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Preparazione e caratterizzazione di fotocatalizzatori per la valorizzazione del CO_2 in reattori a membrana

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Ph.D. thesis

Preparation and Characterisation of Photocatalysts for CO$_2$ valorisation in Membrane Reactors

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Summary

Only the chemist can tell, and not always the chemist,

what will result from compounding

Fluids or solids.

And who can tell

How men and women will interact

On each other, or what children will result?

There were Benjamin Pantier and his wife,

Good in themselves, but evils toward each other:

He oxygen, she hydrogen,

Their son, a devastating fire.

I Trainor, the druggist, a mixer of chemicals,

Killed while making an experiment,

Lived unwedded.

Edgar Lee Masters

Abstract

Carbon dioxide is a gas that is constantly exchanged among the atmosphere, oceans, and land surface due to its continuous production and absorption by many microorganisms, plants and animals. These processes tend to balance the CO_2 content in the atmosphere; however, since the Industrial Revolution, human activities are perturbing this equilibrium causing global warming and climate change. Due to this problem, an increasing concern has bring the scientific community to devote huge efforts to the CO_2 reduction and/or valorisation.

The published researches demonstrate that photocatalytic reduction of CO_2 in the presence of H_2O as reductant is a promising green way to obtain CH_4, CO, CH_3OH, EtOH, HCHO, acetaldehyde, and other products. Albeit, some aspects should be still improved in the use of the current technology, mainly related to the fact that TiO_2, the most known photocatalyst, absorbs light in the ultraviolet region of the electromagnetic spectrum and the use of the visible light is by far desirable. Beside the use of the best light source, also the high recombination hole-electron photogenerated charges (h^+ e^-) should be reduced or, in the best prospective, suppressed.

The aim of the current *PhD* dissertation is the CO_2 reduction by renewable methods, by using sunlight in order to obtain molecules that eventually could be used as fuels. This challenge aims to miming the natural process.
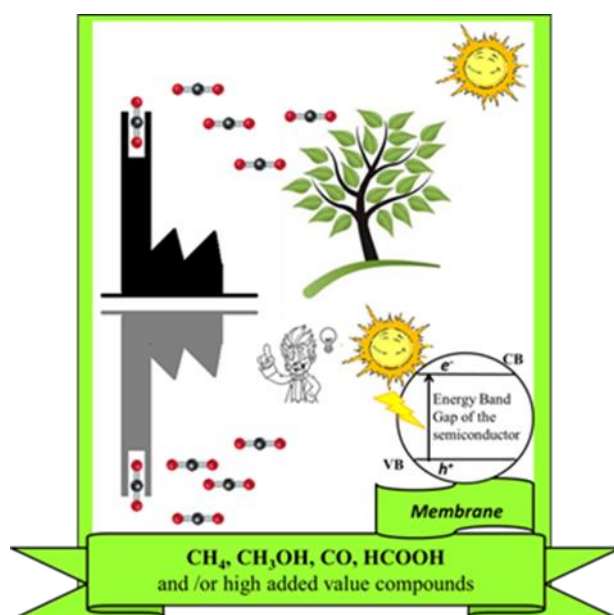
In this contest, heterogeneous photo-catalysis assisted by the choice of reactor such as the continuous membrane reactor can improve the process performance.

The current research is focused to improve the activity in CO_2 reduction by two way: (i) the improvement of catalyst photoactivity and (ii) the optimization of the reactor set up. The first approach regards the catalyst modification by composites formation or doping material. The second approach aims to enhance the performance of the photoreaction by the incorporation of the photocatalyst in a membrane. In this way, the photocatalytic membrane should play a double role: (i) as (photo)catalyst support (ii) as separating barrier shifting the equilibrium versus the products formation, all in one step avoiding also a possible back reaction.

Several materials were prepared: (i) C_3N_4 from melamine by two thermal treatments, (ii) the C_3N_4 composite with TiO_2 sample by mechanical mixing, (iii) the O doped C_3N_4 samples by chemical and/or thermal method, (iv) graphene/TiO_2 composites with a graphene loading percentage weights equal to 0.5, 1, 3 and 10% obtained by a hydrothermal method. Beside to these powder samples, by solvent evaporation method, also the photocatalytic membranes were prepared embedding C_3N_4 and C_3N_4-TiO_2 in to polymeric Nafion matrix. In addition to these materials, also ZrO_2 bare and doped with Er or Ce were prepared. These photocatalysts were characterised and then used to perform CO_2 photoreduction experiments.

By concerning the characterization, FTIR, DRS, and XRD analyses were carried out for all powder samples, whilst the morphology and the structure of the photocatalytic and bare Nafion membrane were studied by SEM image and FTIR-ATR analysis.

In order to evaluate the photocatalytic activity versus the CO_2 photoreduction, all powder sample (TiO_2, C_3N_4, C_3N_4-TiO_2, bare and doped ZrO_2 materials, graphene/TiO_2 were tested in a Pyrex gas/solid batch reactor in the presence of a gaseous mixture CO_2/H_2O, at atmospheric pressure and under simulated sunlight. Besides, the pure and O doped C_3N_4, after immobilisation in a glass supports, were tested in a batch reactor at 2 bar. In both cases, the evolution of the species present in the reacting mixture, during the irradiation time, was followed by a GC-FID-TCD.

The flat sheet photocatalytic C_3N_4 and C_3N_4 /TiO_2 Nafion membranes were assembled in a stainless steel module equipped with a quartz window allowing UV-Vis irradiation of the catalytic membrane surface. Once placed in UV-Vis exposure chamber, the membrane module was fed continuously with CO_2 and H_2O by means of a mass flow controller and an HPLC pump, respectively.

In the case of C_3N_4 Nafion membrane, particular attention was devoted to analysing the effect of contact time (2, 9.8 and 18.7 s) and CO_2/H_2O (0.5, 2 and 5) feed molar ratio on membrane reactor performance. Whilst, in the C_3N_4-TiO_2/Nafion membrane the experimental set up allowed also to define the pressure system effect on reaction performance.

In this photocatalytic membrane reactor, the gaseous fraction of retentate and permeate flows were analysed by means of a GC-FID-TCD. To ensure the catalysts and the membrane photoactivity, in all case, the blank test was carried out in the same experimental reaction conditions but replacing CO_2 by argon.

The results obtained in these three years are below briefly described.

During the test of **graphene/TiO_2** materials, methane was the main product in all case. The highest methane production (1000 μM g^{-1}) was observed for the 1% graphene/ TiO_2 composite and it was the highest ever reported for similar systems in the presence of metal free photocatalysts. This research may open a new doorway for new significant application of graphene for the selective production of methane and methanol as a promising material in membrane photocatalytic continuous reactor. However further investigations are needed.

The tests carried out in the presence of **ZrO_2 based materials** highlight that the new photocatalysts are able to absorb portions of UV (λ=365 nm) and solar light. Pristine ZrO_2 as well as Ce and Er-doped ZrO_2 resulted photoactive in gas-solid regime for CO_2 reduction to form mainly acetaldehyde. This uncommon behaviour for an insulator like ZrO_2 (with a band gap of more than 5 eV) is explained by the formation of intra band gap states due to the O vacancies.

During the tests in the presence of **C_3N_4 and oxygen doped C_3N_4** used as photocatalysts for CO_2 reduction, the detected product was CO. The pure material was

observed to be more active than the oxygen modified analogue. A decrease in the rate of CO generation, under irradiation, was observed during both single runs and repeated test cycles with the same catalyst. During control tests in the absence of CO_2, the production of CO was observed under irradiation, raising questions about the origin of CO and the stability of C_3N_4. Both analyses such as the diffuse FTIR and XPS before and after use, showed that the thermal and the photocatalytic treatments produce similar changes to the functional groups, which are consistent with oxidation of the C_3N_4 structure. This study allowed an interesting examination of where and how oxidation disrupts the material structure, showing changes in the heptazine base units along with changes in the bonds between units due to the thermal oxidation or photocatalytic use.

By using **C_3N_4 Nafion membrane**, photocatalytic CO_2 conversion was carried out in a continuous photocatalytic reactor with an exfoliated C_3N_4-based membrane irradiated by UV-vis light. The effect of H_2O/CO_2 feed molar ratio and contact time on species production, reaction selectivity and converted carbon were investigated. The rate of total converted carbon per gram of catalyst used varied between 5 to 47.6 µmol $g_{catalyst}^{-1}$ h^{-1}, with the latter value obtained at an H_2O/CO_2 feed molar ratio of 5 and 2 s as contact time. Alcohols were prevailing product. The membrane reactor) converted at least 10 times more carbon than the batch system , as a result of the better dispersion of the catalyst which was embedded in the Nafion matrix.

The photocatalytic CO_2 reduction experiments carried out by using **C_3N_4-TiO_2** Nafion membrane produced mainly MeOH and formaldehyde with trace of acetone and EtOH. The obtained MeOH production confirms the trend previously found for C_3N_4 Nafion membrane about the feed molar ratio and residence time effect. In particular the MeOH production increased with the feed molar ratio and is higher at lower residence time (2 s). Then, the best set up conditions were: a H_2O/CO_2 feed molar ratio and residence time equal to 5 e 2 s, respectively. Under these experimental conditions, MeOH production was higher; in addition, at the lower pressure (3 bar) the reaction exhibited ca. 80% of selectivity that decreased at ca. 50% when there action pressure raised to 5 bar.

On the contrary, the selectivity towards formaldehyde increases from 10 to 45% when the feed pressure increases. By comparing the experiments obtained in the presence of

C$_3$N$_4$ loaded Nafion and C$_3$N$_4$-TiO$_2$ loaded Nafion membranes with those present in the literature for TiO$_2$ loaded Nafion membrane, the selectivity toward MeOH production increases with TiO$_2$ content. On the contrary, the C$_3$N$_4$-TiO$_2$ loaded Nafion membrane showed the best value of total carbon converted, equal to 60 μmol g^{-1} h^{-1}, compared with the other two membranes aforementioned. This value is ca. 7 time higher than that obtained in the batch test with the C$_3$N$_4$-TiO$_2$ powder catalyst, confirming the enhancement owing to the continuous membrane reactor versus the batch.

In conclusion, the CO$_2$ was valorised by using several type of catalysts (pure, doped and composite graphitic materials) in different reactors. In all the cases, CO$_2$ photoreduction occurs giving CH$_4$ and CO or alcohol and acetaldehyde as the main products as a function of reactor type (batch or membrane reactor) and experimental conditions operated.

This *Ph.D* dissertation, in the CO$_2$ photoreduction field, provided (i) an interesting structural study of C$_3$N$_4$ before and after use, (ii) a remarkable study of catalyst photoactivity by using oxide and graphitic material in batch reaction, (iii) a promising route for the optimisation of the photocatalytic continuous membrane reactor in terms of feed molar ratio of reagents mixture, residence time and reaction pressure.

Sommario

Il diossido di carbonio (CO_2) è un gas che viene costantemente scambiato tra l'atmosfera, gli oceani e la superficie terrestre grazie alla attività biologica di una grande varietà di microrganismi, piante e animali. I fenomeni di emissione e di assorbimento del CO_2 in questi processi naturali tendono ad equilibrarsi. Tuttavia, a partire dalla rivoluzione industriale, le attività umane hanno perturbato questo equilibrio, causando un preoccupante aumento della concentrazione di CO_2 nell'atmosfera con il conseguente riscaldamento globale i fenomeni climatici ad esso connessi. Questo problema ha portato la comunità scientifica a dedicare enormi sforzi alla riduzione e/o alla valorizzazione del CO_2.

Le ricerche riportate in letteratura dimostrano che la riduzione fotocatalitica del CO_2 in presenza di H_2O come agente riducente è un modo promettente per ottenere CH_4, CO, CH_3OH, C_2H_5OH, $HCHO$, C_2H_4O, etc. Tuttavia i piccoli valori di conversioni ottenuti hanno spinto ad accoppiare la fotocatalisi eterogenea con la tecnologia dei reattori continui a membrana per migliorare le prestazioni del processo.

Questo è il punto di partenza del presente lavoro di tesi il cui obiettivo è di ottimizzare l'attività nella riduzione del CO_2 attraverso: (i) il miglioramento della fotoattività del catalizzatore e (ii) l'ottimizzazione della configurazione del reattore. Il primo approccio riguarda la modifica del catalizzatore mediante formazione di compositi o di materiali dopati, mentre il secondo mira a migliorare le prestazioni della reazione mediante l'incorporamento del fotocatalizzatore in una membrana e l'uso di un reattore continuo. Il reattore continuo fotocatalitico a membrana così ideato conduce la reazione in un unico step e consente di ottimizzare l'esposizione del catalizzatore alla luce e ai reagenti e di spostare l'equilibrio chimico verso la formazione dei prodotti riducendo in tal modo la possibilità che i prodotti possano reagire a loro volta secondo reazioni termodinamicamente più favorite ma indesiderate che diminuiscono l'efficienza globale del processo.

Per perseguire lo scopo prefissato sono stati preparati i seguenti materiali:

(a) nitruro di carbonio (C_3N_4)
(b) C_3N_4 con TiO_2

(c) C_3N_4 dopato con O mediante metodo chimico e/o termico

(d) compositi di grafene/TiO_2 con un peso percentuale di carico del grafene dello 0.5, 1, 3 e 10%

(e) ossido di zirconio (ZrO_2) puro e dopato con Erbio (Er) o Cerio (Ce).

In aggiunta a questi materiali, sono state preparate membrane fotocatalitiche mediante il metodo di evaporazione del solvente. Nella matrice polimerica delle membrane (Nafion) sono stati aggiunti C_3N_4 puro o accoppiato a TiO_2.

Tutti i fotocatalizzatori sono stati caratterizzati attraverso la spettroscopia UV-vis, la spettroscopia ad infrarossi a Trasformata di Fourier (FTIR) e la diffrazione dei raggi X. Alcune polveri sono state caratterizzate tramite spettroscopia fotoelettronica a raggi X (XPS). Per quanto riguarda le membrane fotocatalitiche, l'analisi strutturale, ottica e morfologica è stata condotta tramite spettroscopia a infrarossi, di riflettanza diffusa e tramite microscopia elettronica a scansione. Tutti i materiali preparatati sono stati infine testati per la fotoriduzione del CO_2 in presenza di acqua.

Per valutare l'attività fotocatalitica dei materiali nei confronti della riduzione del CO_2, tutti i materiali in polvere sopra elencati sono stati testati in un reattore batch di Pyrex riempito da una miscela gassosa CO_2/H_2O a pressione atmosferica e sotto irraggiamento UV-vis (luce solare simulata, SOLARBOX). Il C_3N_4 puro e quello drogato con ossigeno, sono stati utilizzati previa immobilizzazione su un supporto di vetro e testati in un reattore batch in acciaio con una finestra in quarzo attraverso la quale si è effettuata l'irradiazione UV-vis necessaria per condurre la reazione. Anche in questo caso la reazione è stata condotta in presenza di H_2O come agente riducente ma ad una pressione di CO_2 pari a 3 bar.

Diversamente dai materiali in polvere, le membrane fotocatalitiche sono state invece testate in un reattore continuo. Il reattore era composto da un modulo in acciaio dotato di una finestra in quarzo per consentire l'irradiazione UV-vis della superficie della membrana posta all'interno del reattore. Il modulo così composto è stato collegato a dei controllori di portata mediante i quali è stato possibile controllare le quantità di reagenti da miscelare e introdurre nel sistema. Questo strumento ci ha permesso di studiare la distribuzione dei prodotti, la quantità di carbonio convertito, la selettività al variare del

tempo di residenza della miscela dei reagenti all'interno del reattore e l'effetto del rapporto molare della miscela reagente H_2O/CO_2.

In tutti i casi, sia in presenza del catalizzatore in polvere, su supporto di vetro o su membrana, l'evoluzione nel tempo della reazione fotocatalitica è stata seguita con campionamenti periodici. Le analisi dei campioni sono state effettuate tramite gas cromatografo dotato di rilevatori a ionizzazione a fiamma e a termo-conducibilità elettrica.

Tutti i fotocatalizzatori hanno mostrato foto-attività nella riduzione del CO_2 e i risultati sono qui di seguito brevemente discussi.

Nel caso dei compositi **grafene/TiO$_2$** il CO_2 è stato trasformato preferenzialmente in metano che ha raggiunto una concentrazione massima per grammo di catalizzatore di 1000 $\mu M\ g^{-1}$ nel caso in cui il grafene era presente al 1%. I risultati in generale hanno confermato quanto riportato in letteratura dimostrando l'esistenza di un caricamento ottimale di grafene sul TiO_2. Successivi studi e implementazioni dal punto di vista reattoristico sono comunque necessari.

Nel caso dei test condotti in presenza dei materiali a base di **ZrO$_2$ drogati e non**, i risultati hanno evidenziato un'attività fotocatalitica di conversione di CO_2 tendenzialmente ad acetaldeide. Lo studio strutturale delle polveri fotocatalitiche ha consentito di comprendere e giustificare l'insolita attività del ZrO_2 che, in quanto semiconduttore con band gap di circa 5 eV, generalmente non assorbe radiazione nel campo UV-vis. La fotoreattività riscontrata è dovuta alla formazione di vacanze di ossigeno nella struttura dell'ossido che si comportano come stati energetici intermedi all'interno del band gap che consentono l'assorbimento di radiazione UV-vis. Inoltre nel caso del ZrO_2 dopato con Er o Ce, è stato possibile identificare la formazione di bande energetiche intermedie all'interno del band gap capaci di generare un "doppio salto dell'elettrone eccitato".

Nel caso dei catalizzatori immobilizzati a base di **C$_3$N$_4$ (puro e dopato con ossigeno)**, i test fotocatalitici di riduzione del CO_2 hanno evidenziato il CO come unico prodotto. Dal confronto delle reattività ottenute con tutti i materiali supportati si evince una maggiore attività del materiale puro C_3N_4 che però diminuisce con il riutilizzo. Lo

stesso andamento decrescente è stato riscontrato per i catalizzatori dopati con ossigeno. A seguito delle analisi FTIR e XPS, effettuate prima e dopo l'utilizzo, è stato possibile identificarne la causa nell'introduzione di atomi di ossigeno all'interno della struttura al posto dei centri di azoto. L'incremento del contenuto di ossigeno interno alla struttura può essere visto come una foto-ossidazione del materiale che quindi ne causa la progressiva perdita di attività fotocatalitica.

Questo studio ha permesso di comprendere dove e come l'ossidazione muta la struttura del materiale a causa dell'ossidazione termica o dell'uso fotocatalitico, mostrando cambiamenti nelle unità di base di eptazina e nei legami tra esse.

Utilizzando la membrana fotocatalitica contenente il C_3N_4, la conversione fotocatalitica del CO_2 è stata effettuata in un reattore fotocatalitico continuo irradiato da luce UV-vis. Sono stati studiati gli effetti del rapporto molare di alimentazione H_2O/CO_2 e il tempo di contatto della miscela all'interno del reattore sulla produzione e la distribuzione dei prodotti, sulla selettività della reazione e sul carbonio convertito totale. In generale, gli esperimenti hanno prodotto principalmente metanolo, etanolo, formaldeide, e tracce di acetone. In termini di efficienza della reazione condotta, gli esperimenti fotocatalitici hanno mostrato valori di carbonio convertito totale tra i 5 e 47.6 μmol g^{-1} h^{-1}. Il più alto valore, in particolare, è stato raggiunto adottando un rapporto molare di H_2O/CO_2 di 5 e un tempo di residenza di 2 s. In ogni caso, comunque, il valore di carbonio convertito totale ottenuto nel reattore continuo a membrana è stato almeno 7 volte maggiore rispetto a quello ottenuto in condizioni analoghe ma in presenza delle polveri di C_3N_4 nel reattore batch. Quest'ultima evidenza sottolinea l'importanza di opportune condizioni reattoristiche per la reazione considerata e in particolare del reattore continuo a membrana per incrementare l'efficienza del catalizzatore in esso disperso.

Gli esperimenti di fotoriduzione del CO_2 effettuati utilizzando la membrana Nafion C_3N_4-TiO_2 hanno prodotto principalmente metanolo e formaldeide con tracce di acetone ed etanolo. La quantità di metanolo ottenuto conferma la tendenza precedentemente menzionata per la membrana di Nafion in presenza di C_3N_4, in merito all'effetto del rapporto molare e del tempo di residenza. In particolare, la produzione di metanolo aumenta con il rapporto molare e con il diminuire del tempo di residenza. Per quanto riguarda l'effetto della pressione di reazione, la selettività verso la produzione di

metanolo mostra valori maggiori (*ca.* 80%) a pressioni minori (3 bar). Viceversa si sono ottenute selettività a metanolo (*ca.* 50%) minori a pressioni di reazione maggiori (5 bar).

La selettività della reazione nei confronti della produzione di formaldeide aumenta dal 10 al 45% quando la pressione di alimentazione aumenta da 3 a 5 bar. Sia negli esperimenti in presenza delle membrane fotocatalitiche in Nafion contenenti C_3N_4 e C_3N_4-TiO_2 che nei risultati di letteratura relativi a membrane in Nafion con TiO_2, la selettività in metanolo aumenta con il contenuto di TiO_2. In termini di carbonio totale convertito, la membrana Nafion C_3N_4-TiO_2 ha mostrato una più alta efficienza raggiungendo un totale carbonio convertito rispetto alle altre due membrane sopra menzionate pari a 60 $\mu m\ g^{-1}\ h^{-1}$. Questo valore come gia detto, risulta essere di *ca.* 7 volte superiore a quello ottenuto nel test in batch con il catalizzatore C_3N_4-TiO_2 in polvere. Questo risultato evidenzia l'incremento delle performance del reattore a membrana fotocatalitico continuo rispetto a quello batch.

In conclusione, diversi tipi di catalizzatori (materiali grafitici puri, drogati e compositi) sono stati preparati, caratterizzati e testati per la trasformazione fotocatalitica delCO_2 in diversi reattori. In tutti i casi, la fotoriduzione di CO_2 si verifica dando metano, monossido di carbonio, alcol e formaldeide come prodotti principali in funzione del tipo di reattore (reattore batch o membrana) e delle condizioni sperimentali utilizzate. Questa tesi di dottorato, nel campo della fotoriduzione della CO_2, ha fornito (i) un interessante studio strutturale del C_3N_4 e dei materiali dopati con ossigeno prima e dopo l'uso, (ii) un ampio studio della fotoattività di catalizzatori ossidici e materiali grafitici in reattori batch, (iii) uno studio per l'ottimizzazione del reattore fotocatalitico continuo a membrana in termini di rapporto molare di alimentazione dei reagenti della miscela, tempo di residenza e pressione di reazione.

Outline

The present dissertation deals with the preparation and characterisation of photocatalysts active under UV-vis light irradiation for CO_2 reduction to high value added compounds. The first chapter introduces the environmental problem of the global warming caused by the increasing CO_2 concentration in the atmosphere. The sections therein survey the various methods investigated in the relevant literature in order to exploit CO_2 as building block for the synthesis of fuels. Due to its green features, photocatalysis is proposed as one of the most promising methods among them, and its basic mechanisms, along with the main photocatalysts and some reactor design issues are briefly presented.

The second chapter describes the synthesis and characterization of all of the photocatalysts tested for CO_2 reduction. Results of the reactivity test in batch reactors are reported in chapter 3. The section 3.1, 3.2 and 3.3 present the CO_2 photoreduction results obtained in the presence of graphene/TiO_2 composites, bare and doped ZrO_2 materials and bare and doped C_3N_4 samples, respectively.

The following 3.4 and 3.5 sections present the results of the fuels production in a continuous photoreactor by using C_3N_4 and C_3N_4-TiO_2 embedded in Nafion membranes.

This dissertation ends with a summary highlighting the main results and the appendix A and B which report the publications and the training Ph.D school activity, respectively.

Chapter 1

The Environmental problem and CO_2 valorisation

1.1 Aim of this dissertation

The presented literature overview testify the attention of the scientific community towards the challenging problem of CO_2 activation. Different materials have been already proposed as promising photocatalysts and their activity has been tested and reported in many papers.

The starting point of the present dissertation was to identify the most promising materials among them and to investigate the relationship between their physico-chemical features and their activity for CO_2 photoreduction. These basic materials were TiO_2, ZrO_2, and C_3N_4. TiO_2 is the most studied semiconductor due to its abundance, non toxicity and chemical stability so that it is often considered as a reference materials for a wide class of photocatalytic reactions. The use of ZrO_2 for CO_2 photoreduction is appealing because of its surface basicity favours CO_2 adsorption. Even if this material has been only rarely used as a photocatalyst due to its wide band gap (ca. 5 eV), recent studies highlighted its visible light harvesting capability due to the presence of oxygen vacancies acting as colour centres. Graphitic carbon nitride (C_3N_4) is very attracting material recently investigated for CO_2 photoreduction because of its narrow band gap, the basicity of the constituting nitrogen atoms and the particularly negative potential of the photogenerated electrons.

With the aim of increasing the CO_2 photoreduction efficiency of these materials, two approaches were adopted: (i) modifying the bare semiconductors by means of metal and non-metal doping or by coupling them with opportune graphitic materials (such as graphene or the graphitic C_3N_4), and (ii) tailoring design and operating parameters influencing the reaction efficiency, by using continuous photocatalytic membrane reactors, different reactants molar ratio, and residence times.

As far as the first point is concerned, TiO_2 was loaded with different amounts of graphitic materials such as graphene and carbon nitride, whilst ZrO_2 was modified with Erbium and Cerium metals. Moreover, C_3N_4 was doped with oxygen in order to enhance its visible light absorption capability.

These materials were tested for CO_2 photoreduction in batch reactors by using water as the reductant. However, in order to avoid back reaction of the products, which is the main hurdle hindering the reaction efficiency, and to optimize the light exposure of the photocatalyst, the activity tests were performed in a continuous photocatalytic membrane reactor. To this aim giving the high versatility, the UV transparency, the photostability and the high proton exchange efficiency of Nafion, the C_3N_4 and C_3N_4-TiO_2 samples were embedded into the Nafion membrane. C_3N_4 materials were chosen to be coupled with Nafion because of the reported compatibility and strong interaction with the sulfonic groups of Nafion.

The photocatalytic materials both powdered and embedded in the membrane were thoroughly characterized in order to evidence the correlation between their physico-chemical properties and CO_2 photoreduction efficiency.

1.2 The Environmental problem

Since the last century, the scientific community is placing particular attention on a world phenomenon called "Global warming".[1, 2] In climatology, the expression global warming indicates the change in the Earth's climate that assumed remarkable effects during the 20th century and is still ongoing.

Atmosphere and oceans have warmed, the amounts of snow and ice have diminished and sea level has risen. These changes are largely attributed to emissions in the Earth's atmosphere of increasing quantities of greenhouse gases and to other factors that the scientific community has identified as attributable to human activity.

By definition, a greenhouse gas is a gaseous compound, generally present in the atmosphere, which is transparent to the solar radiation but consistently retains the infrared radiation emitted by the Earth's surface, atmosphere and clouds. These properties are known from spectroscopic analyses. Greenhouse gases can be of both natural and anthropogenic origin, and absorb and emit at specific wavelengths in the infrared radiation region. This causes the phenomenon known as a greenhouse effect. In fact, these gases are capable to no-radioactively emit into the atmosphere the absorbed solar IR radiation simultaneously blocking the IR emission from the Earth thus causing the above mentioned global warming.

Water vapour, carbon dioxide, nitrous oxide, methane and sulphur hexafluoride (SF_6) are the main greenhouse gases in the Earth's atmosphere. In addition to these gases, there is a wide range of greenhouse gases of exclusive anthropogenic origin, such as halocarbons. Among the most known are chlorofluorocarbons (CFC), and many other chlorine and fluorine containing molecules whose emissions are regulated by the Montreal Protocol.

The molecules mostly contributing to the greenhouse effect are those characterised by a non-linear molecular structure and by an intrinsic dipole moment. In fact, not all of the diatomic gases constituting the atmosphere are IR active as they have a definite linear structure. On the other hand, ozone, water vapour, nitrous oxide, fluorinated gases (hydrofluorocarbons, sulphur hexafluoride, perfluorocarbons, chlorofluorocarbons) behave as greenhouse gases due to their non-linear structure.

As an exception, CO_2, despite its symmetric and linear structure, has a strong IR absorption due to its asymmetric stretching, which affords a significant dipole moment. Even if other gases have a greater greenhouse potential, CO_2 is considered one of the biggest responsible for the global warming due to its greater abundance in the atmosphere.[2]

Before the second industrial revolution (which conventionally began in 1870, along with the large-scale use of electricity, oil and chemicals), the atmospheric CO_2 concentration was 280 part per million (ppm), as shown by measurements in glaciers and poles.

Recently, the World Meteorological Organization published a series of data related to 2016, which show a significant increase in the concentration of carbon dioxide in the atmosphere. For instance, the CO_2 concentration rose from 400 to 403.3 ppm in only one year (from 2015 to 2016).

Due to the strong correlation between the global warming and the CO_2 concentration[3] (Figure 1), the European Commission[4] set greenhouse gas emissions targets in order to limit the warming to well below 2°C above pre-industrial temperatures within 2050.
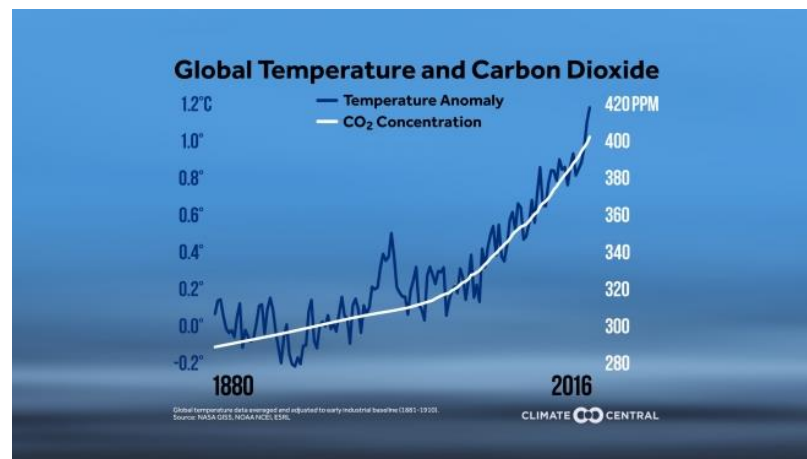

Figure 1. Global temperature and CO₂ atmosphere concentration (ppm) trend from 1880 to 2016.[4]

European key climate and energy targets are set in two particular actions called: (i) 2020 climate and energy package and (ii) 2030 climate and energy framework.

These targets are defined in order to address the EU activities towards a low-carbon economy as detailed in the 2050 low-carbon roadmap. The EU tracks its progress on cutting emissions through regular monitoring and reporting.

1.3 CO_2 utilization: conversion to high added value compounds

Even if naturally present in the atmosphere as a transparent and odourless gas at a low percentage (0.04%) with respect to the other air components, CO_2 plays a key role in the "Carbon cycle", i.e., the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere. In fact, CO_2 is solubilised in the seawater as CO_3^{2-} and HCO_3^- depending on pH, and it is a primary worker in the biological process. In particular, CO_2 represents the building block in the chlorophyll photosynthesis where it is fixed from the plants in the presence of light and from them rejected as waste in the dark.

Carbon is the main component of biological compounds as well as a major component of many minerals such as limestone. Along with the nitrogen and water cycles, the carbon cycle comprises a sequence of events, which are essential to the Earth capability of sustaining life. In theory, being a cycle, it should be capable to balance in the environment the content of carbon, in all of its forms. Unfortunately, this equilibrium is perturbed by human activities, which produce tons of CO_2 per capita at years, as reported in "The global carbon budget 1959–2011" published from Quéré et al. (Figure 2).[5]
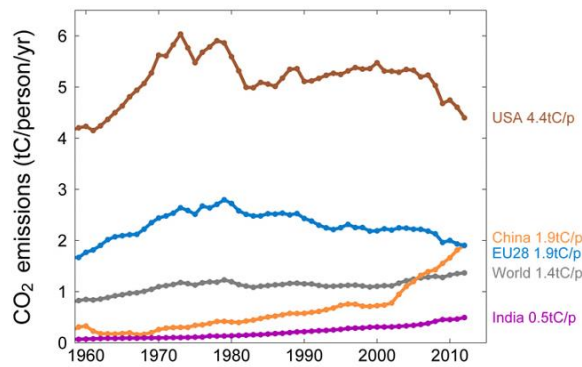
Figure 2. Average emissions per capita from 1960 to 2012.[5]

In a more recent study (2017), Quèrè et al.,[6] in collaboration with sixty world institutes, estimate that ca. 87% of the current anthropogenic CO_2 total emission, derives from fossil fuel combustion (Figure 3a).

In particular, their studies found that the electricity and heat generation is the economic sector that produces the largest amount of man-made carbon dioxide emissions (Figure 3b).

a)   b)
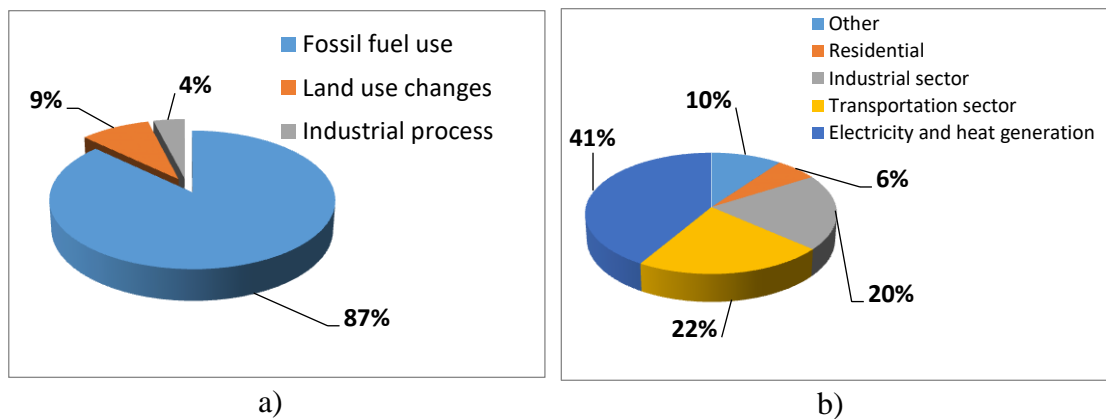
Figure 3. (a)Anthropogenic sources of Carbon dioxide and (b) Carbon dioxide emissions from fossil fuel combustion.

Fossil fuels have been exploit up to now as the main energy source for human activities. This is due to their fundamental characteristics of (i) high compactness concerning the energy to volume ratio, (ii) easy storage, and (iii) low cost. Because of the extremely long process of natural formation of fossil fuels, which makes them a non-renewable energy sources, an inevitable and progressive depletion of

the stocks occurred. This has caused a continuously rising cost of the fossil fuels and of related goods.

Experts from all over the world estimate the predictable exhaustion of resources in a period of around 40 years.

These problems, along with the environmental disasters recently occurred (CO_2 increasing, deforestation, desertification, etc.), moved industrialised Countries to greater attention towards environmental issues by using alternative and renewable energy sources. In particular, the European Union aimed at promoting the use of renewable resources according to targets to be fulfilled within 2020.

In other words, the goal is to generate energy by wind, sun, tides, or other renewable sources, at least at the same rate of consumption. Furthermore, these technologies to produce green energy are environmental friendly, as they do not pollute, not jeopardise the natural resources for the needs of future generations, and not produce emissions of toxic substances or greenhouse gases into the atmosphere.

1.3.1 Activation of CO_2

Even if CO_2 contains polar bonds, it is a nonpolar molecule, due to the high symmetry of its linear structure. Furthermore, CO_2 in principle could give rise to nucleophilic and electrophilic attack through its carbon and oxygen atoms, respectively.

According to the Molecular Orbital Theory, its highest occupied molecular orbital (HOMO), is susceptible to electrophile attack due to the localized electron density of oxygen (lone pairs). On the contrary the lowest unoccupied molecular orbital (LUMO) is susceptible to nucleophile attack due to the antibonding orbital at the lowest energy represented by the central carbon atom.

Furthermore, the CO_2 HOMO degenerated orbitals have four electrons with the same energy ready to be released, while CO_2 LUMO have four unoccupied states to which four electrons can transfer. If one of four electrons from HOMO orbital is released or transferred, the degeneration is broken[7] with the consequent activation

of CO_2. Unfortunately this electron transfer is not favoured so that it has been often represented as a "Holy Grail".[8]

Therefore, CO_2 is a very stable molecule with a $\Delta G^0 = -394$ kJ/mol also because the carbon atom is in its highest oxidation state. Consequently, CO_2 activation is the crucial step in CO_2 transformation to high added value molecules.

1.3.2 Methods

Three principal methodologies are reported to transform CO_2 into useful chemicals:

(i) Use high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds, and organometallics

(ii) Address the selectivity towards oxidized low-energy synthetic products such as organic carbonates

(iii) Supply energy such as light, electricity or biological driving forces.

Selecting the appropriate method and shifting the equilibrium to the product side by removing a particular compound, can lead to a negative Gibbs free energy of the reaction.

Significant researches have been devoted to use CO_2 as the raw material for different reactions, as summarised in Figure 4. In particular, CO_2 reduction performed under photoirradiation, or under electrochemical conditions, generally, affords simple molecules such as carbon monoxide, methane and formic acid [9] or syngas by means of reforming reactions.
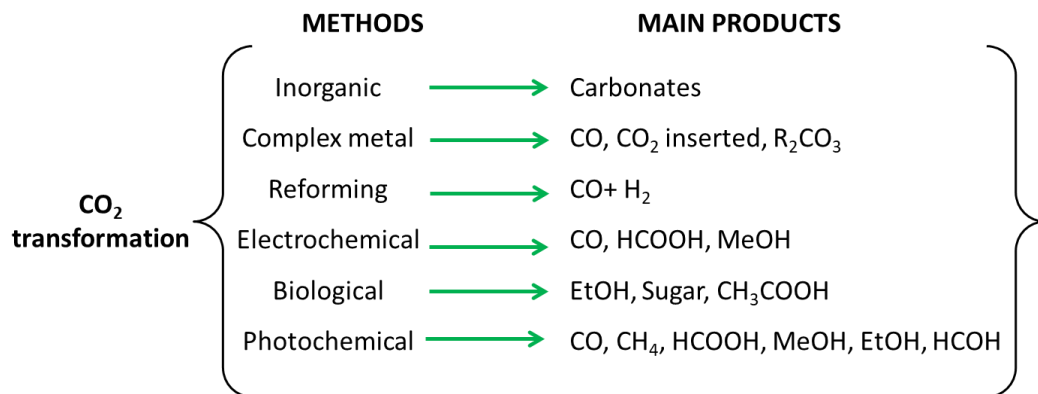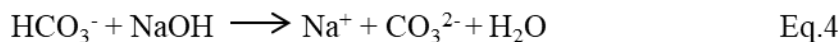
Figure 4. The main reaction/process type from CO_2 transformation to obtain high added value compounds.[9, 10]

The inorganic CO_2 reaction (Eq. 1-2) is just a pH depending to equilibrium as showed in the below reactions (Eq. 3-4).

$$CO_2 + 2H_2O \rightleftarrows H_3O^+ + HCO_3^- \qquad\qquad \text{Eq. 1}$$

$$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^{2-} \qquad\qquad \text{Eq. 2}$$

$$H_2CO_3 + NaOH \longrightarrow Na^+ + HCO_3^- + H_2O \qquad\qquad \text{Eq.3}$$

$$HCO_3^- + NaOH \longrightarrow Na^+ + CO_3^{2-} + H_2O \qquad\qquad \text{Eq.4}$$
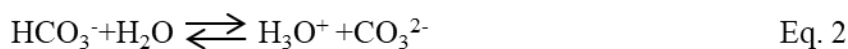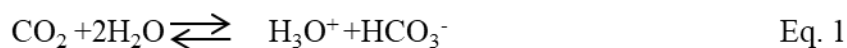
This method is not very useful due to the very low economic value of products (carbonate and bicarbonate salts) and additionally to the large amount of base needed to obtain carbonate.

With the exception of this first kind of transformation, all of the other CO_2 activation routes require the presence of some catalyst to decrease the high activation energy.

Metal complexes (inorganic or organic type) have been used to activate CO_2 in order to obtain high added value compounds as CO or to fix CO_2 in an organic substrate (carboxylation process).

This reaction occurs because CO_2 can efficiently coordinate with transition metal compounds.[11] Figure 5 shows the different coordination modes of CO_2 in transition metal complexes, even at room temperature.[12]

Figure 5. Modes of bonding of carbon dioxide with transition metal.

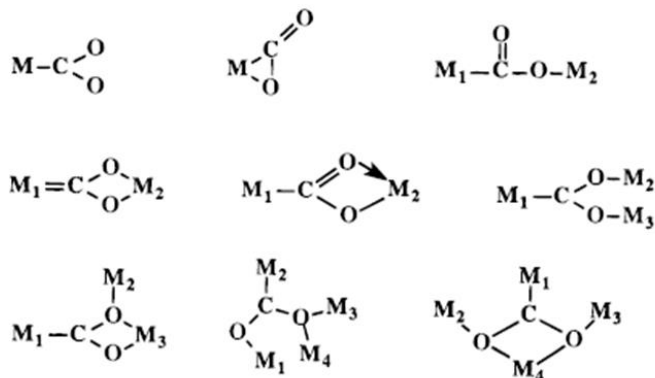In particular, high valence metal complexes with nucleophilic ligands as alkoxides or amides,[13, 14] permit the formation of the carboxyl group through nucleophilic attack to CO_2. This reaction occurs by CO_2 insertion in the M-O or M-N bond giving a metal-alkyl carbonate or metal-alkyl carbamate, respectively. In general, apparently because the metal alkoxide and metal-alkyl carbonate have similar M-O bond strengths, most metal alkoxide complexes react reversibly with carbon dioxide.[15-21] CO_2 insertion has been reported for different transition metals. Zinc complexes, as Zn_2Br_4 (μ-$OCHRCH_2NC_5H_5$)$_2$ (R = H, CH_3),[22] or Cobalt complexes, as [Co (TCT)(OR)]BPh$_4$ (R = Et, Ph; TCT = cis,cis-1,3,5-tris(cinnamylideneamino) cyclohexane),[23] activate CO_2 for insertion reactions. Similar behaviour has been found for organic metal complexes such as Rhenium fac-(CO)$_3$L$_2$-ReOCH$_3$ (L = PMe$_3$; L$_2$ = diars),[24] alkyl vanadium(III) alkoxide,[25] Molybdenum systems[26] like $Mo_2(OiPr)_4(L)_4$ (L = PMe$_3$, HOiPr), or Titanium(IV) butoxide[27], which promote reversible carbon dioxide insertion into the M-O bond. Interestingly, also zirconia catalysts,[28] vanadium based heterogeneous catalysts[29] and organotin alkoxides immobilized on mesoporous silica[30] exhibit similar CO_2 insertion. This kind of reaction was also hypothesized to occur in CO_2-starting syntheses catalysed by tin[31], nickel[32], and niobium[33] complexes.

Metal-organic or inorganic compounds are currently used as catalysts in relevant industrial processes to produce for instance acetic acid, salicylic acid, urea, polycarbonate and propylene carbonate from CO_2.

Even if this type of complexes are used in industrial processes, they suffer several disadvantages mainly because the transition metals are toxic and, especially in the metal-organic form, capable to interact with human tissues and DNA. Some of them are not stable in the presence of water or give leaching making difficult their separation from the reacting mixture and their reuse. Moreover, some transition metals such as Rh, Os, Pt, Au, Ru, and Pd are rare earth elements, which considerably affect the overall cost of the process.

A very efficient alternative method is CO_2 reforming, a thermal catalytic process affording syngas (CO + H_2). This process attracted great attention as a clean and efficient method for hydrogen production from waste material as CO_2. Notably, H_2 is envisaged as the fuel carrier of the future especially for its application to fuel cells.[34]

The industrial CO_2 reforming occurs in the presence of Ni based catalysts,[35] starting from methane and CO_2 as the reagents. (Eq. 5).

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 \qquad\qquad \Delta H_{298°C} = +246\ kJ.mol^{-1} \qquad\qquad Eq.\ 5$$

CO_2 reforming processes are industrially carried out at a high temperature to enhance reaction rates and syngas yields, due to the highly endothermic nature of reaction.

The main drawback of the thermal catalytic reforming processes is the large amount of heat required for the processes.[34] Typically, a temperature ranges of 500-950°C[36] and a pressure between 20-40 bar are applied. These hard operating conditions make the process expensive and energetically demanding. Furthermore, with respect to the steam reforming process (i.e., the analogous process when H_2O is used instead of CO_2), the CO_2 reforming is 40 kJ more endothermic and the higher carbon concentration favours coke deposition, with the consequent faster poisoning of the catalyst.

Albeit the aforementioned drawback, the high interest to obtain H_2 has driven researchers to design opportunely catalysts and reactors in order to improve the efficiency of the process, set mild conditions, and reduce the costs.[36-40]

A promising method to avoid the above-mentioned catalyst poisoning, is to use electricity as the driving force by means of electrochemical processes. These systems are typically comprised of an anode and a cathode placed in two chambers separated by an ionic conducting membrane. In the anodic compartment, water is oxidised to molecular oxygen, while CO_2 (used as carbon source) is reduced at the cathodic side to high added value molecules.

The electrocatalysts used for this application can be divided into three groups: metallic, non-metallic, and molecular catalysts as summarised in Figure 6.[41-59]
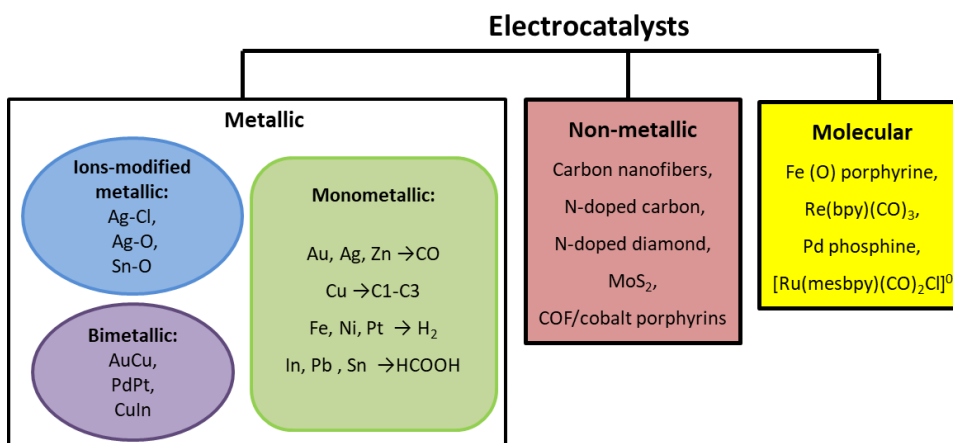
Figure 6. Schematic illustration of the three major categories of electrocatalysts for CO_2 reduction.[60]

Due to the thermodynamically uphill nature of one electron CO_2 reduction (Eq. 6) an external bias is required.

$$CO_2 + e^- = CO_2 \bullet^- \qquad\qquad -1.90 \text{ V vs. SHE (pH 7)} \qquad\qquad \text{Eq. 6}$$
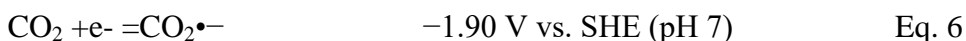
On the other hand, a smaller electromotive force in the range of −0.2 to −0.6 V vs. SHE (Standard Hydrogen Electrode) is required for CO_2 reduction with proton-assisted electron transfer processes.

Unfortunately, due to the similar redox potentials for all of the reaction pathways (i.e., CO_2 to $HCOOH$ and CO_2 to CH_3OH have E_0 equal to -0.58 and -0.51 V, respectively),[60] the proton-assisted processes can lead to a wide range of CO_2-derived products, thus giving rise to poor selectivity towards the desired chemicals. However, generally only CO and $HCOO^-$ are reported as the main products of CO_2 electrocatalytic reduction.[60]

Notably, a key factor, to be carefully controlled is the competition of water with CO_2, which decreases the efficiency of the process producing H_2 instead of the CO_2 reduction products.[60] Furthermore, the costs related to the consumption of electricity are bottleneck for this process. In addition, the electricity is currently mainly produced from fossil fuel oxidation, which in turn is a source of CO_2.

Every living being must extract energy from the environment in order to carry out the metabolic processes. In particular, plants harvest solar light in order to perform photosynthesis, which uses CO_2 as building block to synthesise carbon chains molecules (e.g., glucose and cellulose). For this reason, plants, algae and cyanobacteria are called photoautotrophs, i.e., they are capable to produce complex organic compounds from simple molecules, generally using light as energy source. Photosynthesis is largely responsible producing and maintaining the oxygen content of the atmosphere, and it supplies the organic compounds and the energy necessary for life on Earth. Even if photosynthesis is differently performed by different species, the process always begins when energy from light is absorbed by proteins called reaction centres that contain green chlorophyll pigments. These proteins (enzyme function) coordinate with Cu (Cu(I) and Cu(II)) and Mg, playing a key role on the photosynthesis process.

Different pathways are known for the fixation of inorganic carbon into organic compounds used for cell biomass.[61] Among them the reductive pentose phosphate (Calvin−Benson−Bassham) cycle[61, 62] is the predominant mechanism by which many prokaryotes and all plants fix CO_2 into biomass.

The enzymes required to carry out these important metabolic pathways, which have evolved over billions of years, and they use readily abundant materials from the environment to achieve these important energy conversion processes. All of these

metabolic pathways involve the storage and utilization of energy in the form of chemical bonds. Our ability to carry out the same transformations in a controlled and efficient way will be critical to our future energy security. In fact, a huge number of literature reports focus understand these complex processes in order to convert CO_2 in high added value compounds in vitro and in vivo conditions. In particular, it has been demonstrated the photosynthetic functions of microalgae *Chlorella* or unicellular cyanobacteria *Synechocystis* can be energetically convenient compared to catalytic conversions requiring energy-intensive reaction conditions (high temperature ca. 300–600 °C and pressure higher than 10 bar).[63-66] Furthermore, algae such as *Chlorella*, *Scenedesmus, Spirulina, Nannochloropsis*, and *Chlorococcum* are characterized by rapid growth, tolerance to stress factors, and to high concentrations of CO_2.[67-69] A recent kinetic study on *Chlorella vulgaris* reports the bio-fixation rate and cell concentration value more than 1.4 g/L/day and 1.3×10^7 cells/mL, respectively.[70]

Unicellular microorganisms such as Cyanobacteria have been used in several ways to produce renewable biofuel. However, recent studies suggest that biofuel production from cyanobacteria is unfeasible, as the energy return to energy invested ratio (EROEI) is unfavourable.[71] In fact numerous large, closed loop bioreactors with ideal growth conditions (sunlight, fertilizers, concentrated carbon dioxide, oxygen) need to be built and operated, and this in turn consumes fossil fuels.[71] Additional energy is required to work up the cyanobacterial products.

A hybrid type of photo bioreactor was developed for the growth of algae and cyanobacteria by considering the influence of various parameters such as CO_2 concentration, availability of light, temperature, pH, and O_2 removal rate.[72] For instance, Kumar et al. developed a composite (or mixed) bioreactor getting maximum yield and maximum energy efficiency of the process.[68]

A class of enzymes widely studied are those belonging to the crotonase superfamily, characterized by presence of oxyanion holes that stabilize the formation of enolate anions in their substrates. Furthermore, these enzymes are biotin dependent. Biotin is a vitamin linked to the active site of the enzyme, which plays the role of cofactor in different ATP-dependent carboxylases. The carboxylation reaction involves the capture of bicarbonate by the biotin, which in

turn transfer CO_2 to an acceptor. Generally, the acceptor is Acetil-CoA so that the enzyme operating carboxylation is called Acetyl-CoA carboxylase.

In other words, this vitamin is responsible for the C-C formation through CO_2 fixation.[41, 73-75]

Several possible advantages exist for using biotin-dependent carboxylases as catalysts for fuel production. Firstly, a wide variety of enzymes is available, all of the genes encoding the enzymes have been cloned, and activity overexpressed. Secondly, even if the enzymes operate at low concentration of bicarbonate, it is possible to enhance the reaction rate by using other enzymes, which locally increase the bicarbonate concentration and allow to doubling the turn over number even at room temperature and atmospheric pressure.

The major disadvantage for fuel production is that these processes require a continuous input of ATP and of acceptor molecule (acetyl-CoA).[41] Furthermore, biological systems are based on complex and delicate equilibria whose control is demanding. However, investigating the mechanisms of the biological systems is of paramount importance to mimic their ability of exploiting CO_2 as a building block molecule (i.e., photosynthesis process shown in Figure 7).

Figure 7.Simplified scheme of natural photosynthesis process by plant.

In this way, it would be possible to develop a green industry to produce and to solve the environmental problems. This vision is clearly expressed by the famous sentence of G. Ciamician:

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!" [76, 77]

In this contest, the photocatalysis may be a promising tool to realize this dream.

1.4 Photocatalytic reduction of CO_2

1.4.1 Basic principles of photocatalysis

Sun is considered an unlimited source of energy and a promising driving force for chemical reaction.

The term of Photocatalysis refers to a catalytic process induced by light. Generally, photocatalysts are semiconductors, which are characterized by their unique electric conductive behaviour, intermediate between that of a conductor and an insulator.

In detail, when light of suitable energy is absorbed by the catalyst (semiconductor) one electron is promoted to the conduction band (CB) from the valence band (VB) where a hole is generated (step 1-Figure 8). The energy required to produce this effect is an intrinsic factor for each semiconductor and it is equal to its band gap (ΔE_g), i.e., the difference between the energy of the edges of the conduction and valence bands.

The light absorption occurs when the photon energy (E) is higher or at least equal to ΔE_g. The relationship between the energy of photon E and the wavelength λ of the light is expressed by equation 7,

$$E = \frac{h \cdot c}{\lambda}$$
Eq. 7

where h is Plank constant ($6.626 \cdot 10^{-34}$ J s) and c is light velocity ($2.998 \cdot 10^8$ m s^{-1}).

The charges generated upon light absorption (step 1) can either undergo primary recombination, emitting light or heat (step 2), or can be trapped at reactive surface sites (step 3). The trapped charges can either recombine (secondary recombination, process 4), or undergo an Interfacial Electron Transfer Process, whereby the electron reduces an electron acceptor species A to a primary reduction product A$^{\bullet-}$ (step 5a), and the hole oxidizes an electron donor species to D$^{\bullet+}$ (step 5b). In order to avoid back electron transfer (step 7) A$^{\bullet-}$ and D$^{\bullet+}$ must then undergo a rapid conversion to the final products A_{red} and D_{ox} (from step 5a to 6a and from step 5b to 6b).
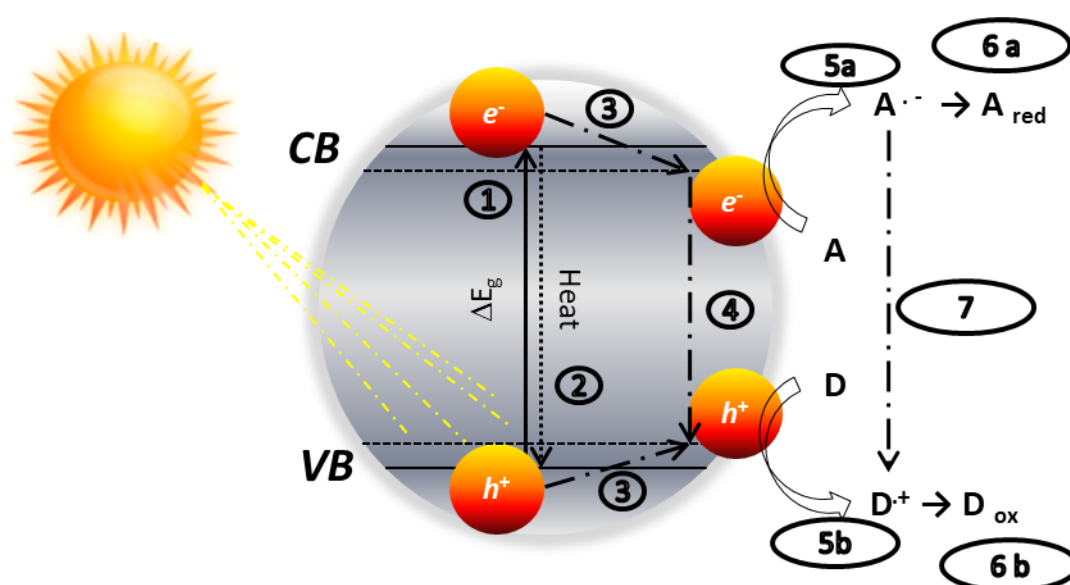

Figure 8. Schematic key processes representation of a photocatalytic reaction at level of a semiconductor particle.

Under the best conditions, thus the electrons and holes may reduce and oxidize, respectively, species adsorbed or in proximity of the surface of the catalyst.

Generally, heterogeneous photocatalysis is carried out in the presence of a solid dispersed in a fluid phase (liquid or gas) similarly to the case of thermal heterogeneous catalysis, and the overall process consists of five independent steps:

1.   Transfer of the reactants from the fluid phase to the surface of the catalyst

2.   Adsorption of a least one of the reactants

3.   Reaction in the adsorbed phase

4.   Desorption of the product(s)

5.   Removal of the products from the interface region.

These steps are summarised in Figure 9 a and b for catalytic and photocatalytic reactions, respectively.
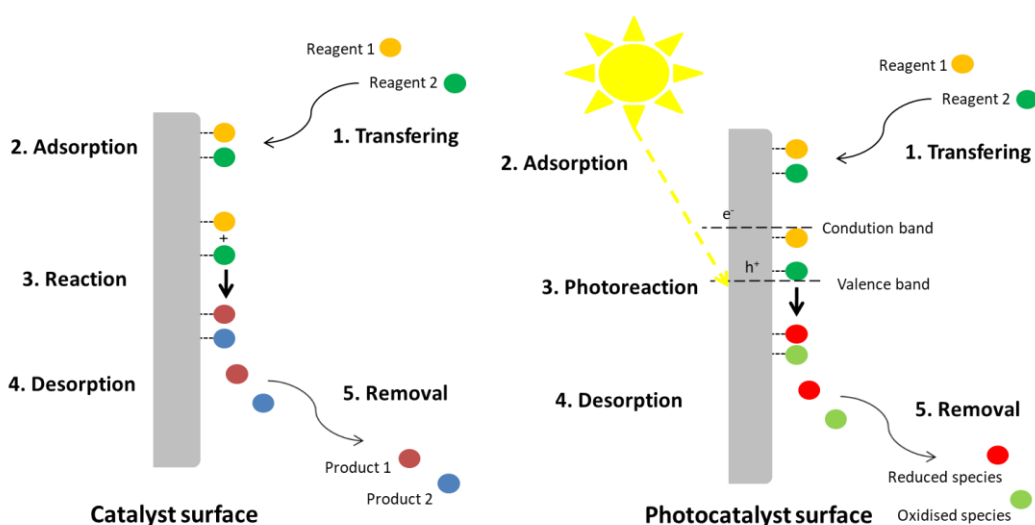

Figure 9. Catalytic and photocatalytic simplified mechanisms.

The main difference between catalysis and photo-catalysis is that the activation process (step 3) is enhanced by heat and light, respectively.

The electron promotion from valence band to conduction band continuously occurs under irradiation, but the consequent reaction of photogenerated charges (e^- and h^+) is lower than the number of promotion events. The charges which are not efficiently trapped or reacted, recombine releasing the surplus of acquired energy either as photons or heat, as above described.

Heterogeneous photocatalysis is a suitable methodology to carry out a large variety of reactions such as metal deposition, organic synthesis, water splitting,

photoreduction, hydrogen transfer, O_2^{18}–O_2^{16} and deuterium–alkane isotopic exchange, water disinfection, anti-cancer therapy, water detoxification, gaseous pollutant removal, isomerisation, etc. [34, 78-90]

In general, several factors affect the catalyst photoactivity as reported by Rajeshwar et al.[91] and summarized in Table 1.

Table 1. Factors responsible of photoreactivity of semiconductors.

Proprieties	Factors
Optical	Band gap, ΔE
Electronic	Carrier mobility, redox potential of the charges
Structural and morphological	Surface Area, crystallinity, particles size, defects, crystal phase, exposed facets, particle morphology
Surface	Acid-base character, surface groups, defects

These effects are crucial to determine the catalyst photoactivity and capability to perform a selected reaction. These properties acting individually or synergistically, affect UV-vis adsorption, quantum efficiency, reactant adsorption and/or orientation, charge recombination, etc. Sometimes the effect of some properties may be contrasting, so that it is difficult to predict the photocatalytic behaviour. For instance, high specific surface areas generally imply higher adsorption and higher reactivity. On the other hand, materials with a high surface area are generally poorly crystalline with the consequent reduced oxidation/reduction power due to the lower mobility of charges in the lattice.[92-94]

From these considerations, it appears clear the importance of the studies on synthesis and characterization of tailored materials. In fact, different techniques are reported to synthesise and to design photocatalysts for specific aims, modulating their proprieties such as crystallinity, defectivity (vacancies in the crystal lattice), surface functionalization, etc.

Titanium dioxide (TiO_2) is the most popular photocatalyst due to its abundance, chemical stability, easy synthesis, no toxicity, low price, easy structural modulation and remarkable photoactivity. The commercial TiO_2 labelled as Evonik ® P25,

comprises of ca. 80% anatase and 20% rutile phases, and it is the most reported one, due to its high activity, so that it is often used as reference catalyst[78] in many photocatalytic studies.

On the other hand, the main drawback of TiO_2, as well as of other semiconductors absorbing in the UV light range, is that it is able to absorb only at wavelengths shorter than 400 nm so that only 4% of the solar irradiation (the UV portion) is useful for its excitation.

In order to exploit a larger part of the solar spectrum, different techniques have been used as summarised below in Figure 10.
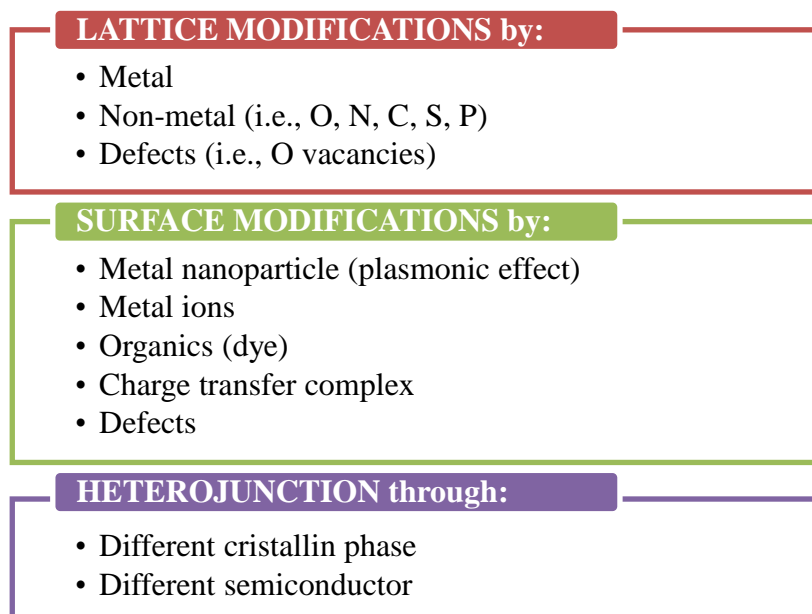
LATTICE MODIFICATIONS by:
- Metal
- Non-metal (i.e., O, N, C, S, P)
- Defects (i.e., O vacancies)

SURFACE MODIFICATIONS by:
- Metal nanoparticle (plasmonic effect)
- Metal ions
- Organics (dye)
- Charge transfer complex
- Defects

HETEROJUNCTION through:
- Different cristallin phase
- Different semiconductor

Figure 10. Schematic presentation of principal catalyst modifications.

Structural (lattice) modifications of the semiconductors are characterised by the introduction of foreign atoms into their lattice. This generates intermediate energy states in the band gap thus endowing the material with visible light activity. Similar effect is also achieved by introducing lattice defects such as O vacancies.

Surface modifications are the most commonly used technique to photosensitise the catalyst. To this aim, several techniques are reported in literature based on modification through chromophoric or chromogenic species. Chromophoric species (dyes, metal nanoparticles, metal organic complexes) can be grafted on the semiconductor surface. They absorb visible light (the adsorbate itself is coloured) and subsequently inject electrons into the conduction band of the semiconductor. This mechanism is also known as *photo-induced electron transfer*.

In particular, the visible light absorption, in the case of metal nanoparticles, is due to the so-called plasmonic resonance. This effect gives rise to a local electric field, which further boosts photoexcitation.

On the other hand, the chromogenic species allow visible light activation of a system in which neither the catalyst nor the adsorbate (generally enediols, chlorophenols) absorb visible light. The adsorbate is colourless but becomes coloured when adsorbed on TiO_2. This mechanism is also known as *optical electron transfer*.

The heterojunction modifications can be built between two or more different semiconductors (TiO_2 and CeO_2) or by means of two different crystal phases belonging to the same type of semiconductor (TiO_2 anatase and rutile). In order to form a heterojunction, the requirement that each material is a semiconductor with unequal band gaps is somewhat lost, especially on small length scales, where electronic properties depend on spatial properties.

There are three typical types of heterojunction: Type I (Figure 11A), Type II (Figure 11B) and Type III (Figure 11C). In all cases, both semiconductors are in a photoexcited state.

In the heterojunction of type I, both photogenerated charges just migrate to SC-I (semiconductor I) from SC-II (semiconductor II) with any effect on charge separation in each semiconductor. Similarly, no separation of charges is caused in type III heterojunction where each couple e^- and h^+ works alone without any cooperative effect, as shown in Figure 11C.

In contrast, the type II heterojunction, as shown in Figure 11B, presents thermodynamic compatibility of valence band (VB) and conduction band (CB) of

SC-I and VB and CB of SC-II. In fact, the photogenerated h^+ migrate from VB of SC-I (more positive potential) to VB of SC-II (less positive potential). The opposite migration occurs for the e^- photogenerated on the SC-II, decreasing the recombination e^--h^+ events.

Clearly, only type II heterojunctions are beneficial because they give rise to enhancement of charges separation, and consequently the photocatalytic activity improves.
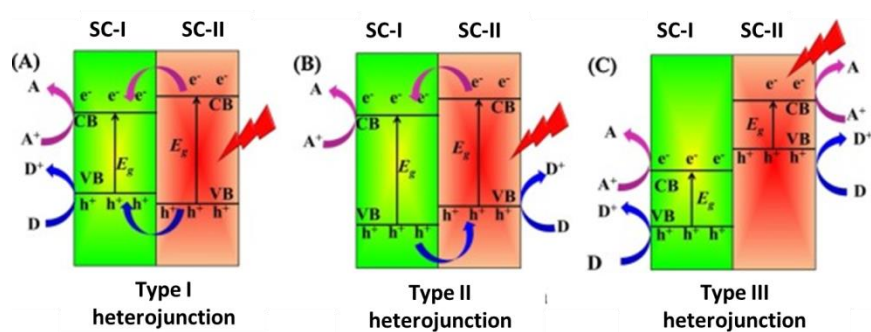

Figure 11. Separation charges in the different types of heterojunctions as reported from Li et al.[95]

A particular situation occurs when the heterojunction is formed by one material with two different crystalline phases. In this case, the enhanced charges separation effect is lower than above reported, due to the very similar values of CB and VB.

Another possible charge migration pathway, which may occur in the type II heterojunction, is called "Z-scheme", due to the Z shaped path of the electron transfer (Figure 12). [96]
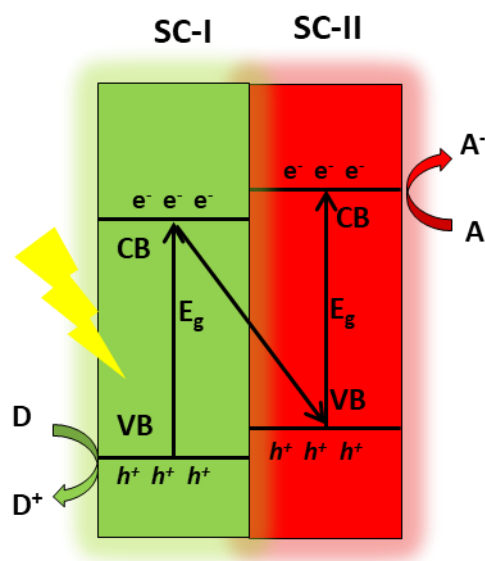
Figure 12. Z scheme representation.

In both cases, spatial charge separation is achieved. However, in the Z-scheme electrons and holes mostly populate CB and VB of SC-II and SC-I, respectively. On the contrary, in the type II heterojunction electrons and holes mostly populate CB and VB of SC-I and SC-II, respectively.

In addition, it should be noted that charge-carrier migration for the direct Z-scheme photocatalyst is physically more feasible than that for type-II heterojunction photocatalysts (Figure 12), since the migration of photogenerated electrons from the CB of TiO_2 semiconductor to the photogenerated hole-rich VB of GaP, for instance, is favourable due to the electrostatic attraction between the electron and hole.[95] Notably, even if it is a difficult task, experimental measurements of the potential of the photogenerated charges may be useful to discriminate between the two mechanisms.

Depending on the desired composite, the synthesis of mixed semiconductors can be carried out by co-precipitation methods (heterojunction formation), by impregnation methods (heterojunction formation or surface functionalization), by hard mechanical treatments by using planetary ball milling (heterojunction formation), by electro or photo-deposition (nanoparticle metal-catalyst), by thermal

treatment in air or in controlled atmosphere (doped-catalyst or nanoparticle metal-catalyst), etc.

Notably, considerations about charges (e^- and h^+) lifetime would result very interesting. In fact once created, these carriers need to transfer to the surface of the catalyst and maintain their separation as long as the desired reactions occur. The carrier lifetimes are on the nanosecond order in typical semiconductors.[97] In contrast, i.e., the water reduction and oxidation half-reaction need milliseconds and seconds, respectively, to proceed. Clearly, the carrier lifetimes are not long enough for single semiconductors. In nano-crystalline materials, the diffusion length is not too small; the problem usually lies in too short lifetime on the surface. To improve the charge separation, and thereby their lifetime, and to increase the rate of the surface reactions, some modification techniques are also used such as introduction in the lattice of metals and non-metals, metal ions and metal nanoparticle surface loading, and the heterojunction formation.

In this contest, a huge number of researches found heterogonous photocatalysis as a promising green method to perform CO_2 valorisation in order to obtain high added value compounds.

1.4.2 Photocatalytic reduction of CO_2: Overview

Photocatalysis has been reported as a method for activating and converting CO_2 into high added value compounds. Given the high CO_2 stability, the adsorption strategy of CO_2 onto a photocatalyst surface is a key factor to decrease the energy barrier. In particular, through adsorption, the linear structure of CO_2 should possible bend in order to decrease the energy of the lowest unoccupied molecular orbital level. Thereafter, sequential of CO_2 reduction should begin with one-electron transfer to form the corresponding anion radical $CO_2^{-.}$ (Eq. 6). Further reactions mostly involve the transfer of electrons or protons, to break C-O bonds, and create new C-H bonds. [98] To this aim the potential of the charge carriers, the operating conditions and the type of reductant play a key role. All of these features influence the different distribution of the final products.[99-101] First of all,

photocatalytic reduction of CO_2 required the presence of reductant species in order to scavenge the photogenerated hole making the electron photogenerated more available. The main reductants used to this purpose are H_2O, H_2, CH_4, and CH_3OH, [102] which, undoubtedly, differently affect the reaction pathways.

It is reported that, carbon-free reductants such as H_2O and H_2 lead to the formation of C_1 and C_2 products. Even if H_2 is favoured in agreement with the eq. 8, its use is not the best choice for economic and safety reasons.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad\qquad \Delta G^0 = -165 \text{ kJ/mol} \qquad\qquad \text{Eq. 8}$$

On the contrary, H_2O being an excellent green and cheap compound represents the best alternative, and it is commonly used to CO_2 photoreduction.

Unfortunately, there is limited knowledge on the actual reaction routes, so that several pathways have been proposed.

The first step is the formation of $CO_2^{\cdot-}$ anion radical through one electron transfer from the CB of the photocatalyst to CO_2 (Eq. 6).[103, 104]

By observing Figure 13, it can be seen that electrons photogenerated in the conduction band of the most candidate semiconductors do not have enough negative potential driving force to carry out the one-electron reduction of CO_2 to $CO_2^{\cdot-}$.[105, 106]

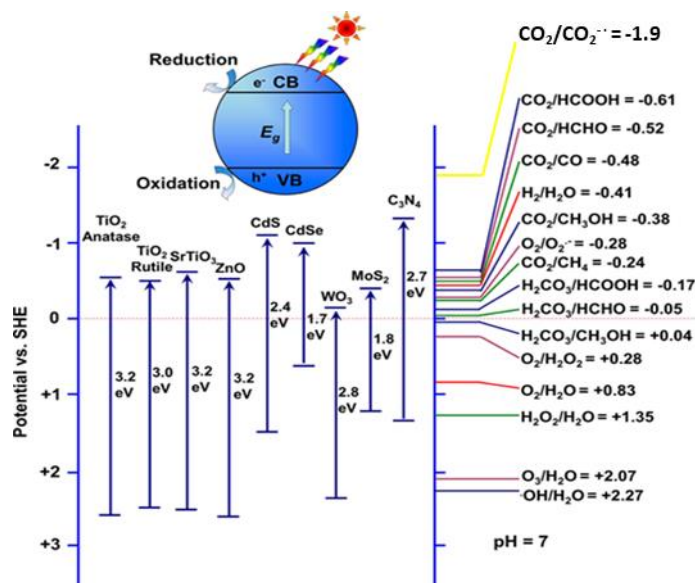*Figure 13. Potentials for various redox couples in water (pH 7) and the band-edge positions of semiconductor photocatalysts reported by Kou et al. [90]*

Figure 13 summarizes the association between band-edge positions of photocatalysts and the potentials for various redox couples in water (pH 7). [90, 102, 107]

The thermodynamic limitations would make impossible the activation of the CO_2 molecule. [10]

However, multi-electron transfer reactions coupled with proton exchange possess suitable redox potential so that the formation of a high-energy $CO_2^{\cdot-}$ radical can be bypassed (Table 2). This Proton Coupled Electron Transfer has been firstly highlighted in a pioneering photoelectro-chemical study carried out in liquid phase from Inoue et al. on 1979.

Table 2. The main products of CO_2 reduction using water as reductant and the corresponding reduction potentials with reference to SHE (Standard Hydrogen Electrode) at pH 7 in aqueous solution, 25 °C and 1 bar gas pressure. [10]

Reaction	E_0 (V vs SHE)	Equation (n°)
$H_2O + 2h^+ = \frac{1}{2} O_2 + 2 H^+$	+1.23	9
$CO_2 + 2H^+ + 2e^- = CO + H_2O$	-0.51	10
$CO_2 + 2H^+ + 2e^- = HCOOH$	-0.58	11

$CO_2 + 6H^+ + 6e^- = CH_3OH + H_2O$	-0.39	12
$CO_2 + 8H^+ + 8e^- = CH_4 + 2H_2O$	-0.24	13
$2CO_2 + 12H^+ + 12e^- = C_2H_5OH + 3H_2O$	-0.33	14
$2CO_2 + 14H^+ + 14e^- = C_2H_6 + 4H_2O$	-0.27	15

By considering the number of electrons transferred, formation of CO and HCOOH, requiring just two electrons (Eq. 10 and 11 in Table 2, respectively), should be kinetically favoured. On the other hand, CH_4 formation should be thermodynamically favoured by considering its reduction potential.

However, in the relevant literature it is reported that the product distribution strongly depends on the operating conditions. For instance, being the same number of electrons required (2e-) formation of CO is favoured in gas phase, whilst formation of HCOOH is favoured in liquid phase. Furthermore, even if CH_4 formation is thermodynamically favoured with respect to CH_3OH, it has been detected only in gas phase reactions while CH_3OH formation (6e$^-$ required, eq. 12 in Table 2) was observed both in liquid and gas phase reactions.

Recently, Olivo et al.,[108] compared the product distribution in vapour and liquid phase tests, and they found that the reduction of H^+ to H^- strongly affects the process activity and selectivity depending on the reaction medium. As shown in Figure 14, in this the study authors pointed out that in the gas phase the deoxygenation step is faster than hydrogenation thus causing the preferential formation of CH_4. On the contrary, in liquid phase CH_3OH, HCHO and HCOOH are the main products as the hydrogenation step is faster than the deoxygenation.

Another method to enhance the reduction efficiency of CO_2 is the use of a hole-scavenger. Several low molecular weight organic compounds such as MeOH, EtOH or TEOA (triethanolamine) are suitable to this aim. Unfortunately, these compounds are also products of CO_2 photoreduction, (Table 2); therefore, their use should be avoided. Inorganic sacrificial agents are more appropriate such as Na_2SO_3 or Na_2S salts.

$$H^+ + e^- \rightarrow \cdot H$$

$$CO_2 \xrightarrow[\text{deoxygenation}]{\text{fast}} \cdot C + O_2 \xrightarrow{4 \cdot H} CH_4$$

$$CO_2 + e^- \rightarrow \cdot CO_2^-$$

$$\cdot CO_2^- + 2 \cdot H \xrightarrow[\text{hydrogenation}]{\text{fast}} HCOOH$$

$$HCOOH + 2 \cdot H \rightarrow HCHO + H_2O$$

$$HCHO + 2 \cdot H \rightarrow CH_3OH$$

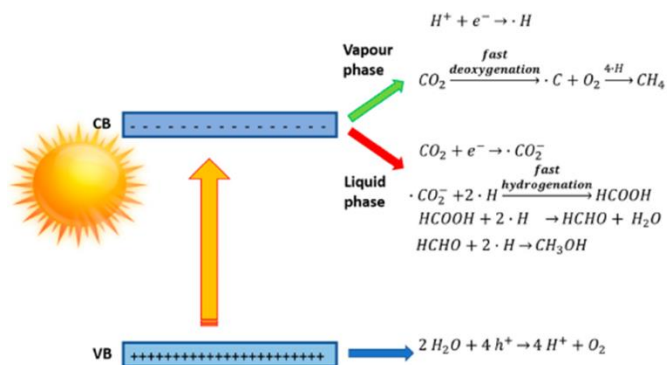$$2 H_2O + 4 h^+ \rightarrow 4 H^+ + O_2$$

Figure 14. Different reaction mechanisms in liquid and gas phase reported from Olivo et al.[108]

Stolarczyk et al.[97] observed that the use of sacrificial agents reduces the overall efficiency of the process. The difference between the redox potentials of the reduction and oxidation half-reaction determines the amount of energy stored in the photocatalytic process. The use of a sacrificial agent provides an additional loss mechanism, because the stored energy is accordingly decreased by the difference between the redox level of the scavenger and that of CO_2 reduction. [97]

From all of the above-mentioned considerations, the choice of the opportune photocatalyst is extremely relevant and still a challenging task. Suitable surface characteristics should allow a better CO_2 reduction and water oxidation.

In the following sections, detail on CO_2 reduction carried out in the presence of TiO_2, ZrO_2, C_3N_4 and graphene based material will be presented because they are relevant for the aim of this Ph. D thesis.

1.4.3 Photocatalytic reduction of CO_2: Metal oxide materials, TiO_2 and ZrO_2

For the first time, Inoue et al.[105] carried out photocatalytic CO_2 reduction in liquid phase by using several semiconductors such as TiO_2, WO_3, ZnO_2, CdS, GaP, and SiC using H_2O as reducing agent. This pioneering work, reported the production of

HCHO, HCOOH, CH_3OH and trace of CH_4, under 500W Xenon or 500 W high-pressure mercury arc lamp.

Titanium dioxide is a white solid, thermal stable, no toxic, and a cheap material used in a huge number of industrial products such as sunscreens, toothpastes, paint, food additives (E171), etc.

TiO_2 is naturally occurring in three allotropic forms named anatase, rutile, and brookite. TiO_2 can be also synthesised starting from inorganic or organic precursor, by hydrolysis of $TiCl_4$, $TiOSO_4$, or alkoxides such as titanium isopropoxide and butoxide. By opportunely tailoring the operating conditions of the synthesis (appropriate precursor, pH, thermal treatment, additives, separation process), it is possible to obtain only one, two or all of the above mentioned crystal phases and to set the particle size and specific surface area.[109-112] Furthermore, with the aim of CO_2 photoreduction, a recent research published by Yang et al.,[113] focused the attention on TiO_2 precursors. By diffuse reflectance infrared Fourier transform spectroscopy and isotopically labelled $^{13}CO_2$, this study demonstrates that carbon residues deriving from precursors and solvents participate to the CO formation. Therefore, authors[114, 115] suggest to "cleaning" the photocatalysts under irradiation prior to their use for CO_2 reduction.

The three allotropic TiO_2 forms have different band gap energies. As reported by Monai et al.,[116] anatase and rutile show band gap approximately equal to 3.2 and 3.02 eV, respectively. The values reported for brookite ranges between 3.1 and 3.4 eV.[116] The conduction band edge for TiO_2 is ca. -0.5 eV (Figure 13). So that, it is a candidate for the CO_2 reduction.

As above-mentioned, until 1979 to now a huge number of investigations on CO_2 reduction were published, especially using titanium dioxide, and some of these reports are summarised in Table 3.

Table 3. Literature survey of photocatalytic CO_2 reduction catalysed by pristine and doped TiO_2 based materials using H_2O as the reducing agent in batch reactor.

Photocatalyst	Light source, phase, Pressure, Temperature, etc	Products, µmol g⁻¹ h⁻¹	Ref.
TiO_2	75 W high pressure Hg, gaseous, 2 °C	CH_4 ($3.5 \cdot 10^{-3}$), CH_3OH ($2.4 \cdot 10^{-3}$), CO traces	[117]
TiO_2	4.5kW Xenon lamp, liquid and gaseous, NaOH, 0.25 µbar, 20°C	CH_4(0.08),CH_3OH (0.15), H_2,(0.18), C_2H_5OH (0.25), C_2H_4 (traces) Total product in gas and liquid phase.	[118]
TiO_2	990 W Xenon lamp, liquid, 65 bar, 25°C	HCOOH (0.6)	[119]
TiO_2 (P25)	15 W GTE F15T8/BLB lamp, liquid, 25°C	CH_3OH (0.41 µM g⁻¹h⁻¹)	[120]
TiO_2 ($TiCl_4$)	400 W medium pressure Hg, gaseous	CH_4(0.01),CH_3CHO (traces),HCHO(0.03)	[110]
TiO_2 (P25)	125 W medium pressure Hg, liquid, 7 bar, 80°C, Na_2SO_3 hole trap	CH_4(0.01),CH_3OH (0-351),HCHO(0-16560), CO (0.7-13),H_2 (0-103),HCOOH (59-2960)	[108]
TiO_2	A300W HRC UV-VIS and 400 W Xe-Halogen lamp, liquid, NaOH, $NaHCO_3$, 25°C	HCOOH (16-23)	[121]
Cu/TiO_2	75 W high pressure Hg, 2 °C	CH_3OH ($6 \cdot 10^{-3}$)	[117]
1% Cu/TiO_2 ($TiCl_4$)	400 W medium pressure Hg, gaseous	CH_4(0.017),CH_3CHO (0.01), HCHO(0.2)	[110]
TiO_2 (P25) GaP/TiO_2	1500Whigh pressure Xe lamp, gaseous, 70°C	CH_4(0) CH_4(0.52)	[122]
Me/Porphirine/TiO_2 (Me=Zn,or Cu)	300W HRC UV-VIS and 400 W Xe-Halogen lamp, liquid, NaOH, $NaHCO_3$, 25°C	HCOOH (6.5-26)	[121]
1-7% Ag/TiO_2	8W Hg lamp, liquid,	CH_4(0.36), CH_3OH (0.072) CO (0.048), H_2 (5.6)	[103]
CuO/TiO_2	250 W high pressure Hg lamp, liquid, 25 °C, MeOH, CTAB	$HCOOCH_3$ (1600)	[123]
TiO_2 CeO_2/TiO_2	500 W Xenon lamp, liquid, NaOH,	CH_4 (6 µmol g⁻¹) CH_4 (18.6 µmol g⁻¹)	[124]
$Pd/RuO_2/TiO_2$ Pd/TiO_2, TiO_2	450 W Xe short arc lamp, liquid, NaOH, NA_2SO_3 hole trap,	$HCOO^-$ (72 ppm) $HCOO^-$ (69 ppm) $HCOO^-$ (20 ppm)	[125]
TiO_2 $N-TiO_2$ nanotube$N-TiO_2$	500 W tungsten–halogen lamp, liquid, NaOH,	HCOOH (20) HCOOH (334), HCHO (70) HCOOH (1040), HCHO (77), CH_3OH (94)	[126]
$Cu/Ce/TiO_2$	125 W UV lamp, liquid, NaOH, 50-70-90 °C,	CH_3OH (5-11.3)	[127]
TiO_2 (P25) $TiO_2/Cu/C$	32 W Hg lamp, liquid, NaOH, 25 °C	CH_4 (1.5), CO (7.7) CH_4 (2.5), CO (20)	[128]
$TiO_2/SBA-15$	120 W high-pressure Hg lamp, gaseous, H_2O or H_2 as reducing agent	CH_4 (4.3-2.1 ppm) C_2H_4 (2.5-1.4 ppm) C_2H_6 (3.7-0.8 ppm)	[129]
$TiO_2/SBA-15$ $Au/TiO_2/SBA-15$	200 W Hg/Xe lamp, gaseous, He	$CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}$ (ca. 30 ppm) $CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}$ (ca. 37 ppm)	[114]

TiO$_2$ TiO$_2$/Y-zeolite Pt TiO$_2$/Y-zeolite	high-.pressure Hg lamp, gaseous, 55 °C,	CH$_4$ (0.5) CH$_4$ (5),CH$_3$OH (0.5) CH$_4$ (8),CH$_3$OH (5)	[130]
Cd/Se/ TiO$_2$	300 W Xe arc lamp, liquid	CH$_4$ (48 ppm g^{-1} h^{-1}), CH$_3$OH (3.3 ppm g^{-1} h^{-1}), H$_2$ and CO (traces)	[131]
TiO$_2$ micro-size 1% Pt/TiO$_2$	300 W Xe lamp, gaseous	CH$_4$ (2.5), CH$_4$ (6)	[132]
P25 TiO$_2$ Pt/ TiO$_2$ Cu$_2$O/ TiO$_2$	300 W Xenon arc lamp, 0.8 bar, gaseous, porous structure	CH$_4$ (3.7 ppm g^{-1} h^{-1}) CH$_4$ (2.4 ppm g^{-1} h^{-1}) CH$_4$ (3.2 ppm g^{-1} h^{-1}) CH$_4$ (28.4 ppm g^{-1} h^{-1})	[133]
TiO$_2$ Anatase Ni- TiO$_2$ Ni-CNT/TiO$_2$	75 W visible daylight lamp, gaseous	CH$_4$ (0.04) CH$_4$ (0.05) CH$_4$ (0.07)	[134]

As reported in Table 3, TiO$_2$ has been differently modified in order to improve the CO$_2$ reduction efficiently. For instance, TiO$_2$ has been decorated with metal (Ag, Pt, and Rh) nanoparticles in order to take advantage of the plasmonic effect and of the resulting visible absorption. Metal ions loaded on the TiO$_2$ surface acting as electrons sink in order to enhance the available electrons. TiO$_2$ has been also coupled with other metal oxide such as CeO$_2$ able to increase the CO$_2$ absorption.

Another promising way to increase the TiO$_2$ photocatalytic performance toward the CO$_2$ reduction is its coupling with graphitic materials such as graphene or carbon nitride (C$_3$N$_4$). In the first case the electron hole recombination phenomena, generally limiting the TiO$_2$ efficiency, are reduced due to the outstanding conductivity of graphene. Coupling TiO$_2$ and C$_3$N$_4$ not only favours spatial charges separation (see section 1.3.1), but also enlarges the absorption of the composite towards visible light, being C$_3$N$_4$ a yellow coloured powder. The graphitic C$_3$N$_4$ and graphene TiO$_2$ composite will be discussed later in the 1.3.4 and 1.3.5 sections.

While the TiO$_2$ based materials have been extensively investigated, few researches have explored the potential of Zirconium dioxide (ZrO$_2$) to obtain high added value molecules from CO$_2$ photoreduction. ZrO$_2$ is a white solid, most naturally occurring in its monoclinic crystalline structure, in baddeleyite minerals (ZrSiO$_4$).

ZrO_2 is industrially prepared from natural ores, $ZrSiO_4$, by the alkali fusion, plasma fusion or a carbon reduction methods. Zirconium is a transition metal electronically similar to titanium. Due to its ion conductivity[135, 136] high chemical stability and resistance to corrosion, ZrO_2 is used for biomedical application[137] as an implant biomaterial, [138] for dental crown,[139] femoral heads for total hip replacement.[140]

Due to its proprieties, ZrO_2 finds also applications as solid oxide in fuel cell[141] and catalysis,[135, 141] for reaction of hydrogenation, dehydration and skeletal isomerization of hydrocarbons.[142-144]

The reason for the poor interest to use ZrO_2 as photocatalyst is due to the wide band gap value ranging from 5 to 7 eV depending on the phase (cubic, tetragonal, monoclinic, or amorphous). However, due to its outstanding thermal stability and to the presence of both surface acid and basic sites, ZrO_2 has found applications in photo-oxidation of chemicals[145-147] and water photo splitting. [148]

Furthermore, the very negative potential of photogenerated electrons makes ZrO_2 a good candidate for photoreduction reactions. In fact, the conduction band edge lies at ca. −1.0 V (vs. SHE, pH 0),[148] i.e., much more negative than that of TiO_2 anatase (−0.1 V), whereas the potential of the valence band is ca. +4.0 V, more positive than that of TiO_2 (+3.1 V). Introduction of new electronic states in the wide band gap ZrO_2 by defects or doping with rare earth elements modifies the optical properties of ZrO_2 giving rise to an active photocatalyst, which can absorb also fractions of the visible light as reported by Gionco et al.[147, 149]

Furthermore, favourable CO_2 adsorption onto ZrO_2 is reported in the relevant literature. In fact, structural studies, reported high concentration of acid and basic sites, as measured by the amount of irreversibly adsorbed ammonia and CO_2, respectively.[143] In detail, ZrO_2 calcined at 600°C exhibits 0.6 µmol/m^2 of acidic and 4 µmol/m^2 of basic sites. Additionally, infrared spectroscopic studies revealed the presence of Lewis type acid sites, but not protonic (Bronsted acid) sites.

Some studies report ZrO_2 induced CO_2 photoreduction by water as the reductant. For instance, Lo et al., obtained 0.1 µmol g^{-1} h^{-1} of CO from CO_2 and H_2O under UV light set at 43°C and at 1.1 bar in the presence of ZrO_2.[150] In particular high

products yield was obtained using H_2-H_2O mixture or just H_2 but not with only water. [150]

However, the best results are reported by Sayama et al., which tested ZrO_2, 0.1% Pt-ZrO_2, 0.1% Au-ZrO_2, 1% Cu-ZrO_2, 1% RuO_2 – ZrO_2 photocatalysts. The highest values of CO and H_2 formation i.e., 1.1 and 285 µmol h^{-1} respectively, were obtained in the presence of bare ZrO_2.[148]

1.4.4 Photocatalytic reduction of CO_2: Graphene composite materials

Graphene is a planar 2D material characterized by a honeycomb-like structure of sp^2 carbon atoms. The synthesis of graphene from graphite essentially involves mechanical or chemical exfoliation.[151] The mechanical exfoliation represents the easiest method, but unfortunately affords low yields and requires long production time.[152] On the contrary, chemical exfoliation appears suitable for large-scale production. One of the most common chemical exfoliation methods is called colloidal suspension and it was developed by Brodie, [153] Staudenmaier,[154] and Hummers.[155] In the presence of strong acids and oxidants, graphite is converted to exfoliated graphene oxide, which in turn can be chemically reduced to graphene.

Graphene is a low cost material with high versatility, tuneable physicochemical, mechanical and chemical stability, opto-electronic proprieties, excellent electron and thermal conductivity. [156-159] The number of layers, the lateral size, dimensionality, edge structure, defect density, and reduction degree can be also easily controlled.[160, 161]

Because of these peculiarities, this material finds several applications in electronics,[162] optoelectronics,[163] and mass and energy transport. [164]

Graphene has been used as support for various nano-hybrids materials as semiconductors, being an electron collector and transporter capable to efficiently hinder electron-hole recombination.[165] This action extend the lifetime of the photo-generated charge carriers, [166] making electrons more available for the reduction of

species present in the reacting mixture, while the holes remain localised in the semiconductor valence band. This results in a high spatial charge separation of the photo-induced electron-hole pairs.

Graphene nanosheets present huge theoretical specific surface area,[167] commonly believed as the highest among all of the known materials. Another peculiarity of this material concerns the possibility, during the synthesis by chemical method, to improve the nanoparticles dispersion, and to reduce their size owing to the large volume/surface ratio and to the presence of opportune functional groups. Recent studies demonstrate that these functional groups (i.e., C=O, COOH, etc.) can act as anchoring sites and allow the growth of the photocatalyst particles on their surface.[168] Hence, photocatalysts can be uniformly deposited on the surface of graphene nanosheets, thus inhibiting aggregation. Additionally, because of its black colour and being a conductor (zero band gap), graphene can absorb almost throughout the whole spectrum of solar light, enhancing light absorption of composite. Unlike the good light absorption ability, graphene does not create active electrons or holes for the photocatalytic reactions but it can efficiently transport electrons. Finally, graphene can increase the temperature around the photocatalyst to create a confined photothermal effect.[169, 170]

Due to the lower cost with respect to noble metals and because of its peculiar physic-chemical proprieties, the photocatalytic application of graphene has been largely investigated. A huge number of researches reports the graphene as cocatalyst for a wide range of photocatalytic applications.[171] For example, graphene can prevent CdS from photocorrosion in the visible-light photocatalytic H_2 production.[172] It can address the selectivity of CdS towards aldehydes in alcohols oxidation reactions, under mild conditions.[173]

By wrapping the photocatalyst such as Cu_2O and CdS and avoiding their photocorrosion induced by the attack of active species, such as •OH radicals,[174] graphene increases the cocatalyst stability.

Furthermore, graphene can be used as cocatalyst to increase the reduction ability such as in the case of metal oxide. As shown in Figure 15, the best photocatalysts

for the occurring of reduction reactions are carbon nitride (C_3N_4), CdS, Cu_2O, ZnS. Notably, on the contrary, the metal oxide material exhibits oxidation ability.
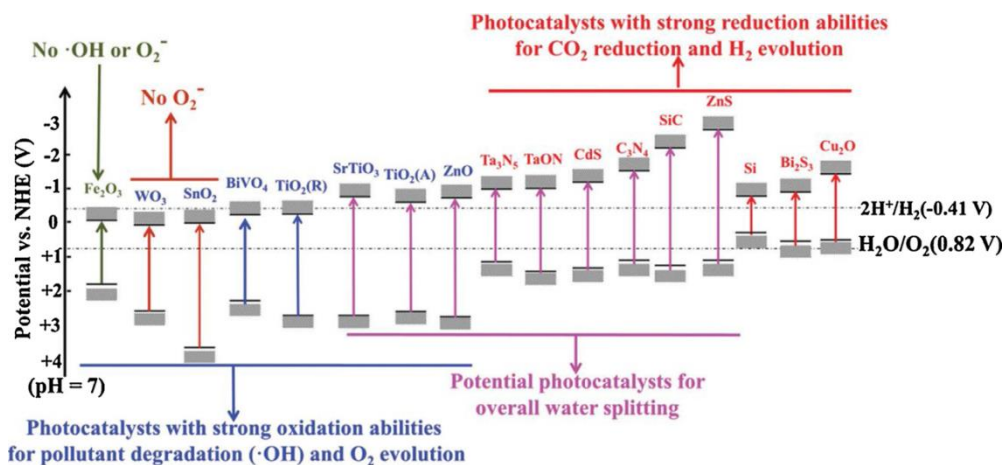

Figure 15. Band positions and potential applications of some typical photocatalysts at pH = 7 in aqueous solutions, reported from Li et al.[175]

In fact, several researches propose the graphene/TiO_2 heterojunctions as promising photocatalysts in the field of energy conversion and environmental applications. [165, 166, 176]

Two key points make graphene a promising cocatalyst for the photocatalytic CO_2 reduction: (i) Electron conductivity: the electron density[177] on the graphene nanosheet is high and favours multi-electron reactions for photocatalytic CO_2 reduction (Table 2). (ii) CO_2 adsorption and activation. Due to the graphene large 2D π-conjugated structure and the delocalized π-conjugated binding π^4_3 of CO_2, a $\pi-\pi$ conjugation interaction can be established between graphene and CO_2. The graphene $\pi-\pi$ conjugation interaction can significantly facilitate the adsorption of CO_2 molecules on the graphene-based photocatalysts, thereby improving the photocatalytic CO_2 reduction activity. Notably, this interaction can also cause destabilization and activation of CO_2 molecules enhancing photocatalytic CO_2 reduction reactions.[174]

Table 4. Literature survey of photocatalytic CO_2 reduction catalysed by G based materials, focusing to TiO_2/graphene composites, using H_2O as reductant in batch reactor.

Photocatalyst	Light source, phase, Pressure, Temperature, etc.	Products, $\mu mol\ g^{-1}\ h^{-1}$	Ref.
0.27 % G/P25 (0.27, 0.55, 1.09, 2.15 G%)	100W Hg lamp or 60W,Halco Lighting, Pure Lite Neodymium Vis lamp, gas phase, film catalyst 6.45 cm^2	CH_4 (8.3$\mu mol\ m^{-2}\ h^{-1}$) under UV CH_4 (4 $\mu mol\ m^{-2}\ h^{-1}$) under Vis	[178]
8.5 %G/TiO$_2$ (2.21, 8.5, 16.39 G%)	150W Vis lamp, 25 °C, liquid phase, 1 mol/L NaOH	CH_3OH (15) HCOOH (16)	[179]
0.5 % G/P25$_2$ (0.25, 0.5, 1 G%)	100W Hg lamp or 60W,Halco Lighting, Pure Lite Neodymium Vis lamp, gas phase, film catalyst 6.45 cm^2	CH_4 (9.3$\mu mol\ m^{-2}\ h^{-1}$) under UV CH_4 (0.15 $\mu mol\ m^{-2}\ h^{-1}$) under Vis	[180]
2 %G/P25$_2$ (0, 1, 2, 5 G%)	300 W Xe lamp, gas phase	CH_4 (8) C_2H_6 (16.8)	[181]
TiO$_2$/G N–TiO$_2$/G	15 W Vis Lamp TORNADO 220–240 V Philips, 25 °C, gas phase	CH_4 (3.21) CH_4 (3.60)	[182]
GO/P25 G/P25 B-G/P25	300 W Xe lamp, 25 °C, liquid phase, Na$_2$SO$_3$ hole trap	CH_4 (0.32) CH_4 (0.7) CH_4 (1.25)	[183]
G/WO$_3$	300 W Xe lamp, 1 mL H$_2$O, gas phase,	CH_4 (1.11)	[184]
GO N doped G N doped G/CuC	20W-F-Hope LED Opto-Electric, DMF and H$_2$O, liquid phase,	CH_3OH (16) CH_3OH (31) CH_3OH (70)	[185]
1% NiO$_x$– Ta$_2$O$_5$/G	400 W metal halogen lamp, liquid phase, HCO$_3^-$, CO$_2$, NaOH	CH_3OH (1 $\mu mol\ h^{-1}$) H_2 (0.82 $\mu mol\ h^{-1}$)	[186]
Cu$_2$O/ G	six lamps at 8.3 mW/cm^{-2} USHIO G8T5, gas phase, NaOH, 35 °C	$CH_3\ CH_2OH$ (20) H_2 (140)	[187]
GO/TiO$_2$ Cu-GO/TiO$_2$	UV/vis Heraeus TQ 150 medium-pressure Hg vapour lamp, 25°C, liquid phase, He/CO$_2$, at different pH, several Cu precursor	CH_3OH (12-45) $CH_3\ CH_2OH$(17-150) CH_3OH (8-60) $CH_3\ CH_2OH$(17-90)	[188]
G/TiO$_2$ in spheres of PMMA or PEI	300 W Xe arc lamp, gas phase,	CH_4 (1.2) CO (9)	[189]

*where GO and G are graphene oxide and graphene respectively.

Table 4 presents a survey of relevant reports focusing on the use of graphene-based materials for CO$_2$ photoreduction, in particular between graphene and TiO$_2$.

As reported in the Table 4, the graphene-based materials produce preferentially CH$_4$ and methanol from CO$_2$ photoreduction. In all the reported studies, the materials are generally synthesised by means of solvothermal, hydrothermal, or electrostatic self-assembly strategies ultrasound assisted methods or through.

1.4.5 Photocatalytic reduction of CO_2 by C_3N_4 pristine, O doped and composite TiO_2/g-C_3N_4

Recently, due to its facile synthesis, no toxicity, reduction activity, enhanced photoexcited charge conductivity,[190] appealing electronic band structure and high (claimed) physicochemical stability, [191]2D graphitic carbon nitride (g-C_3N_4), a new metal free polymer has been introduced as an emergent photocatalyst.

g-C_3N_4 consists of earth-abundant C and N elements bond in a π rich aromatic structure easy to be modify without significant structural and composition changes.[191]

The g-C_3N_4 exists in seven different phases, i.e., α-C_3N_4, β-C_3N_4, cubic C_3N_4, pseudo cubic C_3N_4, g-h-triazine, g-h-heptazine and g-o-triazine with band gap energy of 5.49, 4.85, 4.30, 4.13, 2.97, 2.88 and 0.93 eV, respectively. [192, 193] Although all these phases are semiconductors, only g-h-heptazine and g-h-triazine, containing 14 and 28 of C and N atoms respectively in the elementary cells, possess suitable band gap and band edge potentials to drive photocatalytic processes.[192, 193] However, by considering the position of the valence band, only the g-h-heptazine phase meets the potential requirements for water oxidation. [192, 193] For this reason g-C_3N_4 in this form, is one of the most frequently investigated photocatalysts for H_2 production. Additionally, in principle, the CB edge of g-C_3N_4 is enough negative to reduce CO_2 (Figure 16). [191, 194, 195]
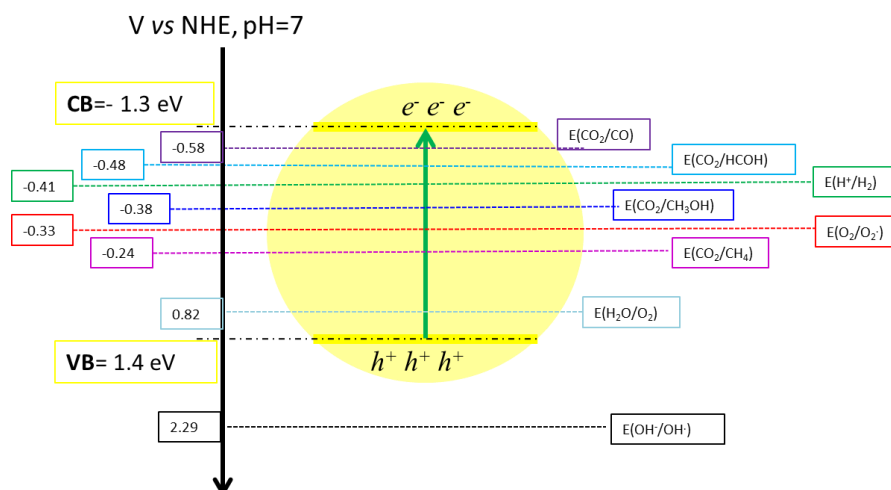
Figure 16.The redox potentials of the relevant products of CO₂ reduction with respect to the estimated position of the g-C₃N₄ conduction and valence band edges (CB and CV) at pH 7.[195]

g-C_3N_4 shows other advantages for CO_2 photoreduction because it is rich of N basic sites, which favour the CO_2 adsorption step. Due to these outstanding properties, several reports was published on different synthetic strategies affording specific crystal phase, surface area, band gap position and band gap energy.

The most common g-C_3N_4 synthesis consists in the thermal condensation of Melamine, or of its precursors (cyanamide or dycianamide), as reported by Ong et al. (Figure 17). [191]

g-C_3N_4 results from condensation of various melem units (monomer) having C/N molar ratio of ca. 0.75, which is the theoretical value of the final polymer (Figure 17).
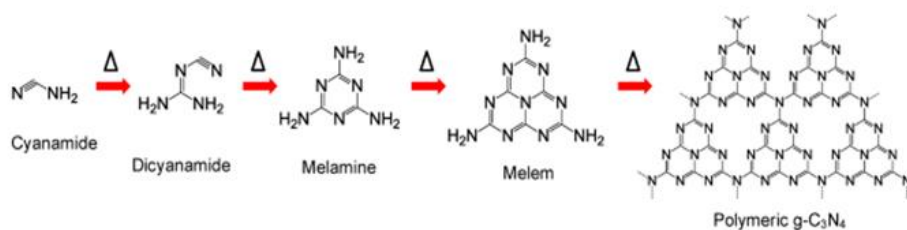
Figure 17. Schematic g-C₃N₄ synthesis by three different precursors, reported by Ong et al.[191]

The as synthesised polymer generally presents low specific area (ca. 10 m^2 g^{-1}), so that the exfoliation process, that can occur by chemical and thermal methods, is used to increase the exposed surface. The thermal treatment seems to be a most simple and effective method also to enhance the photocatalytic and electronic proprieties of g-C_3N_4. [196, 197] In fact, thermal treatments reduce the starting bulky material to a layered one.

In this field, computational studies demonstrated that the number of layers influences also the light absorption ability and the corresponding photoactivity (photoelectric proprieties),[198] as reported in Table 5.

Table 5. Band gaps (ΔE_g) of heptazine and triazine g-C_3N_4 nanosheets with different thickness, obtained by means of computational studies.

Geometry	ΔE_g Heptazine g-C_3N_4, eV	ΔE_g Triazine g-C_3N_4, eV
1 layer nanosheet	3.03	3.81
2 layer nanosheet	2.85	3.51
3 layer nanosheet	2.79	3.42
4 layer nanosheet	2.75	3.38
Bulk	2.70	3.31

In order to increase the CO_2 photoreduction activity of carbon nitride, doping is a suitable method to change the band structure and the adsorption properties. By changing opportunely the precursor, it is possible to introduce non-metal atoms into the lattice of g-C_3N_4, as shown in Figure 18.
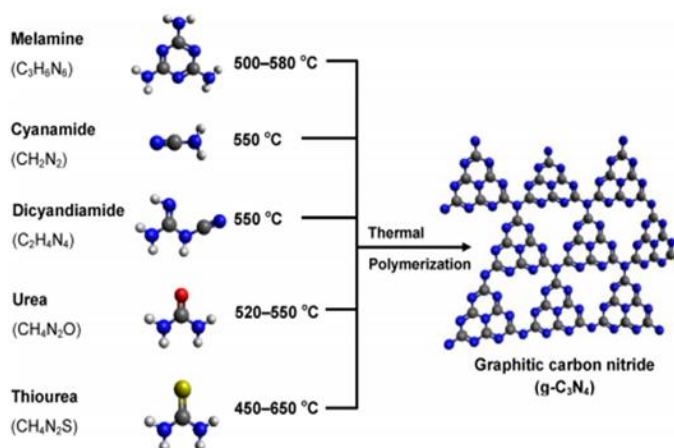
Figure 18. Thermal synthesis to obtain pure and non-metal doped g-C$_3$N$_4$, reported by Ong et al. [191]

S doping is generally obtained by using thiourea like precursor O doping derives from urea like precursor or from successive oxidation of g-C$_3$N$_4$ with H$_2$O$_2$. [199] Treatment of g-C$_3$N$_4$ with ethylene diphosphonic acid [200] or with red phosphor[201] produces P doping.

The incorporated heteroatoms increase the delocalization of π-electron in the g-C$_3$N$_4$ structure. This effect causes a red-shift of the optical absorption toward longer wavelengths[194] and generally enhances the photocatalytic activity. The operating conditions used during the doping such as the precursor, additives such as barbituric acid, temperature, pressure, etc.,[202, 203] affect the dopant position (C or N site), the molar ratio relative C/dopant and, consequently, the theoretical C/N ratio. Recently, Huang et al. reported the formation energies of O-doped g-C$_3$N$_4$ (O-C$_3$N$_4$) by substituting N and C atoms using O atom.[204] Additionally, this study analyses the formation energy of O-C$_3$N$_4$ distinguishing the different C and N positions present in the C$_3$N$_4$ structure shown in Figure 19.
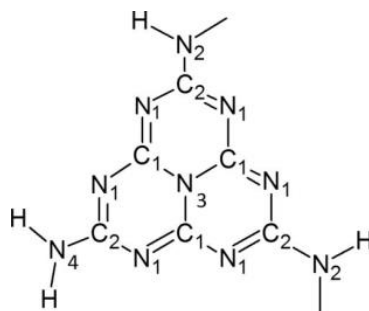
Figure 19. Melem structure repeated in the polymeric C_3N_4 with the corresponding atomic assignation according to XPS analysis as Dante et al. report.[205]

In general, doping generates a "second semiconductor" whose heterojunction may decrease the charge recombination[199, 206] increasing the photocatalytic activity. In particular, non-metal dopants generate a cathodic shift of the valence band edge in combination with a higher conduction band minimum causing a slightly reduced absorbance. The effect of O doping is to promote a downshift of the CB minimum by 0.21 eV without modifying the valence band maximum. Furthermore, the O-doping induces intrinsic electronic and band structure modulations, leading to improved surface area, extended visible light response, and enhanced separation efficiency of the photo-generated charge carriers [199]. By taking into account these properties, a recent study develops a promising O doped C_3N_4 for CO_2 reduction.[206]

g-C_3N_4 was successfully coupled with metal oxides to promote CO_2 photoreduction. In fact, it has a more negative conduction band edge (ca. -1.2 eV) than the most common oxide semiconductors (Figure 15), and this should favour CO_2 reaction even under visible light irradiation.

Hydrothermal methods[207] coupled with thermal treatments[208-210], impregnation methods [211] and vigorous mixing by milling ball[212] are the principal strategies used to form heterojunction between TiO_2 and g-C_3N_4.

g-C_3N_4/TiO_2 composites showed enhanced CO_2 photoreduction activity towards high added value compounds with respect to the pristine materials.

Some reports on CO_2 photoreduction reactions induced by using g-C_3N_4 pure, O-C_3N_4 and C_3N_4/TiO_2 catalysts, are summarised in Table 6.

Table 6. Literature survey of photocatalytic CO_2 reduction catalysed by pristine, O doped and based C_3N_4 materials, using H_2O as reductant in batch reactor.

Photocatalyst	Light source, phase, Pressure, Temperature, etc.	Products, µmol g^{-1}h^{-1}	Ref.
m-g-C_3N_4 u-g-C_3N_4	300 W Xe-lamp with 420 nm cut off filter, liquid phase, NaOH, 1 bar, 20 °C	CH_3OH (traces), CH_3CH_2OH (3.64) CH_3OH (6.28), CH_3CH_2OH (4.51)	213
u-g-C_3N_4 0.03 ba-u-g-C_3N_4 0.03 ATCN-u-g-C_3N_4	300 W Xe-lamp with 420 nm cut off filter, liquid phase, 2.2 bypiridine, TEOA, $CoCl_2$, 1 bar and 30 °C, several loading of BA	H_2 (ca. 1 µmol),CO (2.3 µmol) H_2 (ca. 5 µmol),CO (31.1µmol) H_2 (ca. 7 µmol),CO (37.9 µmol)	214
t-g-C_3N_4 u-g-C_3N_4	300 W Xe-lamp with 420 nm cut off filter, gas phase	CH_4 (traces), CH_3CHO (0.3), CO (0.4) CH_4 (traces), CH_3CHO (0.5), CO (0.6)	215
t-g-C_3N_4 u-g-C_3N_4 P25(TiO_2)	300 W Xe-lamp with 200 nm cut off filter (UV-Vis light), gas phase	CH_4 (0.14), H_2 (0.17), CO (2.1) CH_4 (0.154), H_2 (0.22), CO (1.46) CH_4 (0.1), H_2 (0.39), CO (0.22)	215
t-g-C_3N_4 m-g-C_3N_4	300 W Xe-lamp UV-vis light, liquid phase, $NaHCO_3$ HCl, H_2PtCl_6, 1 bar	CH_3OH (0.37) CH_3OH (0.3)	216
m-g-C_3N_4 O-C_3N_4 tube	350 W Xe-lamp with 420 nm cut off filter, gas, $NaHCO_3$ and H_2SO_4	CH_3OH (0.17) CH_3OH (0.88)	206
u-g-C_3N_4 BTN (TiO_2 nanotube) C_3N_4/BTN	300 W Xe-lamp with 420 nm cut off filter, gas phase, $NaHCO_3$ and H_2SO_4	CH_4 (1.80), CO (7.10) CH_4 (0.17), CO (0.74) CH_4 (5.21), CO (0.84)	208
u-g-C_3N_4 BTN (TiO_2 nanotube) C_3N_4/BTN	300 W Xe-lamp with 200 nm cut off filter, gas phase, $NaHCO_3$ and H_2SO_4	CH_4 (2.5), CO (9.3) CH_4 (0.73), CO (3.31) CH_4 (6.94), CO (1.27)	208
m-g-C_3N_4 m-porous-g-C_3N_4	300 W Xe-lamp with 420 nm cut off filter, gas phase	CO (4.37) CO (0.94)	217
m-bulk-C_3N_4 m-g-C_3N_4	300 W Xe-lamp with 420 nm cut off filter, 15 °C, 25 kPa, gas phase	CH_4 (0.33) CH_4 (0.94)	218
dc-g-C_3N_4 B-dc-g-C_3N_4 B-dc-g-C_3N_4/ TiO_2	300 W Xe-lamp with 420 nm cut off filter, liquid phase	CH_4 (5) CH_4 (44) CH_4 (67)	219
dc-g-C_3N_4 B-dc-g-C_3N_4 B-dc-g-C_3N_4/ TiO_2	300 W Xe-lamp, liquid phase	CH_4 (14) CH_4 (50) CH_4 (70)	219
u-g-C_3N_4 u-g C_3N_4/ N-TiO_2	300 W Xe-lamp, gas phase, 30°C	CO (3.8) CO (12.2)	220
m-g-C_3N_4 m-g-C_3N_4/ TiO_2	8 W Hg lamp, gas phase, 120 kPa, 50 % humidity	CH_4 (4.7), CO (1), H_2 (17.5) CH_4 (8.7), CO (2.8), H_2 (41.3)	221
g-C_3N_4 g-C_3N_4/Cu g-C_3N_4/Cu/TiO_2	Mercury gas UV lamp with an intensity of 5.4 mW/cm^2, liquid phase, UV light, 25°C, NaOH	CH_3OH (40), HCOOH (1200) CH_3OH (210), HCOOH (2250) CH_3OH (470), HCOOH (1000)	222
m-g-C_3N_4 m-g-C_3N_4/Cu m-g-C_3N_4/Cu/TiO_2	500 W Xe-lamp, liquid phase, visible light, 25 °C, NaOH	CH_3OH (240), HCOOH (2250) CH_3OH (350), HCOOH (3100) CH_3OH (450), HCOOH (2250)	222

(*)Where m, u, t, dc and ba indicate melamine; urea, thiourea, dicyanamide and barbituric acid, respectively.

1.4.6 Photocatalytic Reactors for CO_2 reduction: batch vs continuous

The systems currently used for artificial photocatalytic CO_2 reduction result still inefficient and the maximum quantum yields are estimated much below 0.1 %.[223, 224] Therefore, the design of proper reacting systems and the investigation of the related engineering issues are of paramount importance to enhance the efficiency of this reaction.

In general, a chemical reactor used to perform a catalysed reaction must exert at least three functions. In particular, it has to (i) guarantee a proper residence time to perform the chemical reaction, (ii) implement heat exchange, and (iii) allow the direct interaction between reactants and catalyst to facilitate the reaction.

In the case of photocatalytic reactor photons can be considered as immaterial reactants, so that phenomena related to the presence of light must be carefully considered. First of all the materials of which the photoreactor is comprised may absorb light acting as filters for the impinging radiation. Therefore, transparent materials such as quartz or Pyrex should be used. In this dissertation, the batch reactors are made of Pyrex, which cut off light at wavelengths less than 320 nm. In these conditions, the photocatalyst is the light absorbing species and the occurrence of photolytic reactions can be neglected.

Furthermore, an optimal light distribution within the reactor must be ensured so that all of the photocatalysts particles can efficiently activated. For this reason the reactor configuration, the amount of photocatalyst, and light penetration depth are key parameters to be optimised.

Different reactor configurations can be used, which can be mainly divided into two groups: batch and continuous.

A typical batch reactor consists of a tank with agitator mixer with an integrated heating/cooling system where reagents and catalyst are loaded. A batch reactor is a closed reactor where there is not exchange of mass between the reactor and the environment during the reaction. Depending on the aims, also open reactors can be used where one or more reagents are fed to ensure the best conditions (i.e., flux of

oxygen or air in oxidation photoreaction). These vessels may vary shape and size (from less than 1 litre to more than 15,000 litres). They are usually fabricated in steel, glass, stainless steel, glass-lined steel, or other alloys. Liquids and solids are usually charged via connections in the top cover of the reactor. Vapours and gases can be discharged through connections in the top. Liquids are usually discharged out of the bottom. A batch system is the generic term for a type of vessel widely used in the process industries for a variety of process operations such as solids dissolution, product mixing, chemical reactions, batch distillation, crystallization, liquid/liquid extraction and polymerization. Batch reactors are frequently used in wastewater treatment. They are effective in reducing BOD (biological oxygen demand) of influent untreated water. There are also many laboratory applications, such as small-scale productions, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert into continuous operations. They are also used for experiments of reaction kinetics and thermodynamics. Batch reactors are generally considered expensive to run, as well as with variable product distribution reliability.

The photocatalytic CO_2 reduction has been generally performed in batch reactors. This reaction mainly produces volatile compounds; thus, after the introduction of reagents and catalyst, the vessel is generally closed. In this type of system, the residence time coincides with the reaction time. Therefore, generally, the concentration of products (or the amount of consumed reactants) is calculated as a function of the reaction time per gram of catalyst present in the reactor (or per irradiated specific surface area and per number of catalytic sites).

The advantages of the batch reactor consist in its versatility and easy design. A single vessel can carry out a sequence of different operations without any lost in performance terms. This is particularly useful when processing toxic, highly reactive compounds. However, this type of reactor suffers some disadvantages such as high processing costs, difficulties in large-scale productions and in treating unstable reacting mixtures. Furthermore, reactions carried out in batch reactors present low selectivity values especially when undesired secondary routes or back reactions are thermodynamically favoured.

In order to enhance the selectivity towards a target compound, the residence time must be carefully optimized. In fact, if the target compound is a reaction intermediate it may undergo further transformations thus reducing the selectivity of the process. In a batch system, this can be achieved only by stopping the reaction when the target compound concentration reaches its maximum, with relevant disadvantages in terms of plant flexibility and operational costs. On the other hand, in a continuous reactor the residence time distribution can be simply controlled by optimizing the fluid dynamics of the system. The relevance of this issue is even more evident in synthetic applications, especially in cases where the back reaction of the products is faster than their formation, as for instance in the semiconductor induced photocatalytic CO_2 activation for the synthesis of high value added products such as fuels.

Continuous-flow systems may assume two extreme configurations, named continuous stirred tank reactor (CSTR) and plug flow reactor (PFR). In the CSTR system, the flow is perfectly mixed so that the concentration is constant throughout the reactor. On the other hand, the concentration decreases along the flow direction in the PFR. Although PFR has been chosen as the configuration used in the ISO norms for standardization of photocatalytic reactions, CSTR presents relevant advantages. Even if a PFR is more efficient than a CSTR having the same volume,[225] in a CSTR all the catalyst surface is exposed to the same (output) concentration.[226] In steady state conditions, the CSTR can be mathematically described by a set of algebraic equations whereas the PFR requires a set of ordinary differential equations. For these reasons, the European Standard Organization is currently working on standard test methods performed in CSTR configurations.

Continuous processes are used in the chemical industry since decades. Recently, they are used for pharmaceutical,[227, 228] water treatment,[229-231] and fine chemicals [232-235] applications due to the high safety and quality standards, cost efficiency and overall production flexibility. Furthermore, continuous reactors allow to well performing highly exothermic reactions impossible in discontinuous reactors.

In general, continuous reactors possess several advantages such as the possibility of easy scale-up and the efficiency to control the fluid dynamics and the residence time of reactants and products to enhance the selectivity towards target compounds.

Even if batch systems were often applied for CO_2 photo-reduction, fluidised bed reactors and fixed bed reactors are generally the most efficient configurations. In fluidised bed reactors, the photocatalyst is in a fluid-like state so that substrate adsorption and reaction rate are maximized. The problem of product-catalyst separation is in this case negligible by considering the rather volatile nature of the obtained compounds. However, the problems of low surface-area-to-volume ratio, of non-uniform light distribution and poor light utilization efficiency are usually encountered in existing photoreactors.

Notable, being the CO_2 photoreduction strongly depending on parameters such as reactor type, catalyst type and structure, intensity and range of wavelength, pressure, temperature, pH, residence time and reactants molar ratio, comparing results reported in literature research is very difficult due to the various experimental conditions used.

Recently, Hurtado et al. demonstrated under the same experimental conditions the higher efficiency of continuous reactors with respect to the batch reactors for CO_2 photocatalytic reduction. In detail, the reaction has been carried out in water and in the presence of Cu_2O supported on multi-layers graphene in a slurry batch reactor and in a continuous capillary reactor with the catalyst immobilized on the wall. In both cases, authors detected hydrogen as the major photoproduct in the gas phase, along with traces of ethanol in the aqueous solution. The maximum production rates of hydrogen and ethanol were respectively 2031 and 545 μmol g^{-1} h^{-1} in continuous mode and 140 and 20 μmol g^{-1} h^{-1} in batch reactor.[187]

Table 7 reports the relevant literature on CO_2 photoreduction carried out in continuous systems.

Table 7. Literature survey of photocatalytic CO_2 reduction, using H_2O as reductant, in continuous reactors.

Operative conditions	Products, $\mu mol\ g^{-1}\ h^{-1}$	Selectivity, %	Ref
G-Pt/TiO_2 (1.7 cm × 1.7 cm), 500W W–halogen lamp with a high-pass UV filter, gas phase, 100 mL min^{-1}	CH_4= 3 $\mu mol\ m^{-2}\ h^{-1}$	100	[236](2015)
NiO/$InTaO_4$, 500 W halogen, liquid phase, $KHCO_3$ continuous flow	CH_3OH= 1.4	100	[237] (2007)
TiO_2 , 200 UV lamp, He/CO_2 feed 50 mL min^{-1} , gas phase, H_2O/CO_2 molar ratio 0.1	H_2= 50 CH_4= 3.5 CO= 6	84 6 10	[238](2015)
Metal NP/TiO_2 , 200 W Hg lamp, 8 mL min^{-1} , gas phase, 25°C	CH_4= 1.6 C_2H_6= 0.2	89 11	[239] (2017)
Pt/ TiO_2, 400 W Xe lamp, gas phase, 3 mL min^{-1}	CH_4= 1361	100	[240] (2012)
Cu_2O/TiO_2, six USHIO G8T5 lamps, NaOH, liquid phase, 9 mL min^{-1}	H_2= 2031 CH_3CH_2OH= 545	79 21	[187] (2016)
CuO/SiC, 500W Xe lamp, UV filter $NaNO_2$ solution, liquid phase, NaOH, Na_2SO_3	CH_3OH= 38	100	[241] (2011)
Metal/TiO_2, 500 W Halogen lamp, gas phase, 1 bar, 4 mL min^{-1}	H_2= 63 CH_3OH= 26 CH_3CH_2OH =19 CH_3CHO= 20	49 20 15 16	[242](2015)

*NP is nanoparticle

Recently, the combination of continuous photoreactor and membrane technologies resulted in a promising hybrid system called Photocatalytic Membrane Reactor. Such combination offers several advantages. First of all, membranes can allow separation of the photo-catalytically produced target compounds thus avoiding their overreaction and increasing the selectivity of the process. Furthermore, membranes offer large surface-area-to-volume ratio, uniform light and catalyst distribution, better catalyst exposition to light and to reactants, enhanced mass transfer and fine flow control.

1.5 Photocatalytic Membrane Reactor

1.5.1. Membrane reactors: basic principles and applications

A huge number of natural processes occur in the presence of membranes such as vegetal or animal cellular membranes. By definition, membrane is a thin sheet of natural or synthetic material that is semipermeable to substances in solution. Membranes can be constituted of organic, inorganic or hybrid materials. Inorganic membranes are generally made of glass, metal or ceramics. A general classification distinguishes the membranes on the basis of their shape in flat sheet and tubular.[243] Tubular membranes can have different diameter size and can be divided in hollow fiber, capillary, and tubular membranes as shown in Figure 20.
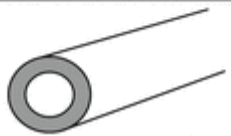
Figure 20. Diameter range of tubular membranes.

The principal function of a membrane is to exert the selective separation of species in a homogeneous or heterogeneous mixture in gas or liquid phase.

This function is possible owing to a dense or porous structure. Generally, dense structures are suitable for gas separation while the porous one for filtration processes. As reported in Table 8, the field of application of the membranes changes depending on their (i) pore size, (ii) molecular weight cut off, (iii) membrane matrix, (iv) type of compounds to be separated, and (v) applied pressure as the driving force of the separation process.

Table 8. Membrane process and corresponding characteristics required.[244]

Parameter	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Pore size, μm	0.01-1.0	0.001-0.01	0.0001-0.001	<0.0001
Molecular Weight Cut off	>100,000	1,000-300,000	300-1,000	100-300
Operating Pressure, psi	<30	20-100	50-300	225-1.000
Membrane Materials	Ceramics, polypropylene, polysulfone, polyvinyldenedifluoride	Ceramics, polysulfone, polyvinyldenedifluoride, cellulose acetate, thin film composite	Cellulose acetate, thin film composite	Cellulose acetate, thin film composite, polysulfonated polysulfone
Membrane Configuration	Tubular, hollow fiber	Tubular, hollow fiber, spiral wound, plate and frame	Tubular, spiral wound, plate and frame	Tubular, spiral wound, plate and frame
Types of micro-organisms and Species Removed	Clay, bacteria, viruses, suspended solids	Proteins, starch, viruses, colloid silica, organics, dyes, fats, paint solids	Starch, sugar, pesticides, herbicides, divalent anions, organics, BOD, COD	Metal cations, acid, sugars, aqueous salts, amino acids, monovalent salts, BOD, COD

A further structural grouping can be done for porous membranes in symmetric and asymmetric type (Figure 21). In symmetric membranes, the structure and the mass transport properties are identical over the entire cross section, and the thickness of the membrane determines the flux. Asymmetric membranes present a not homogeneous pore distribution so that structural and transport properties vary over the cross section. They generally consist of an extremely thin surface layer supported on a much thicker porous, dense substructure. The surface layer and its substructure may be formed in a single operation or in different steps. An asymmetric membrane consists of a 0.1 – 1 μm thick 'skin' layer on a highly porous 100 – 200 μm thick substructure. The skin represents the actual selective barrier whose nature determine the separation properties and the permeation rate. The thickness is an important parameter influencing the mass flux. The separation properties and permeation rates of the membrane are determined by the surface layer, while the substructure acts as a mechanical support. The advantages of asymmetric dense membranes are generally related to the higher fluxes provided

and to the good mechanical stability, so that almost all of the commercial pressure driven processes such as reverse osmosis and gas and vapour separation, are based on this kind of membranes. An important application is the desalination of sea, river, or brackish water. Desalination plants were built especially in the USA, in Israel, and recently in Germany. The permeate water is sterile, desalted, and completely free from particles.[245]

Two techniques are generally used to prepare asymmetric membranes. The first is the phase-inversion process, which in a single step leads to an integral overall structure in which the skin and the support are comprised of the same material. The second is a two-step process producing a (multilayers) composite structure where a thin barrier layer is deposited on a porous substructure. In this case, barrier and support structures are generally made of different materials.
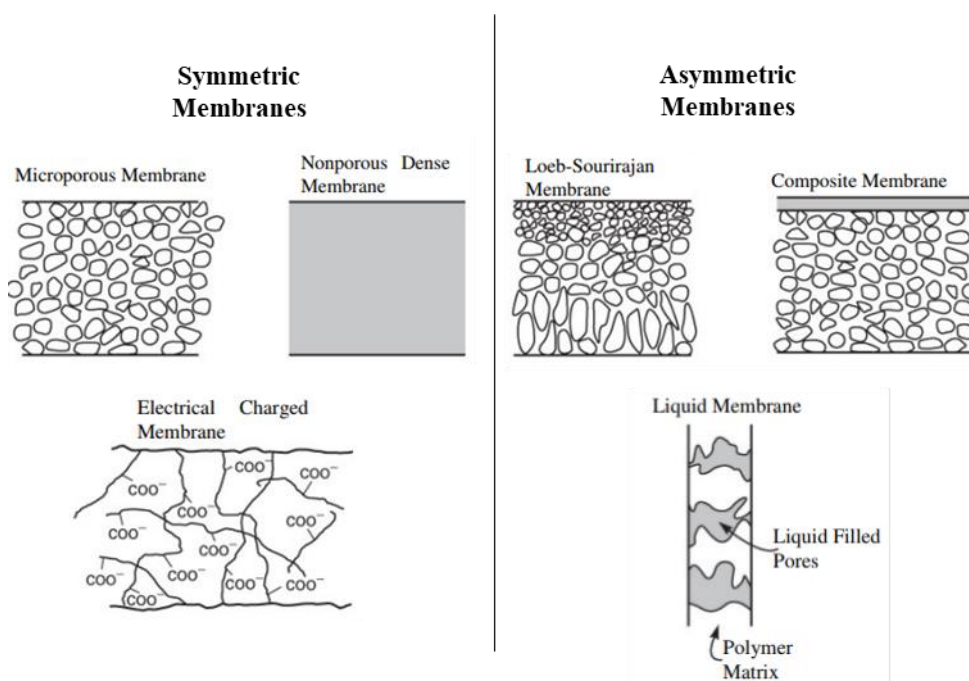
Figure 21. Simplified scheme of symmetric and asymmetric membrane[246].

As above mentioned in Table 8, gradient of partial pressure between the retentate and permeate sides is one of the parameters generally driving the separation process. However, species migration can be also performed through an electrochemical or concentration gradient between the two chambers (donor and acceptor phases) as shown in Figure 22.
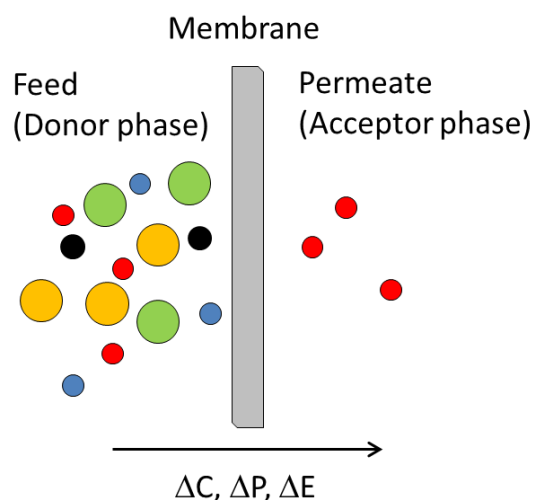
Figure 22. Permeation through a membrane of liquids or gases where ΔC, ΔP, ΔE are the concentration, pressure and electrochemical gradient, respectively.

In detail, when a driving force is applied through a membrane, three different streams can be distinguished: (i) the feed, (ii) the permeate, and (iii) the retentate. The species pass through the membrane with a concentration profile, which affect the mass transport phenomenon.[247] In addition, the transport rate of a species through the membrane is inversely proportional to its thickness. High transport rates are desired in membrane separation processes for economic reasons, so that it is important to use membrane as thin as possible. A crucial point is the mechanism of mass transport through membranes. Two basic models can describe the mass transfer: (i) the solution-diffusion model and (ii) the hydrodynamic model. In the first case, typically occurring in dense membranes, the transport occurs only by diffusion, thus the component that needs to be transported must first dissolve (solution) within the membrane. The hydrodynamic model described satisfactorily the behaviour of porous membranes and the mass transport mechanism is a pure convective motion of molecules through the membrane pores due to the superimposed pressure gradient.

Several methods have been developed to synthetize the membranes with specific properties as reported in Figure 23.
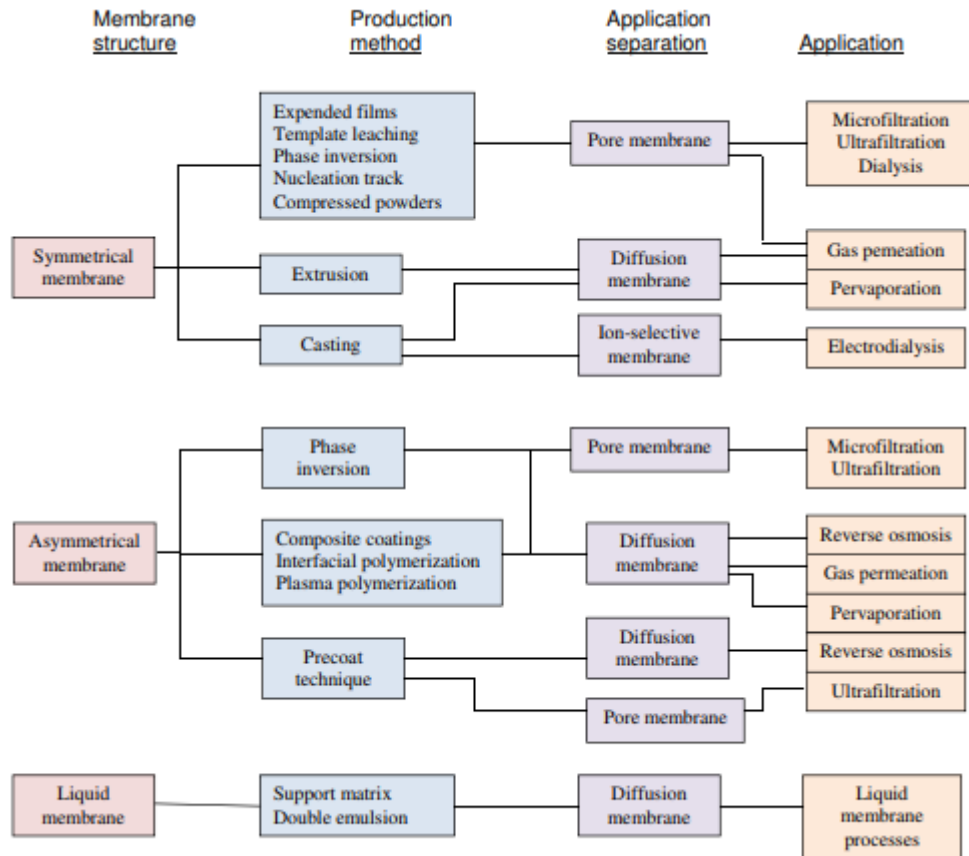
Figure 23. Membrane production methods and application fields of the obtained membranes.

For instance, dense membranes are generally polymeric. The selection of the starting polymer is not arbitrary, but based on the specific properties, which the membrane should possess, mainly structural factors, such as molecular weight, chain flexibility, and chain interactions. In fact, structural factors determine the thermal, chemical and mechanical properties of polymers, but also permeability.

The polymeric membranes used in this dissertation work have been prepared by means of the solvent evaporation method. The polymer is dissolved in a solvent and a homogenous solution (named casting) is obtained. Then, the solution is casted on a suitable support, e.g., a glass plate or another type of porous (non-woven fabric) or non-porous (polymer) support. Thereafter, the solvent is evaporated in controlled atmosphere (e.g., room chamber maintained at constant temperature and humidity) thus leading a dense and homogenous membrane.[248] Tuning the experimental conditions permits to tailor the properties of the polymeric dense membrane.[249]

The Perfluorinated ionomer known as Nafion (Figure 24) is the most widely used polymer for the synthesis of polymeric membrane for PEM fuel cells. [250, 251] The resulting membranes show high proton conductivity, super acidity and high mechanical and chemical stability.

$$\left[\left(CF_2-CF_2 \right)_x \left(CF_2-CF_2 \right)_y \right]_n$$
$$\left[OCF_2-CF \right]_z - O(CF_2)_2-SO_3^-H$$
$$CF_3$$
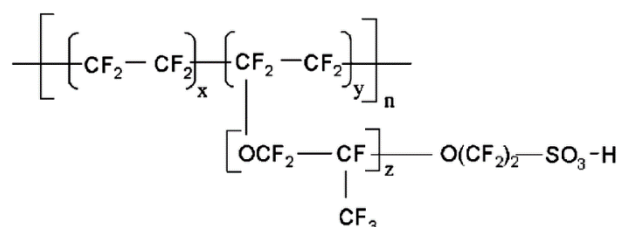
Figure 24. Chemical structure of Nafion polymer.

In general, to enhance the physic-chemical properties of the membranes, various additives can be used during their synthesis. The compounds can be homogeneously embedded inside the matrix or just functionalize the membrane surface. For instance, C_3N_4 or graphene oxide embedded into a Nafion membrane, showed an improvement toward water selectivity and a higher performance of Nafion membrane in fuel cells, respectively. [252, 253]

The latest development in membrane material design is the use of hybrid (inorganic–organic) materials, which overcome most of the limitations associated with polymeric membrane systems. Inorganic materials explored to this aim are metal oxides (e.g., Al_2O_3, TiO_2, SiO_2, ZnO, and Fe_2O_3), metals (e.g., Cu, Ag) and carbon-based materials (e.g., graphene and carbon nanotubes). Introducing inorganic moieties into a polymeric matrix system can offer multi-functionality beyond the mere separation and can enhance hydrophilicity, mechanical strength, water permeability, rejection rate, antifouling properties and/or introduce photocatalytic activity. [254]

The main role of membranes is known to be the separation of desired species. However, membranes can be used also as expositors or contactors. The membrane acts as an expositor when it enables or facilitates, for instance, the exposition of a photocatalyst to the light. In this case the photocatalyst particles, dispersed in the membrane matrix, harvest more photons (increasing the efficiency of the reaction) and at the same time may be better exposed to reactants (higher available surface

contact area). The membrane acts as a contactor when merely contact two phases and enhance the mass transport between them. Membrane contactors have been widely studied by Boyadzhiev et al. for recovery of organic acids, antibiotics, alkaloids, bio-surfactant, and metals.[255]

Membrane reactors are an interesting alternative to traditional reactors owing to their unique characteristics.[256]

Membrane reactors can consist of one or more modules. As shown in Figure 25, two operating ways are possible: single pass or recirculated reactors. In order to increase the productivity, several modules can be added and located in parallel. On the contrary, in series arrangement it is preferred to enhance the selectivity of the process.
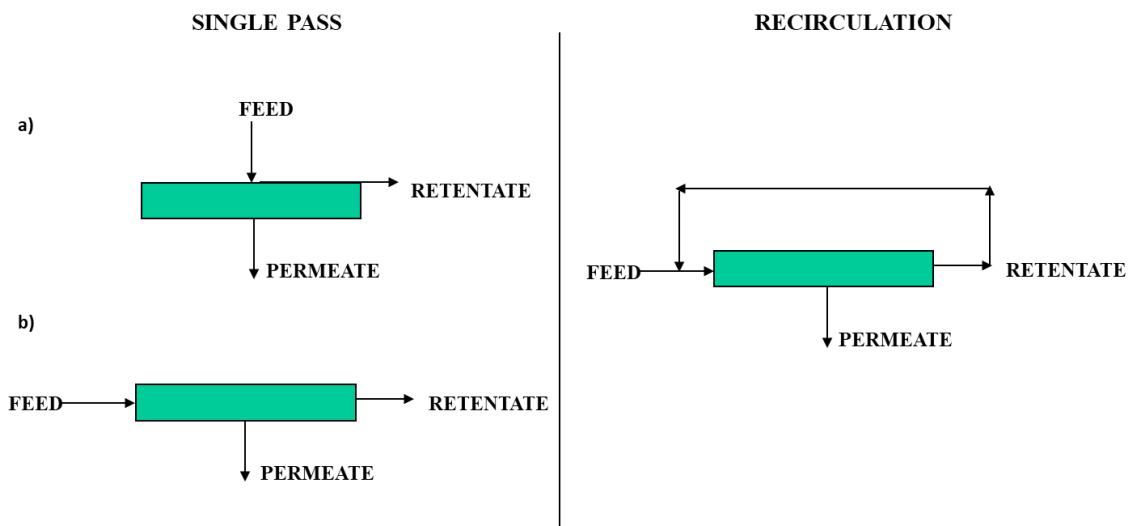
Figure 25. Module arrangements: two types of single pass (a and b) and recirculation mode.

Due to the high potential offered, the use of membranes is continuously increasing in several fields such as water treatment, food and pharmaceutic industries,[257] chemistry, etc. Cold separation using membrane technology is widely used in food, biotechnology and pharmaceutical industries. In fact, it was demonstrated that among polymeric materials, polymeric membranes are attractive for their selectivity and bio-stability characteristics in the use of bio-hybrid systems for cell culture. Semipermeable membranes act as a support for the adhesion of anchorage-dependent cells and allow the specific transport of metabolites and nutrients to cells

and the removal of catabolites and specific products. Moreover, new membrane systems that have been recently realized might also potentially contribute to regenerative medicine and tissue engineering.[258] Furthermore, using membranes enables to separate species impossible to be performed by using thermal separation methods. For example, it is impossible by distillation to separate the constituents of azeotropic liquids or solutes, which form isomorphic crystals by distillation or recrystallization, but such separations, can be achieved using suitable membranes. For instance, several studies report this technology as a promising method for H_2 and N_2 separation, air-drying and in particular for CO_2 capture.[259,260] Important technical applications include the production of drinking water by reverse osmosis (worldwide approximately 7 million cubic metres annually), filtrations in the food industry, the recovery of organic vapours such as petro-chemical vapour recovery and the electrolysis for chlorine production. In wastewater treatment, membrane technology is becoming increasingly important. With the help of ultra/microfiltration it is possible to remove particles, colloids and macromolecules, so that wastewater can be disinfected. About half of the market is dedicated to medical applications such as the use of membranes for artificial kidneys to remove toxic substances by haemodialysis and as artificial lung for bubble-free supply of oxygen in the blood. The importance of membrane technology is growing in the field of environmental protection (NanoMemPro IPPC Database). Even in modern energy recovery techniques, membranes are increasingly used, for example in fuel cells and in osmotic power plants which generates renewable and emissions-free energy and thus contributes to eco-friendly power production by water treatment at different salinity.

The integration of photocatalysis with a membrane based separation unit has been recently proposed as a promising tool to transfer photocatalytic syntheses from lab to industrial scale. The reason why photocatalytic membrane reactors could produce great advantages is based on a simple idea. The target molecule, generally a reaction intermediate, can be continuously separated from the photocatalytic system by means of suitable membranes in order to avoid its further oxidation. This not only provides higher selectivity and efficiency with respect to the sole photocatalytic process, but also enables direct separation of the product of interest.

Furthermore, the dense membranes are generally not affected by possible fouling and allow the complete retention of the photocatalytic powder. This avoids further separation steps, thus strongly reducing the operating costs. Finally, the possibility of operating in a continuous or semi-continuous mode, the easy control and the modularity of the system endow the integrated process with versatility and flexibility. It is worth to note that the integration of the two processes is straightforward due to the similar operating conditions at which they generally operate (mild temperature, low pressure, diluted solutions, low energy demand). This solution has been often applied for environmental[261] (i.e., water treatment) purposes by considering the synergistic effects of the integration, i.e., the possibility of pollutant removal with rates higher than the sum of those obtained by the single technologies.[262] On the other hand, applications for the synthesis of high value added compounds might be still defined at a nascent level. Notably, while some interesting syntheses have been investigated from a "chemical" point of view, the highly specific engineering issues related to them should be still approached. Therefore, various competences and different research approaches must be interdisciplinary connected and scientific collaborations are often required to prove the applicative viability of photocatalytic membrane reactors (PMRs)for synthetic purposes. Up to now a limited number of photocatalytic oxidation, reduction and syntheses of high added value chemicals were carried out in PMRs.[261, 263-265] In fact, few photo-oxidation reactions (i.e., partial oxidation of benzene to phenol and alcohols to aldehydes and the synthesis of vanillin), photo-reduction (i.e., reduction of nitrate to ammonia and acetophenone to phenylethanol) and only two photocatalytic synthetic reductions (CO_2 to fuels and the synthesis of phenylethanol) have been carried out in PMRs, to the best of my knowledge.

More recently, the incorporation of photocatalyst into membrane matrix was studied to develop a newly PMR for the CO_2 photoreduction with good performance.

1.5.2 Photocatalytic membrane reactor for CO_2 reduction

Despite the attractive features of PMRs, their application to heterogeneous CO_2 photoreduction has been up to now scarce.

Pioneering researches on CO_2 reduction in a photocatalytic membrane reactor have been carried out from Pathak et al. in a batch reactor at 139 bar.[266] [267] Authors reported that homogeneously dispersing the photocatalyst in Nafion thin films resulted in improved efficiency of CO_2 photocatalytic reduction with respect to the case where the photocatalyst was dispersed in the reacting mixture. In their first report[266] commercial TiO_2 (Degussa) was immobilized in Nafion matrix films and tested in the presence of supercritical CO_2. The products detected were $HCOOH$, CH_3OH and CH_3COOH (190, 280 and 30 μmol $g_{catalyst}^{-1}$, respectively) after 5 hours of irradiation.

Recently, an innovative CO_2 photoreduction system in mild conditions (pressure of ca. 3 bar) was reported by Sellaro et al.[268]. TiO_2 (1.2% wt.) was embedded in a Nafion membrane prepared by solvent method evaporation. The main product was methanol with a production rate of 45 μmol $g_{catalyst}^{-1}$ h^{-1}, which is one of the highest values reported for photocatalytic systems operating in similar conditions. This work showed that PMRs might be a promising technology for CO_2 reduction.

Both the above-mentioned papers demonstrated the Nafion capability of dispersing and supporting photocatalysts active for the CO_2 photoreduction. Being a stable and UV-vis transparent material with high proton conductivity, Nafion seems to be the best polymeric choice in order to carry out CO_2 photocatalytic reduction in PMRs.

Recently, the influence of reactants molar ratio and contact time on CO_2 photoreduction efficiency has been demonstrated in optofluidic membrane microreactor.[269] In this study, a mesoporous $CdS/TiO_2/SBA-15@carbon$ paper composite membrane was used for the reaction affording an outstanding methanol production of ca. 800 μmol $g_{catalyst}^{-1}$ h^{-1}.

In general, microreactors show several advantages such as: minimal amounts of reagent required under precisely controlled conditions, rapid screening of reaction

conditions, improved overall safety conditions of the process,[270] excellent mass and heat transfer, shorter residence time, lightweight and compact system design, laminar flow, effective mixing and better process control.

By taking into consideration all of the mentioned advantages, it is obvious that they could have many areas of application but those systems are still not perfect. Frequently quoted disadvantages of microreactors are high fabrication cost, low throughput, incompatibility with solids and the omission of cost reduction by scale up effects which lead to still poor industrial acceptance.[271] To ensure a stable flow in microreactors it is necessary to use low pulse or pulseless pumps; pumps are one of the most expensive parts of the microreactor apparatus. Due to the small dimensions of micro-channels one of the biggest problems is clogging[272] when operating with small diameter solids (for example enzyme dispersion) in a microreactor or with highly viscous solvents. It is also important to mention that microreactors can operate a very short residence time so in this case a fast reaction is carried out. Fast reactions also require very active catalysts with high stability in the microreactor. Consequently, microreactors still cannot be used as a replacement for all traditional processes. Another very important problem concerns the analysis of the products. In fact, off-line analyses, although easy to perform, are time demanding. Therefore, there are many efforts in developing on-line analytical techniques for micro-structured devices.

From these considerations, only few reports are available to the best of my knowledge, focus on CO_2 reduction in PMRs, so that further investigations are needed.

Chapter 2

Experimental section

2.1 Material and Methods

All the following materials were used as received without any further purification: $ZrOCl_2$ (Sigma Aldrich, 98%), $Ce(SO_4)_2$ (Sigma Aldrich, 100%), $Er(NO_3)_3 \cdot 5H_2O$ (Sigma-Aldrich, 99.9%), TiO_2 P25 (Evonik, 100%), melamine (Sigma Aldrich, 99%), H_2O_2 (Sigma Aldrich, 30% wt./wt. in H_2O), Graphite (Sigma Aldrich, -), H_2SO_4 (Sigma Aldrich, 95-98%), $NaNO_3$ (Sigma Aldrich, 99%), $KMnO_4$ (Sigma Aldrich, 99%), Nafion solution (Quintech e.K Brennstoffzellen Technologie, 5 wt. %). Distilled deionized water used throughout the experiments, for washing processes, as solvent and reagent was purified by means of a Milli-Q system. All liquid analytical standards such as methanol (anhydrous, 99.8%), absolute ethanol (reagent ISO, reagent Pharmacopoeia European, ≥99.8%), acetone (analytical standard), acetaldehyde (ACS reagent, ≥99.5%), propanal (reagent grade 97%), propanol (anhydrous, 99.7%) and formaldehyde (37% wt. in H_2O contains 10-15 % methanol as stabiliser) were obtained from Sigma-Aldrich.

Gasses such as CO_2, CO, CH_4, Ar, He and N_2 were purchased from Air Liquide with a purity of 99.998%.

2.2 Material synthesis

2.2.1 ZrO_2 based materials

The ZrO_2 based samples have been prepared by means of a hydrothermal process, starting from an aqueous solution containing the zirconium precursor ($ZrOCl_2 \cdot 8H_2O$) in 1.0 M concentration and the rare earth precursor, ($Ce(SO_4)_2$ or $Er(NO_3)_3 \cdot 5H_2O$). The pH of the solution was then adjusted to 11 by using a 4.0 M NaOH aqueous solution. The solution, with the precipitates, was then transferred into a 125 mL Teflon lined stainless steel autoclave, 70% filled, which was heated at 175 °C overnight in an oven. The precipitates were hence centrifuged and washed three times with deionized water, then dried at 60 °C. For comparison, pure ZrO_2 was prepared by the same procedure, without the presence of the rare earth metal. Finally, the prepared powders were calcined at 500 °C for 2 h. For each dopant (Ce or Er), two samples were prepared with different rare earth metal

content, namely 0.5%, and 10% molar percentage. Samples will be labelled indicating the molar percentage of the dopant, then the dopant followed to the ZrO_2.

2.2.2 G/TiO$_2$ composites

Graphene oxide was prepared from graphite flakes via an improved Hummers method.[155] In detail, 4 g of graphite were added to 2 g of $NaNO_3$ in 92 mL of H_2SO_4 and stirred for ca. 15 minutes at 0°C in an ice bath. Because of heat evolution due to the exothermic process, 12 g of $KMnO_4$ were slowly (in 15–20 min) introduced to maintain the temperature below to room value (20°C). Then, after removal of the ice bath, the solution was stirred for 90 minutes assuming a green colour. Firstly, 184 mL of Milli-Q H_2O (reaching 98 °C) were added to the acid solutions, and later 560 mL of Milli Q hot H_2O. A change of the solution colour, from green to yellow, was observed after treatment with 20 mL of H_2O_2.

Upon treatment with the peroxide, to reduce the residual permanganate and manganese dioxide to colourless soluble manganese sulphate, the suspension was filtered resulting in a yellow-brown filter cake. It was washing three times with a total volume of 560 mL of warm H_2O. Filtering was carried out while the suspension was still warm to avoid precipitation of the slight soluble salt of mellitic acid formed as a side reaction.

Unlike the Hummer's method, the resulting product was dispersed in H_2O under stirring using ultrasound in order to obtain a 2D material. The solid was separated by centrifugation at 1000 rpm for 2 minutes. This procedure was repeated 2 times. However, to remove all possible residues from the synthesis steps, the resulting solid was washed by water and centrifuged for 15 minutes at 800 rpm. The precipitated powders were dried at 70°C overnight and labelled GO.

The graphene/commercial TiO$_2$ composites was obtained via hydrothermal method based on modified Nethravathi's work at four different G percentage weights equal to 0.5, 1, 3 and 10%.[273] Briefly, 6 mg of GO was dissolved in a solution of H_2O (60 mL) and ethanol (30 mL) by ultrasonic treatment for 1 h, and 0.6 g of TiO$_2$ was added to the obtained GO solution and stirred for 2 h to get a homogeneous

suspension. The ethanol was used to facilitate both the dispersion of reagents and as reductant of GO to G in these hydrothermal conditions. The suspension was then placed in a 100 mL Teflon-sealed autoclave and maintained at 120 °C for 3 h to simultaneously achieve the reduction of GO and the deposition of TiO_2 on the carbon substrate. The system pressure reached the 25 psi as result of CO_2 formation from ethanol oxidation. Finally, the resulting composite was recovered by filtration, rinsed by water several times, and dried overnight at 60°C. The resulting powder was labelled as 1% G/TiO_2. By following the same procedure, also the 0.5% G/TiO_2, 3% G/TiO_2 and 10% G/TiO_2 composites were prepared.

2.2.3 Pristine and base g-C_3N_4 materials

Graphitic carbon nitride (g-C_3N_4) was prepared by heating (at 2 °C min^{-1}) 10 g of melamine up to 520 °C, temperature kept for 2 h, in a covered crucible exposed in static air. The yellow solid was pounded and then heated again, without coverage, at 3 °C min^{-1} up to 500 °C keeping this temperature for 4 h.

g-C_3N_4-TiO_2 photocatalyst was prepared by mechanically milling both solids with a Retsch RM200 mortar grinder. The procedure of preparation was as follows: 3 g of TiO_2 (commercial P25) powder were mixed in the ball-milling tank with 1 g of g-C_3N_4 (ratio of 3:1) for 1 h at 250 rpm (30 minutes clockwise, 5 minutes of pause, and 30 minutes by inverting the rotation).

2.2.4 g-C_3N_4 pure and O doped materials and their immobilization: g-C_3N_4, O_R-C_3N_4 and O_T-C_3N_4

Oxygen doped g-C_3N_4, was prepared by a modified thermal polymerization method.[274] Briefly, 1 g of g-C_3N_4 (as synthesized previously, see section 2.2.4) was dispersed in 80 mL of 30% H_2O_2 solution and placed in a Teflon vessel of 100 mL. The vessel was then heated up to 130 °C and kept at this temperature for 24 h in an autoclave. After cooling, the dispersion was filtered, and the orange colourised powder was washed with hot water to remove the H_2O_2. Once no H_2O_2 was

detected in the washings (by $KMnO_4$ method), the powder was dried at 60°C and designated O_R-C_3N_4. g-C_3N_4 and O_R-C_3N_4 catalysts were immobilised in a glass supports by the following procedure. 8 mg of powder was immobilized on borosilicate glass (3 x 2.5 cm^2) by spray coating using a water dispersion of 25 g L^{-1}. Each coated borosilicate glasses were dried at 70 °C. The g-C_3N_4 powder coated was used without further treatment or annealed at 450 °C (2 h with ramp up and down rate 2°C min^{-1}) to produce O_T-C_3N_4 prior to testing.

2.2.5 Pristine Nafion and photocatalytic C_3N_4 and C_3N_4-TiO_2 Membranes

Nafion and photocatalytic Nafion membranes were prepared following the same procedure reported by Sellaro et al.[268] Nafion 5 wt. % solution (20 g) was dried at ca. 60−70 °C under stirring; then, the resulting powder was dissolved in EtOH/H_2O = 50:50 w/w at room temperature under stirring for 1 h to obtain the polymeric solution. Two types of flat sheet membranes were prepared: a Nafion membrane (not including catalyst) and a photocatalytic Nafion membrane (Table 9). For the catalytic membranes, after complete polymer dissolution, the catalyst (C_3N_4 or C_3N_4-TiO_2) was added to the obtained solution, and the resulting dispersion was left under stirring for 1 h more. Then, it was sonicated for 3 h more at room temperature to favour the homogenization of the dispersion. The catalyst-polymer dispersions obtained were then cast in a Petri dish (diameter = 7.1 cm), and the solvent evaporation was carried out in a climatic chamber (60 ± 4 °C and 12 ± 5% as relative humidity) for about 20 h. The membranes obtained were treated thermally, heating at 10 °C min^{-1} up to 100 °C, then at 0.5 °C min^{-1} up to 120 °C, and kept at this temperature for 4 h. No specific investigation on catalyst loading content was carried out, and the chosen photocatalyst percentage was 1.23 wt. %. In the case of the Nafion membrane, the same procedure was followed but without catalyst dispersion. Then, the flat sheet membranes obtained were detached from the Petri dishes with a small amount of water and then dried at room temperature. In all the membranes, two membrane sides were distinguished as the casting-plate-facing and air-facing surfaces.

Table 9. Composition of solutions used to prepare pristine and photocatalytic membranes

	Membrane, wt.%	
	Photocatalytic Nafion	**Nafion (bare)**
Polymeric solution		
Solvent (EtOH:H$_2$O, 50:50)	97.8	97.827
Polymer	2.173	2.173
Catalyst addition		
Catalyst	0.027	0
Resulting membrane		
Catalyst in membrane	1.23	0
Polymer in membrane	98.77	100

2.3 Materials characterizations

2.3.1 Powder characterizations

Bulk and surface of all catalysts prepared in the above (2.2.1 - 2.2.4) sections and commercial TiO$_2$ were characterised for defining the physicochemical properties of the powder.

Their crystalline phase structures were analysed at room temperature by powder X-ray diffraction by using a Panalytical Empyrean instrument, equipped with Cu Kα radiation and a PixCel-1D (tm) detector.

The Brunauer−Emmett−Teller specific surface area of the synthesized catalysts was measured by nitrogen adsorption−desorption isotherms using a Micromeritics Asap instrument. Infrared spectra of the samples in KBr (Aldrich) pellets were obtained with an FTIR-8400 Shimadzu spectrophotometer and recorded with 4 cm^{-1} resolution and 256 scans.

The diffuse reflectance spectra were measured in air at room temperature in the 200−800 nm wavelength range using a Shimadzu UV-2401 PC spectrophotometer, with BaSO$_4$ as the reference material.

However, in order to define the fine structure of the graphene materials, the Raman spectra were also performed in three points for each sample. The spectra were recorded by a Reinshaw in-via Raman equipped with an integrated microscope and

with a charge-coupled device (CCD) camera. He/Ne laser operating at 532 nm was used as the exciting source (20x lens, focal length ca. 4-5 μm and work power ranged from 1% to 50% of 100mW).

Additionally in collaboration with Giamello's group of University of Turin, Electron Paramagnetic Resonance analyses were carried out on ZrO_2 base materials in order to explain the unusual photoreactivity. Then, Electron Paramagnetic Resonance spectra were recorded at room temperature and at liquid nitrogen temperature (-196 °C) on an X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation. The effect of light on EPR spectra was investigated by using 1600W Mercury/ Xenon lamp (Oriel Instruments) and an IR water filter. A 400 nm cut off filter was used to eliminate part of the UV radiation, leaving a 5–8% of UVA component comparable to that present in the solar spectrum.

2.3.2 Characterisations of supported materials

All the materials supported on glass (2.2.4 section) were characterized, before and after their use, by a Perkin Elmer Varian 640-IR FTIR was used for FTIR characterization. FTIR analysis was performed with a resolution of 10 cm^{-1} step size, compiled from 50 scans and measured in triplicate.

The crystalline phase structures were analyzed at room temperature by powder X-ray diffraction by using a Panalytical Empyrean, equipped with Cu $K_α$ radiation (1.5406 Å) and PixCel-1D (tm) detector.

Diffuse reflectance was used to determine the optical characteristics of the materials and measured with a Shimadzu UV-2401 PC spectrophotometer, with $BaSO_4$ as the reference material. X-ray photoelectron spectroscopy (XPS) of the used and unused material plates were recorded by means of a Kratos Axis Ultra system equipped with a monochromatic Al $K_α$ X-ray source (hυ 1486 eV). Triplicate analysis was performed, sampling from different areas of the material plates. For all the elements, the coefficient of variance was less than 10%. The binding energy at 284.8 eV was used for calibration of C 1s chemical shifts. Survey

scans covering the entire energy range were performed with 160 eV energy window, whilst high-resolution scans of specific elemental regions were performed at a reduced 20 eV. The data were fitted using a mixed Gaussian-Lorentzian (GL30) function on a Shirley background.

2.3.3 Characterization of membranes

After cleaning as described in the section 3.4.2, the membranes prepared (2.2.5 section) were characterized by different techniques. The morphologies of the membrane surfaces (air- and plate-facing) and cross section were examined by an EVO MA10 Zeiss Scanning Electron Microscope. The samples were sputtered with gold prior to these analyses.

A PerkinElmer Spectrum One was utilized for Fourier Transform Infrared spectroscopy analyses in attenuated total reflectance mode of both air-facing and casting-plate-facing membrane surfaces.

Diffuse reflectance spectroscopy (Shimadzu UV-2401 PC) analyses were carried out in three different points for both casting sides.

Permeability to N_2 and CO_2 were also measured to evaluate the membrane mass transport properties and integrity.

Chapter 3

Results and discussion

3.1 Doped and pristine ZrO_2 for CO_2 photoreduction

The results presented in this chapter have been published in:

E.I. García-López, G. Marcì, F.R. Pomilla, M.C. Paganini, C. Gionco, E. Giamello, L. Palmisano. ZrO_2 Based materials as photocatalysts for 2-propanol oxidation by using UV and solar light irradiation and tests for CO_2 reduction. *Catalysis Today* 313, **2018**, 100–105.[147]

3.1.1 Photocatalytic test conditions

Previously the photocatalytic test, a possible presence of products deriving from C impurities was checked by treating the photocatalysts under irradiation (before the photoactivity experiments in the presence of CO_2) with a flow of humid inert gas according to Strunk et al.,[114] which allowed also to clean the surface. Notably no organic species were observed during the treatment.

The CO_2 photoreduction tests were carried out by using a batch photoreactor constituted by a Pyrex vessel with a volume of 25 mL and equipped with a septum to permit the sampling (Figure 26). 0.06 g of photocatalyst were spread in the bottom of the photoreactor and N_2 was flushed for 2 h inside the system under irradiation in order to photo-desorb possible impurities and/or carbon residues from the catalyst surface. Subsequently, the photoreactor was saturated with CO_2 containing the vapour pressure of water at 25 °C. In order to start the experiment in the presence of humid CO_2, the stream of CO_2 was continuously flushed for at least 1 h inside the reactor, after bubbling it in a flask containing water. Then the reactor was closed and the lamp (1500W high-pressure Xenon lamp) of SOLARBOX (CO·FO.ME·GRA) apparatus, simulating the solar light, was switched on.
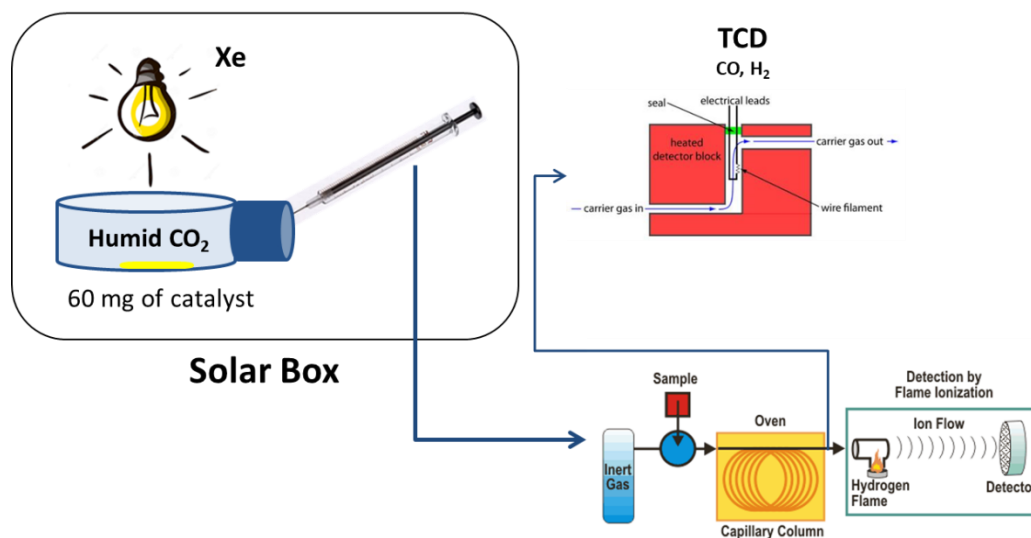
Figure 26. Photocatalytic apparatus consisting by Solar Box and glass batch reactor equipped with GC TCD-FID instruments.

Aliquots of the gaseous reaction mixture were withdrawn from the reactor at fixed irradiation times by using a gas-tight micro syringe. The evolution of the formed organic products was followed by a GC-2010 Shimadzu equipped with a Phenomenex Zebron Wax-plus column by using He as the carrier gas and a FID. CO was analysed by a HP 6890 GC equipped with a packed column GC 60/80 Carboxen-1000 and a TCD. The latest analysis were useful to check the tight of the system by monitoring the amount of N_2 and O_2 inside the reactor.

3.1.2 Characterisation of ZrO_2 based materials

XRD patterns of prepared samples are reported in Figure 27. A mixture of both monoclinic (m-ZrO_2) and tetragonal (t-ZrO_2) polymorphs of zirconia was observed in all of them. In agreement with Gionco et al.[275] the increasing of rare earth (RE) dopant amount led to the stabilization of the tetragonal polymorph.
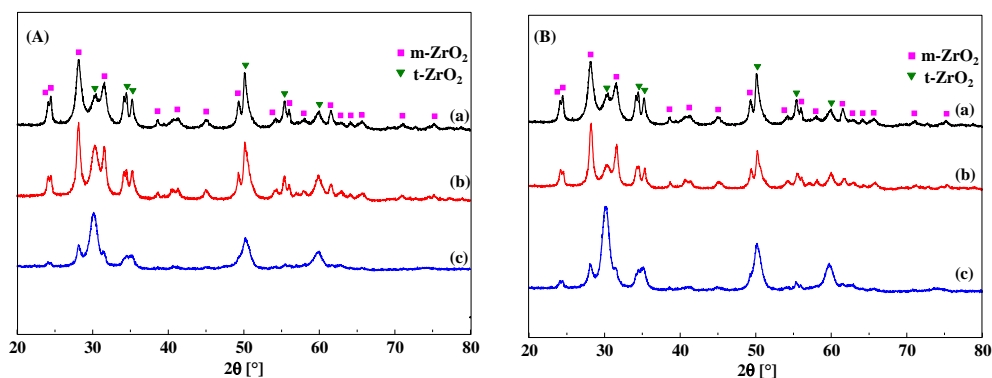
Figure 27. XRD patterns of the prepared samples. Ce doped (A) and Er doped (B) ZrO₂ samples, along with the pristine ZrO₂. (A): ZrO₂ (a); 0.5%Ce/ZrO₂ (b) and 10%Ce/ZrO₂ (c) and (B): ZrO₂ (a); 0.5%Er/ZrO₂ (b) and 10%Er/ZrO₂ (c).[147]

A Rietveld refinement was performed on the XRD patterns and the results are reported in Table 10.

Table 10. Cell parameters, weight percentage and crystallite size obtained from Rietveld refinement: (wt.) weight percentage of a given phase; (a), (b) and (c) lattice parameters; (β) angle between a and c axes for the monoclinic cell; (D) and (d) maximum and minimum crystallite sizes for the anisotropic m-ZrO₂; (d') crystallite size for t-ZrO₂; (E$_g$) estimated band gap for all of the samples prepared.[147]

Sample	Phase	wt. [%]	a [Å]	b [Å]	c [Å]	β [°]	d, d' [nm]	D [nm]	E$_g$ [eV]
ZrO₂	m-ZrO₂	66	5.18	5.22	5.34	99.59	9	43	5.2
	t-ZrO₂	34	3.58		5.23		7		
0.5% Ce/ZrO₂	m-ZrO₂	61	5.19	5..22	5.35	99.71	13	40	5.1/4.0
	t-ZrO₂	39	3.62		5.16		10		
10% Ce/ZrO₂	m-ZrO₂	24	5.16	5.20	5.32	99.35	17	20	3.0
	t-ZrO₂	76	3.62		5.17		10		
0.5% Er/ZrO₂	m-ZrO₂	76	5.17	5.21	5.33	99.51	15	31	5.2
	t-ZrO₂	24	3.61		5.16		11		
10% Er/ZrO₂	m-ZrO₂	28	5.18	5.22	5.35	99.58	12	63	5.1
	t-ZrO₂	72	3.64		5.16		12		

The weight percentages of phases obtained are in agreement with the qualitative considerations. The cell parameters of the m-ZrO₂ phase are poorly influenced by the insertion of the RE dopant, while the lattice constants of t-ZrO₂ undergo a distortion which increases with the RE content, as shown in Table 10. Moreover,

the m-ZrO_2, both in the bare and doped oxides, presents some degree of anisotropy. Indeed, the peaks broadening is not constant; for this reason it was used the Popa model[276] for the refinement of this phase and we have listed in Table 10 the maximum (D) and minimum (d) crystallite sizes obtained from the Rietveld refinement, along with the (110) and (-111) plans, respectively. The maximum crystallite sizes for the monoclinic phase are generally larger than those tetragonal. Raman spectra obtained for all of the samples are reported in Figure 28 and Figure 29
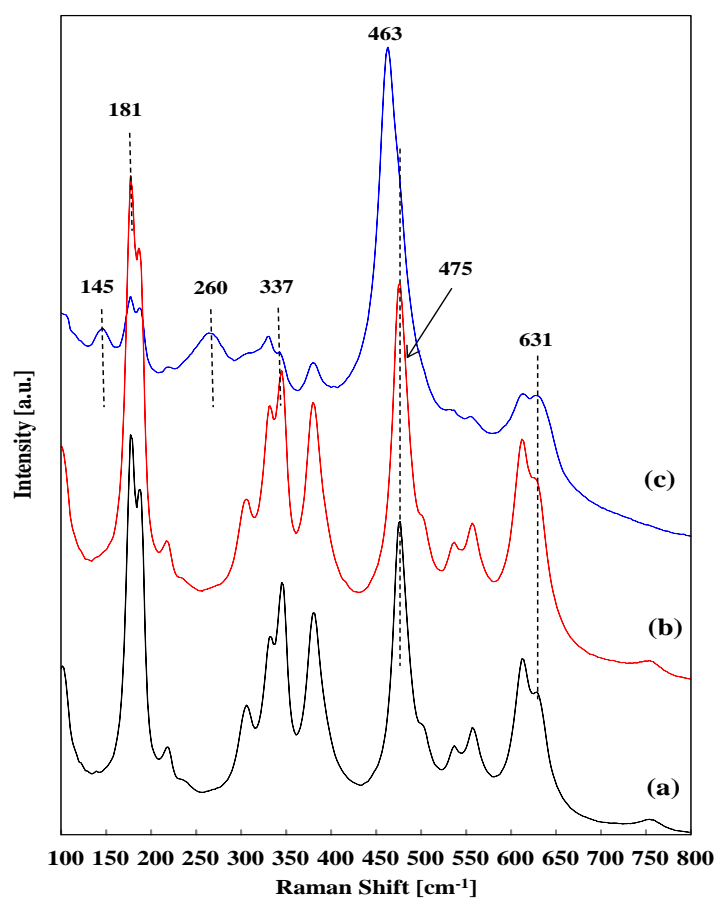
Figure 28. Raman spectra of the samples: ZrO₂ (a); 0.5% Ce/ZrO₂ (b) and 10% Ce/ZrO₂ (c).[147]

Raman spectroscopy has been used to further investigate the structural features of the synthesized samples. Figure 28 shows micro-Raman spectra of Ce doped samples along with that of pristine ZrO_2 in the range from 100-800 cm^{-1}. Each measurement has been done at different positions on the surface of the powders in order to verify the homogeneity of the material. Raman spectroscopy is a very

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sensitive technique to determine the phase composition in transition metal oxides. According to the literature, tetragonal ZrO_2 presents six active modes: 148, 164, 266, 322, 339, 467, 609, and 642 cm^{-1}[277] whereas monoclinic ZrO_2 shows sixteen active modes in the range 100-700 cm^{-1}: 102, 179, 190, 224, 235, 270, 305, 320, 334, 360, 375, 385, 476, 500, 553, and 636.[278]

The micro-Raman spectrum of the pristine ZrO_2 showing the bands reported in literature results the presence of monoclinic and tetragonal phases in good agreement with the crystalline phases revealed by XRD. The Raman bands located at 145 and 260 cm^{-1} can be assigned only to the tetragonal phase and the bands at 181 and 337 cm^{-1} to the monoclinic phase. The perusal of Figure 28 indicates that the mentioned bands, attributed to the tetragonal phase, are more evident in the sample 10% Ce/ZrO_2 than in the ZrO_2, indicating the stabilization of the tetragonal polymorph in agreement to XRD results. The bands at 475 and 631 cm^{-1} are close to those typical of both polymorphs and could change their relative intensities for the two phases; often these two bands present ca. the same intensity in the tetragonal phase, but the band at 475 cm^{-1} becomes much stronger than that at 631 cm^{-1} in the case of the monoclinic phase. This insight, also observed in Figure 28, confirms the previous conclusion, i.e., the consolidation of the tetragonal phase by increasing Ce in the ZrO_2 sample. It is very important to note that in Figure 28, line (c), the spectrum of the 10% Ce/ZrO_2 sample shows a peak at 463 cm^{-1} that corresponds to the typical band attributable to the presence of the cubic fluorite structure of CeO_2. Because of the high Raman scattering of the CeO_2 cubic phase, the intensity of this band corresponding to the F_{2g} first-order symmetrical stretching mode of the Ce-O vibration unit, is remarkable. Hence, the Raman spectrum confirms the presence of CeO_2 in the 10% Ce/ZrO_2 sample. Further differences between the spectrum of the ZrO_2 pristine sample and that of the doped samples, particularly 10% Ce/ZrO_2, are attributable to distortions in the structure due to the presence of Ce.

In Figure 29(A) the micro-Raman spectra of Er doped samples are reported along with that of pristine ZrO_2 in the range from 100 to 800 cm^{-1}. As observed for the 10% Ce/ZrO_2 sample, also in the Raman spectrum of the 10% Er/ZrO_2, the 475 cm^{-}

[1], band decreased in intensity indicating the consolidation of the tetragonal polymorph in the 10% Er/ZrO$_2$ powder.
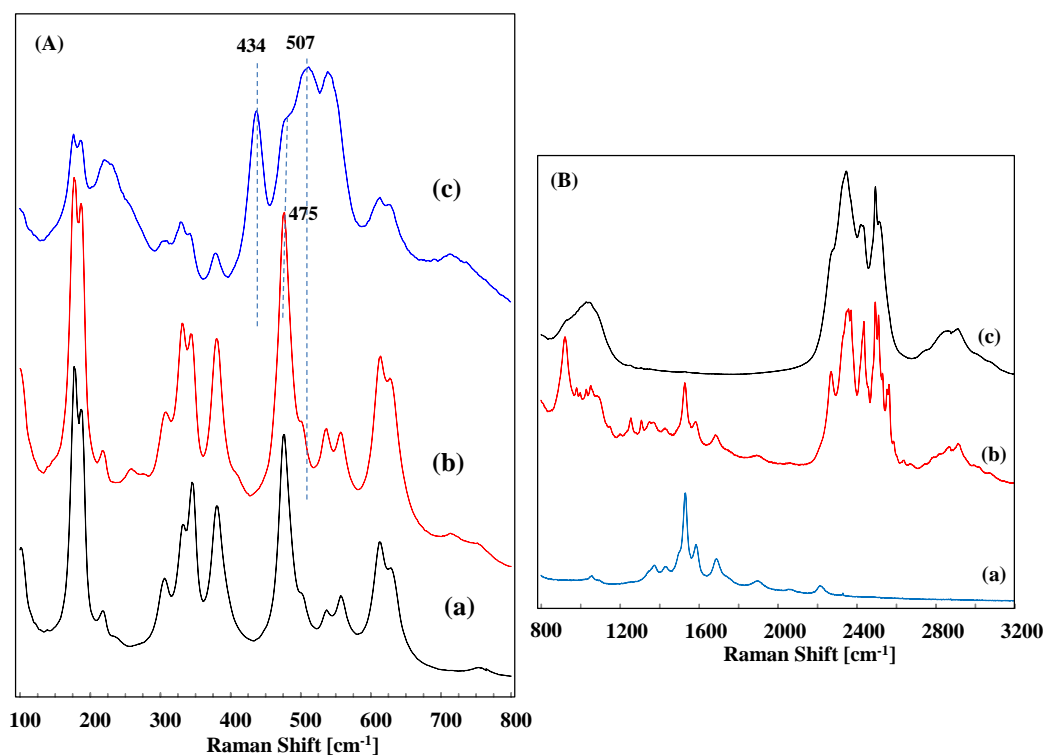
Figure 29. Raman spectra of the samples: ZrO$_2$ (a); 0.5% Er/ZrO$_2$ (b) and 10% Er/ZrO$_2$ (c).[147]

By taking into account the ionic radii size of Zr^{4+}, Ce^{4+} and Er^{3+}, it should be considered that the incorporation of the rare earth ion into the zirconia structure is expected to modify the host lattice. Raman spectroscopy is an appropriate technique to detect the incorporation of dopants and the possible host lattice disorder and defects appearance due to their presence. The lattice defects induce disorder, which breaks the symmetry in Raman transitions giving rise to variations of some signals of spectrum. This occurs for the Er containing ZrO$_2$, where some Raman transitions appeared shifted with respect to the pristine ZrO$_2$ due to the doping with the trivalent cations Er^{3+} by virtue of the size of this cation (ionic radium Er^{3+} 0.881 Å, Zr^{4+} 0.790 Å) generating oxygen ion vacancies, as before reported.[279, 280] Notably, Ce^{4+} presents an ionic radium of 0.92 Å, so the difference in size between Zr^{4+} and Ce^{4+} can favour also the partial segregation of CeO$_2$.

Figure 29(A) the band at 434 cm^{-1} of the 10% Er/ZO$_2$ sample can be due to the presence of Er$_2$O$_3$. The bands at about 507 cm^{-1} can be assigned to the t-ZrO$_2$ (ca. 475 cm^{-1} in the pristine ZrO$_2$) and to the presence of Er$_2$O$_3$.[281] Consequently, for the sample 10% Er/ZrO$_2$ the presence of some segregated distorted sesquioxide species cannot be excluded. Indeed, the study of the spectra at higher energies (Figure 29(B)) appeared completely different from that of the pristine ZrO$_2$, but no data about the bands present in the range 2200-2600 cm^{-1}, confirming the presence of Er$_2$O$_3$, were found in literature.

Concerning the band gap measurements, Figure 30 shows the Kubelka-Munk transformation of the diffuse reflectance spectra normalized to 1 for all of the previous mentioned samples.
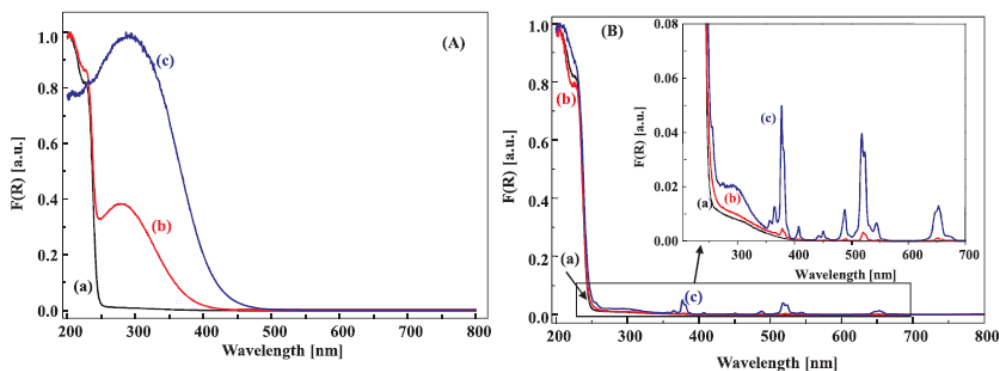
Figure 30. Absorbance spectra of the samples obtained by applying the Kubelka-Munk function, F(R∞), to the diffuse reflectance spectra. (A): ZrO$_2$ (a), 0.5% Ce/ZrO$_2$ (b), 10% CeZrO$_2$ (c) and (B): ZrO$_2$ (a), 0.5% Er/ZrO$_2$ (b), and 10% Er/ZrO$_2$ (c) The inset is a magnification of the squared region.[147]

An absorption shoulder, centred at ca. 300 nm, is clearly observed for the Ce doped samples in Figure 30(A). The absorption in the UV–vis range increases for all of the samples by adding the RE but the effect of Ce and Er ions is largely different as reported before.[275] The presence of the absorption band centred at 300 nm dominates the spectra of the 10% Ce/ZrO$_2$ sample overlapping the fundamental transition of zirconia. The shape of the spectrum is strongly similar to that of pure CeO$_2$ indicating that this absorption could be related to the charge transfer transition from O 2p to Ce 4f. This finding could indicate the presence of CeO$_2$ on the surface of ZrO$_2$ for the X% Ce/ZrO$_2$ samples in accord with Raman results. Probably the CeO$_2$ was very well dispersed on ZrO$_2$ and consequently its presence

was not revealed by XRD analysis. The Er containing samples, on the other hand, show a smaller modification of the optical properties of the materials; indeed all of the spectra are very similar each other, except for the small region enlarged in the inset of Figure 30(B). Both the Er/ZrO_2 samples present many absorption bands which are the fingerprint of the Er^{3+} ion, and the shoulder centred at 300 nm already present in the undoped materials. This band intensity increases with the Er content. The values of E_g (eV) were calculated by using the Tauc plot[282] and are reported in Table 10. The values were calculated by considering a direct transition for all of the samples except for 10% Ce/ZrO_2, where an indirect transition was considered due to the high concentration of CeO_2. Thus, the CeO_2, as in the case of TiO_2 (anatase structure), shows an indirect band gap.[283] For the 0.5% Ce/ZrO_2 sample two values are reported, one ascribable to the fundamental VB→CB transition of ZrO_2, and a second one due to the absorption band ascribable to the O 2p→Ce 4f charge transfer transition. The value of the band gap of ZrO_2 is not highly affected by the insertion of dopants, while the overall absorption is largely modified. Both 10% Er/ZrO_2 and 10% Ce/ZrO_2 samples are indeed coloured.

The photoluminescence emission spectra at λ_{exc}=365 nm (i.e., 3.40 eV) are reported in Figure 31.
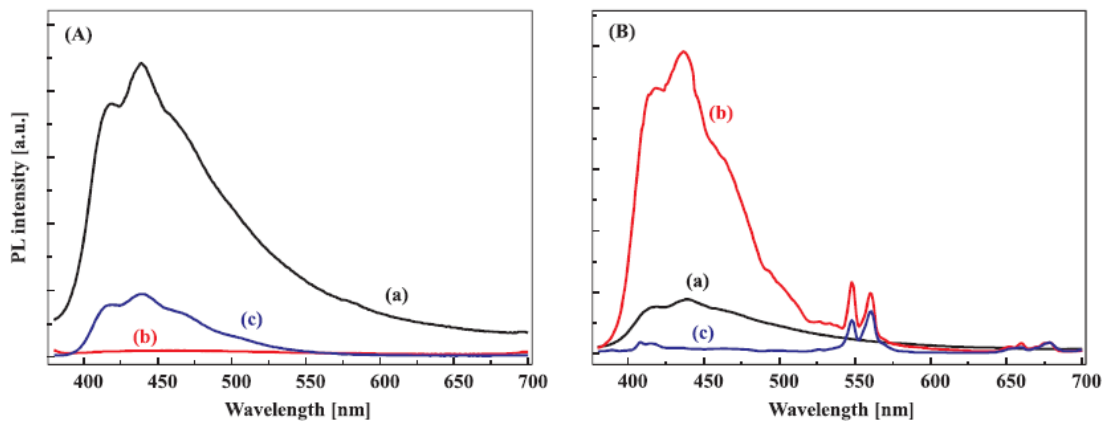
Figure 31. Photoluminescence spectra of (A): ZrO₂ (a); 0.5% Ce/ZrO₂ (b) and 10% Ce/ZrO₂ (c) and (B): ZrO₂ (a); 0.5% Er/ZrO₂ (b) and 10% Er/ZrO₂ (c).[147]

Since the excitation energy is lower than Eg, the PL spectra can reflect the intra band gap defects present in the ZrO_2 samples. The pure ZrO_2 (Figure 31(a) both (A) and (B)) presents a broad, asymmetric emission band centred at around 440 nm

(i.e., 2.82 eV). This emission band was already reported in literature, and it is generally assigned to the radiative recombination of photogenerated holes with electrons occupying oxygen vacancies.[284-286] In the case of Ce doped samples (Figure 31(A)), there is an evident suppression of the luminescence intensity, indicating a lower amount of intra band gap defects and thus a lower electron hole recombination rate. This effect is higher for the 0.5% Ce/ZrO_2 sample for which the luminescence intensity is nearly zero, while in the case of the 10% Ce/ZrO_2 sample the luminescence intensity is lower than that of pure zirconia but higher than that of the 0.5% Ce/ZrO_2 sample, probably because the 10% Ce/ZrO_2 sample absorbed more energy during the excitation due to its lower band gap (presence of well dispersed CeO_2). In the case of Er doped samples (Figure 31(B)), the effect is different, depending on the rare earth metal concentration. The 0.5% Er/ZrO_2 sample, indeed, shows an enhanced luminescence, indicating the formation of many oxygen vacancies as charge compensation for the introduction of Er^{3+} ions. The 10% Er/ZrO_2 sample, on the contrary, shows a total suppression of the luminescence intensity, except for the bands related to its f–f transitions, suggesting that in this case the main recombination centres are actually the Er ions and not the formed oxygen vacancies. EPR is a suitable technique to monitor the photo-induced charge separation process and, thus, to assess the photoactivity of a material under irradiation. Indeed, the direct charge separation is obtained by irradiating in situ the solid at the temperature of liquid nitrogen to avoid the rapid recombination of the carriers. If the photogenerated charges are stabilized by the solid (at different sites of the oxide, usually a cation for the electron and an oxide anion for the hole), paramagnetic centres can be formed (i.e. the O− ion) and they can be monitored by the electron paramagnetic resonance. The effect of UV–vis light on hydrothermally synthesized ZrO_2 was already reported by Gionco et al.[275] The as prepared sample does not show paramagnetic centres and its spectrum is a barely flat line. Upon irradiation, a new signal appeared ascribable to the photogenerated holes localized at an anion centre.

Figure 32reports the EPR spectra recorded at liquid nitrogen temperature for the Ce/ZrO_2 (Figure 32(A)) and Er/ZrO_2 (Figure 32(B)) samples.
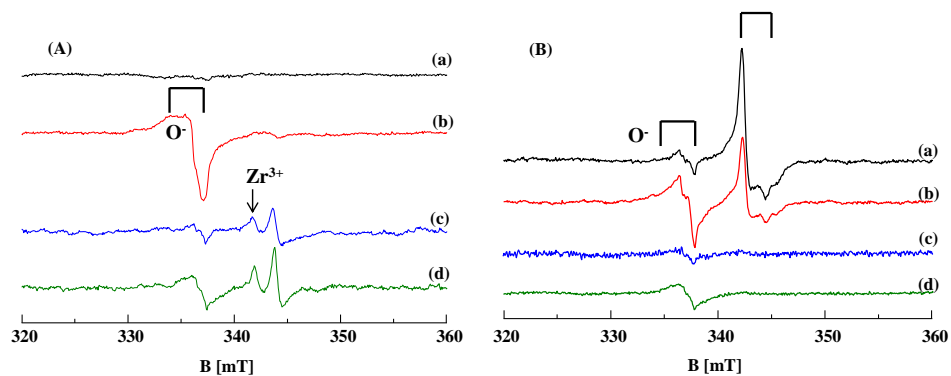
Figure 32. EPR spectra recorded at liquid nitrogen temperature for the Ce/ZrO$_2$ (A) samples: (a) 0.5% Ce/ZrO$_2$ before irradiation; (b) 0.5% Ce/ZrO$_2$ after irradiation; (c) 10% Ce/ZrO$_2$ before irradiation; (b) 10% Ce/ZrO$_2$ after irradiation and Er/ZrO$_2$ (B) samples: (a) 0.5% Er/ZrO$_2$ before irradiation; (b) 0.5% Er/ZrO$_2$ after irradiation; (c) 10% Er/ZrO$_2$ before irradiation; (d) 10% Er/ZrO$_2$ after irradiation. Irradiation time: 15 min.[147]

For all of the samples, both the spectra before ((a), (c)) and after ((b), (d)) irradiation for 15 min, are reported. The spectrum of the as prepared 10% Ce/ZrO$_2$ sample shows some intrinsic defectivity. Spectra in Figure 32 are reported against the external applied magnetic field B$_0$. Eq. 16 allows extrapolating the related values of the g factors.

$$\Delta E = h\upsilon = g_e * \mu_B * B_0 \qquad \text{Eq. 16}$$

The factor g$_e$ is very useful being a dimensionless quantity that characterizes the magnetic moment and gyromagnetic ratio of electron. In fact, it is essentially a proportionality constant that relates the observed magnetic moment μ of a particle to its angular momentum quantum number and a unit of magnetic moment, usually the Bohr magneton (μ$_B$) or nuclear magneton (eq. 16).

In detail, Figure 32 A (spectrum c) shows two signals: the one centred at g=1.978 (B=342) is assignable to Zr^{3+} species[149], the assignment of the one at B = 344, related with g∥=1.96 and g⊥=1.94, reported in literature, is still under debate.[287-289] Under irradiation a new signal ascribable to O− species appears in both 0.5% Ce/ZrO$_2$ and 10% Ce/ZrO$_2$ samples. The effect of irradiation is much more evident in the case of the 0.5% Ce/ZrO$_2$ sample, whilst for 10% Ce/ZrO$_2$ the intensity of the new signal is much lower. This can be due to spin-orbit coupling effects that affect the localization of the photogenerated charges. The spectrum of the as prepared

0.5% Er/ZrO_2 sample also shows the presence of a well-defined axial signal at g∥=1.978 and g⊥=1.955, which is assigned to Zr^{3+} ions, probably due to the Er^{3+} ions and the consequent formation of oxygen vacancies. Upon irradiation, both the spectra of the 0.5% Er/ZrO_2 and 10% Er/ZrO_2 samples show the formation of the signal related to the localized hole. In addition, in this case the intensity of the spectrum of 0.5% Er/ZrO_2 is higher than that of 10% Er/ZrO_2.

3.1.3 Photocatalytic activity study

Concerning the photoreactivity experiments, blank tests, carried out under the same experimental conditions (section 3.1.1) and they ensured that no organic compounds were produced in the absence of catalyst as well as under dark or in the absence of CO_2.

On the contrary, in all of tests carried out in the presence of CO_2, all of the samples showed activity for CO_2 photo-reduction giving rise to small organic molecules and CO which increased by increasing the irradiation time as shown in Figure 33, i.e., in the presence of ZrO_2 catalyst.
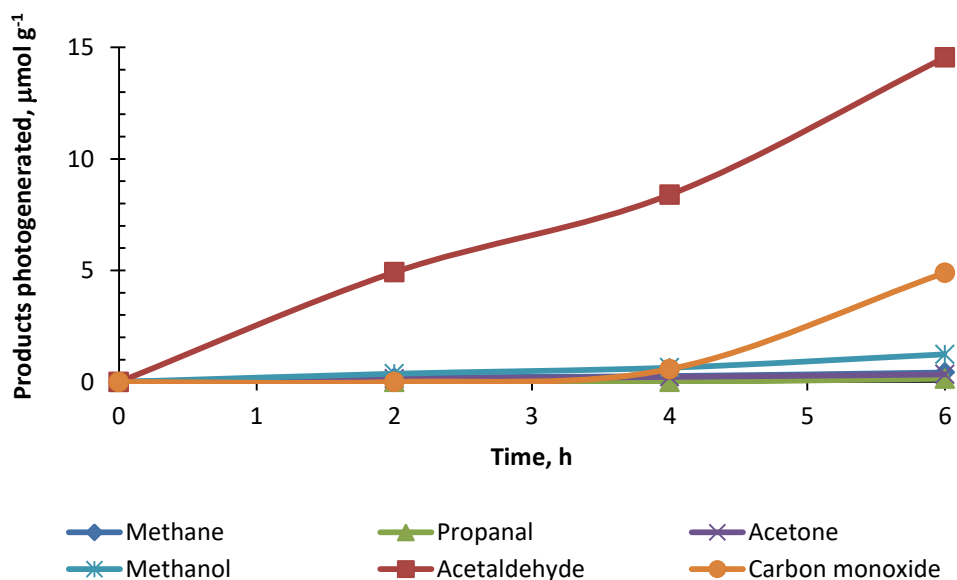
Figure 33. Photogenerated products versus irradiation time in the presence of ZO_2 catalyst, CO_2 and H_2O.

Generally, during the first 6 h of irradiation acetaldehyde, CO and traces of methane, methanol, methanal, propanal and propanone were obtained for all of the catalysts used. Data are summarized in Figure 34.
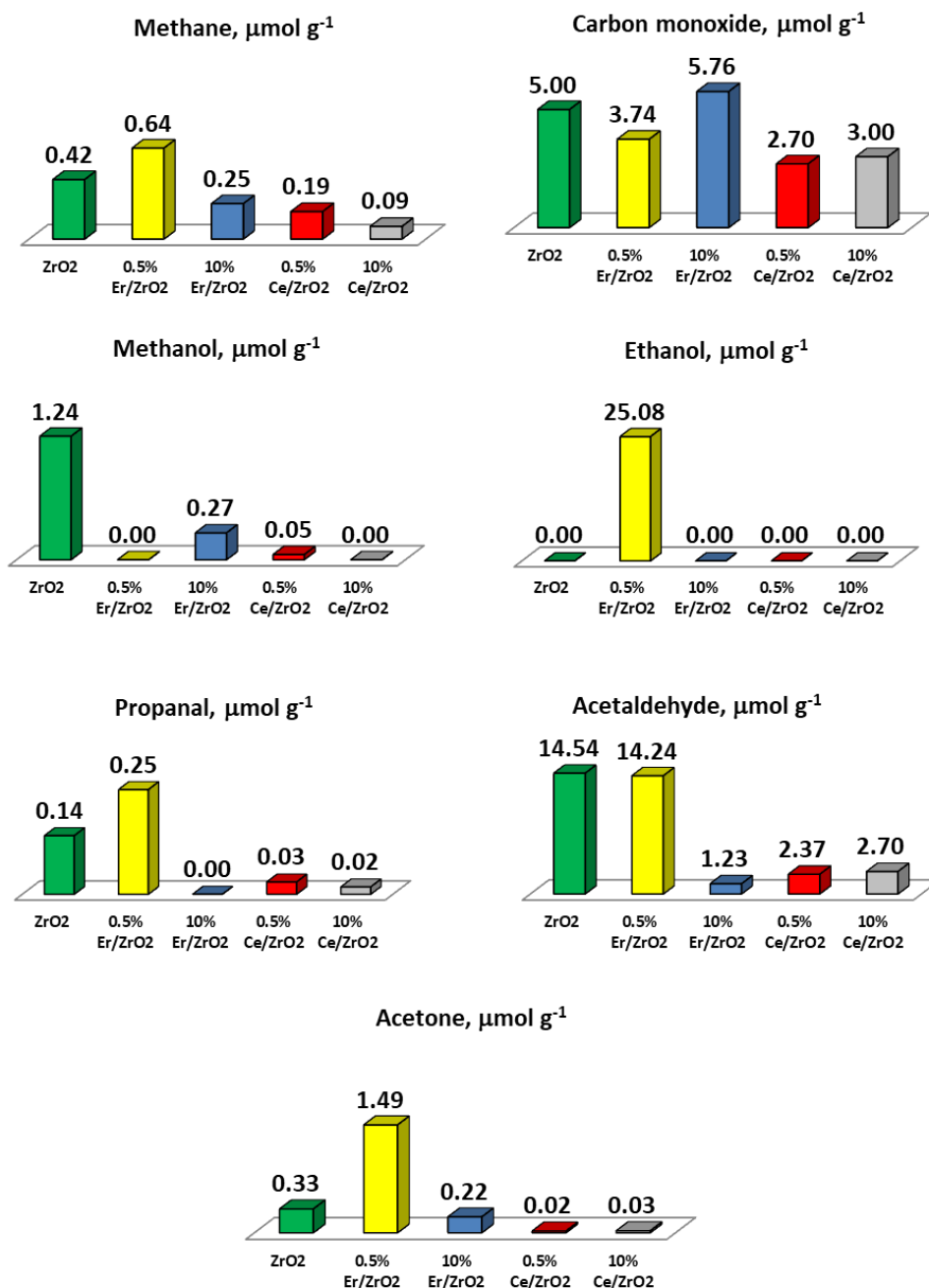
Figure 34. Photocatalytic reactivity (in terms of μmol g^{-1}) towards CO$_2$ reduction after 6 hours of irradiation time obtained with the following catalysts ZrO$_2$, 0.5% Er/ZrO$_2$, 10% Er/ZrO$_2$, 0.5% Ce/ZrO$_2$ and 10% Ce/ZrO$_2$ coloured green, yellow, blue, red and grey, respectively.

The presence of ZO_2 catalyst induces formation of ca. 5 and 15 μmol g^{-1} of CO and acetaldehyde, respectively.

At longer irradiation times (up to 24 h) the maximum amount of acetaldehyde increased from ca. 15 μmol g^{-1} (after 6 h) to 25 μmol g^{-1}. Similar behaviour was observed in the presence of 0.5% Er/ZO_2 sample, where acetaldehyde production increased from 14 to 17 μmol g^{-1} after 6 h and 24 h of irradiation, respectively. For both samples the CO_2 reduction rate declines for long-term irradiation. Although this effect is more pronounced in the presence of 0.5% Er/ZO_2, this sample showed the best activity producing also 25 μmol g^{-1} of ethanol after 6 h irradiation. This amount remained constant even after 24 h irradiation.

As shown in Figure 34, increasing the extent of Er doping on ZrO_2 (10% Er/ZO_2 sample) results in a reduction of the CO_2 conversion efficiency and no ethanol could be detected. In detail, in the presence of 10% Er/ZO_2 sample the amount of acetaldehyde produced decreased more than 10 times with respect to 0.5% Er/ZO_2, while a slight increase of the photogenerated CO was observed (from 3.74 to 5.76 μmol g^{-1}), which hence becomes the main product.

A different behaviour was observed in the presence of Ce doped photocatalysts. CO and acetaldehyde remained the main products of CO_2 photoreduction, but the amount of photoreduction products increased with increasing the Ce doping. However, the overall efficiency of Ce doped materials was always lower than both that of bare ZO_2 and Er doped materials.

Therefore, in all photocatalytic test, traces of methane, methanol, propanal and acetone detected were lower than 1 μmol g^{-1}, excepted for the acetone (1.49 μmol g^{-1}) and methanol (1.24 μmol g^{-1}) produced in the presence of 0.5% Er/ZO_2 and ZO_2 respectively, after 6 h of irradiation time.

As above discussed, ZO_2 and 0.5% Er/ZO_2 catalysts exhibited the best photoreduction performance towards CO_2 reduction. This fact are highlighted in Figure 35 where the total carbon converted after 6 h irradiation time, is calculated according to eq. 17.

Carbon converted, μmol g⁻¹
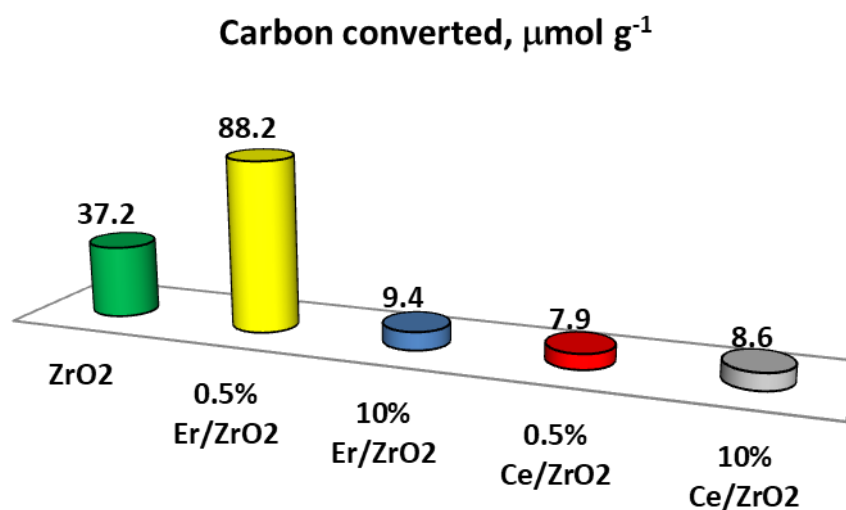
Figure 35. Carbon converted obtained after 6 hour of irradiation time with the following catalyst ZO₂, 0.5% Er/ZO₂, 10% Er/ZO₂, 0.5% Ce/ZO₂ and 10% Ce/ZO₂.

$$\frac{Converted\ carbon}{catalyst\ weight} = \frac{\sum Carbon\ for\ each\ produced\ species}{Amount\ of\ catalyst}, \frac{\mu mol}{g_{catalyst}} \quad \text{Eq. 17}$$

By comparing the obtained results, the best photoreduction activity was achieved in the presence of 0.5% Er/ZO₂ and ZO₂ affording ca. 88 and 38 μmol g⁻¹ of carbon converted, respectively. 0.5 % Er doping enhanced the ZrO_2 performance more than 2 times. An opposite trend was observed by increasing the amount of Er from 0.5 to 10%, which caused a drastic reduction in the CO_2 reduction efficiency (3 times less with respect the ZO₂ sample and ca. 10 times less with respect to 0.5% Er/ZO₂ catalyst). Ce doped materials presented the lowest efficiency. However, increasing Ce doping resulted in higher amount of carbon converted (from 7.9 to 8.6 μmol g⁻¹) comparable with that obtained with 10% Er/ZO₂ catalyst (9.4 μmol g⁻¹).

As literature reports, the same reaction has been carried out by using the same set-up in the presence of TiO_2 photocatalysts obtained from $TiCl_4$ as the precursor.[110] In that case, depending on the type of catalyst, a different selectivity was observed, but the main reaction product observed was also ethanal in a maximum amount of ca. 1 μmol g⁻¹ after 5 h of irradiation. Also, GaP/TiO₂ materials were used before in the same system.[122] In that case, the main product obtained by the CO_2 reduction

was methane in an amount of ca. 12 μmol g^{-1} after 6 h of irradiation. However, a more thorough investigation is necessary in order to understand the different selectivity of the various photocatalysts reported in the literature.

The photo-activity of bare ZrO_2 under UV irradiation can be explained by taking into account the photoluminescence and EPR studies indicating that this material was able to photo-produce electron-hole pairs under UV light irradiation (in the PL λ_{exc}=365 nm), although its band gap is 5.2 eV.

To sum up, the CO_2 photoreduction activity of the ZrO_2 based samples can be explained by considering their defectivity, which mainly consists in the presence of oxygen vacancies. Even if ZrO_2 presents a wide band gap (5.2 eV), the high defectivity not only induces visible light harvesting capability, but also the possibility of dissociative adsorption of CO_2. In fact, as schematically depicted in Figure 36 and reported in the relevant literature,[290] oxygen vacancies allow formation of intermediate complexes (a) characterized by lower activation energy with respect to the species formed by interaction of CO_2 with a perfect ZrO_2 surface (b).

a   b
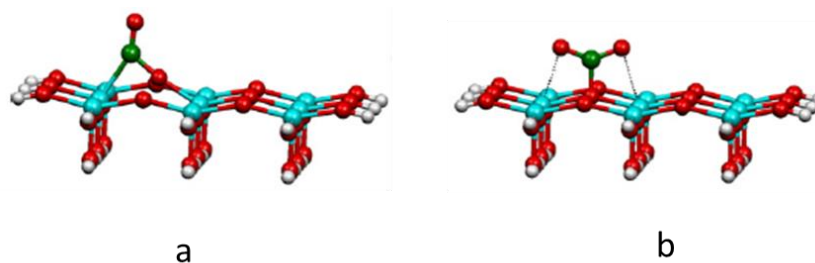
Figure 36. CO_2 adsorption on defective (a) and perfect (b) ZrO_2 surface.

Doping with Ce^{4+} stabilizes the tetragonal polymorphous structure of ZrO_2 thus diminishing the defectivity. As a result, CO_2 conversion for all of the Ce doped materials was lower than that observed for the bare ZrO_2 sample. On the other hand, low amounts of Er^{3+} in the ZrO_2 lattice (0.5% Er/ZO$_2$ sample) increase the defectivity of the material as demonstrated by EPR and Raman spectroscopy results. As a result, this sample showed the highest photocatalytic CO_2 reduction efficiency. However, increasing the Er doping extent tentatively favoured

segregation of erbium containing oxides, which led a detrimental effect on the CO_2 reduction activity.

3.1.4 Conclusion

The preparation of ZrO_2 by a solvothermal method and the introduction of new electronic states in this high band gap semiconductor by doping with Ce and Er, led to new photocatalysts able to absorb portions of UV (λ=365 nm) and solar light. Pristine ZrO_2 as well as Ce and Er-doped ZrO_2 resulted photoactive in gas-solid regime for CO_2 reduction to form mainly acetaldehyde. This uncommon behaviour for an insulator like ZrO_2 (with a band gap of more than 5 eV) is explained by the formation of intra band gap states due to the O vacancies. The intra band states are responsible for the "double jump" absorption leading to excitation of the electrons from the valence band to the conduction band. In the doped materials, the lanthanides doping showed two opposite CO_2 reduction capability. In the Er doped materials, lower doping resulted in an enhancement of the activity due to the increasing of O vacancies with respect to bare ZrO_2. At higher Er contents and in both Ce doped materials, lower photoreduction capability was achieved with respect to pure ZrO_2. Seen the promising behaviour, further investigation could be useful to improve the structure understanding and the reduction capability of this type of catalysts.

3.2   G/TiO$_2$ composites for CO$_2$ photoreduction

The results presented in this chapter have been published in:

3.2.1 Photocatalytic test conditions

In order to test the G/TiO$_2$ catalysts at different graphene loadings (0.5, 1, 3 and 10) for CO$_2$ photoreduction, the same apparatus described in the section 3.1.1 was used. In addition, in this case, blank tests were performed.

3.2.2 Characterization of G/TiO$_2$ materials

FTIR spectra of the home-prepared G/TiO$_2$ samples are reported in Figure 37. The FTIR spectrum of graphene oxide (GO) in Figure 37 (black spectrum) shows the presence of abundant hydroxyl, carboxyl, and epoxide groups, as indicated by the characteristic peaks of the C=O stretching vibration at 1733 cm^{-1}, the O-H deformation at 1404 cm^{-1}, the C-O (epoxy) stretching vibration at 1227 cm^{-1}, the C-O (alkoxy) stretching vibration at 1049 cm^{-1}, and the epoxy or peroxide group peak at 957 cm^{-1}. After reduction of GO by hydrothermal synthesis in the presence of TiO$_2$ (see section 2.2.2), the intensities of the bands related to oxygen containing groups significantly decrease in all of the spectra of the composites G/TiO$_2$, while the peak at 1624 cm^{-1}, which corresponds to non-oxidized graphitic domains remains virtually the same. This confirms the reduction of GO to graphene.[176] In addition, it is evident the broad band in the low frequency region (600-1000 cm^{-1}) of the spectra of the

composite materials due to the presence of TiO_2 (Ti-O-Ti stretching). However, the band centre shifts towards higher wavenumbers at higher graphene loadings. This effect has been reported in literature[176] and it is due to the presence of Ti-O-C vibrations which combine with the Ti-O-Ti vibrations of TiO_2. This result confirms formation of G/TiO_2 composites by chemical interaction of TiO_2 and graphene.
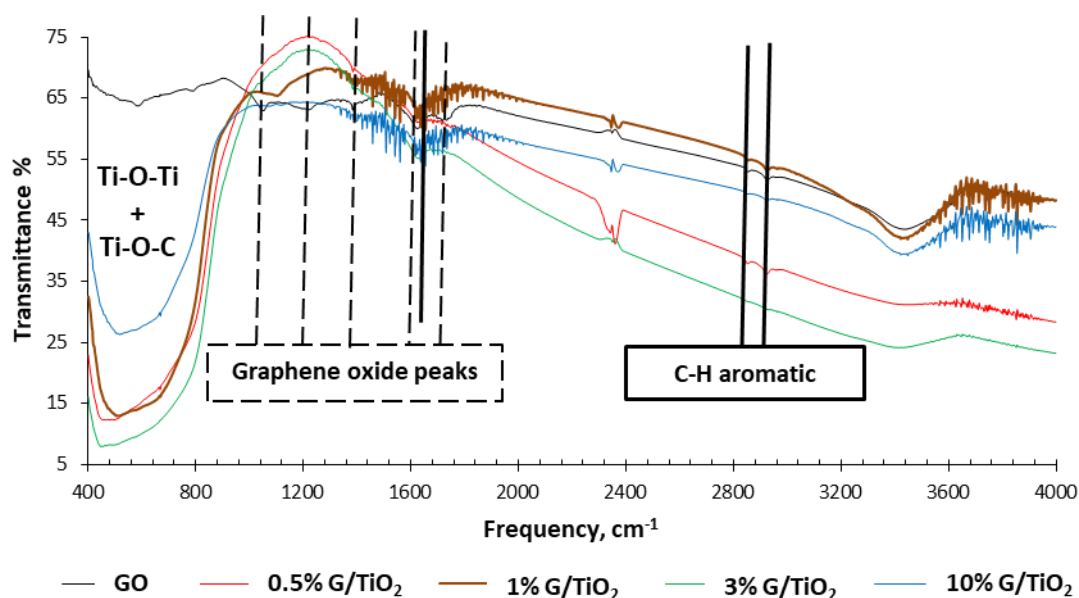
Figure 37. FTIR spectra recorded from 400 to 4000 cm^{-1} of pure graphene oxide (black) and G/TiO₂ composites at different graphene loading. The vertical black dashed and full black lines indicate the graphene oxide (GO) and graphene (G) characteristic peaks, respectively.

In order to obtain information about structural defects of graphene, Raman analysis has been performed and the results are reported in Figure 38. By the analysis of the characteristic peaks labelled in Figure 38 as D and G, Raman spectroscopy is capable not only to identify the presence of graphene but also to provide information such as the amount of disorder, doping, and the atomic arrangements at the edges.[291] Briefly, all carbons show common features in their Raman spectra in the 800–2000 cm^{-1} region, the so-called G and D peaks, which lie at around 1580 and 1360 cm^{-1}, respectively.[292] The D peak is due to the breathing modes of sp^2 rings and requires a defect for its activation.[293] This band derives from transvers optical phonons around the K point of the Brillouin zone.[292] The G peak corresponds to the E_{2g} phonon at the Brillouin zone center.[292] The Raman spectra of graphite and graphene also show

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second-order scattering.[294] The *D* peak and its second-order peak *2D* are activated by resonance processes.[295, 296] Notably, the G peak of the composites is shifted towards higher frequencies with respect to the G peak of the spectrum of bare GO. This indicates that the graphitic structure present in the composites is graphene rather than graphene oxide as reported in literature.[297]

The D band is an indication of disorder, which may arise from certain defects such as vacancies, grain boundaries,[293] and amorphous carbon species.[298] The intensity ratio of these two bands indicates the quality of the product. The band intensity ratio I_d/I_g found equal to 1.00 for GO, decreased a little bit for all the G/TiO$_2$ composites. This difference indicates a decrease of defects by recovery of the aromatic structures. Lee et al. reported,[299] in fact, an increase of the I_d/I_g ratio of reduced graphene oxide treated with hydroiodic acid and acetic acid, indicating that the reduction process altered the structure of GO with a large quantity of structural defects.
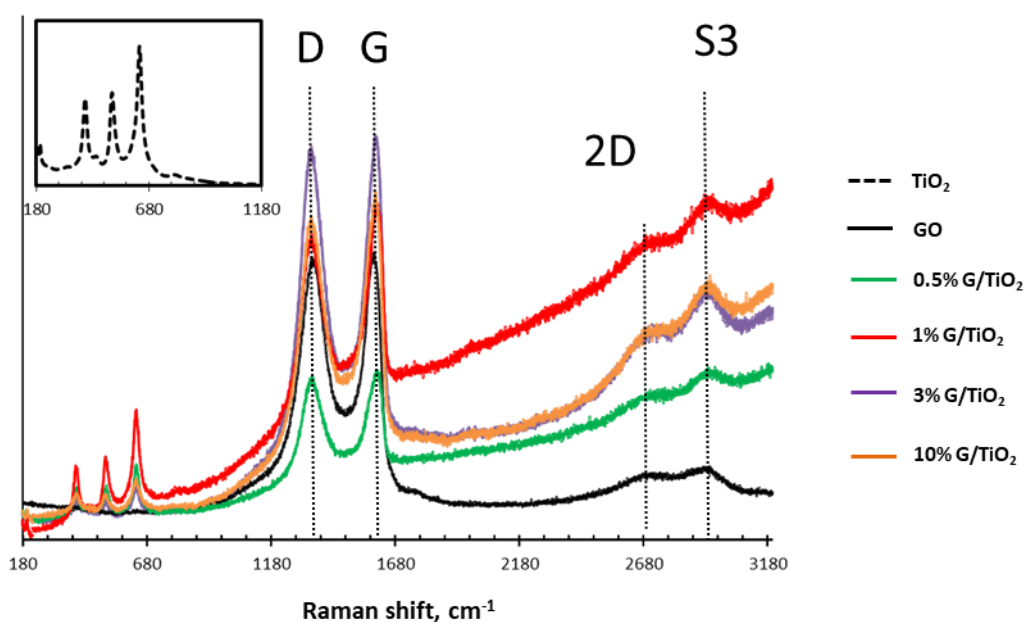
Figure 38. Raman spectra analysis of G/TiO$_2$ composites, pure GO and TiO$_2$ by using a laser at 532 nm. The TiO$_2$ Raman spectrum is shown in the inset (dashed line).

Based on this information, it can be deduced that the composite prepared herein contains less defects than the GO. The band at 2700 cm^{-1} is particularly interesting.

Monolayer graphene shows a sharp peak at ca. 2700 cm^{-1} known as the 2D band. Hence, the width of this band is considered an indicator of the number of graphene layers. Casiraghi found that while the intensity of the *G* peak is not affected by doping, the *2D* peak intensity is strongly sensitive to doping and in particular to the dynamics of the photoexcited electron-hole pairs.[291] In Figure 38, the band at 2700 cm^{-1} is related to the graphene structure.

The band, known as S3 (2900 cm^{-1}), is a second-order peak derived from the D–G peak combination. The intensity ratio between the bands S3 and 2D is proportional to the decrease of the defects.[297] The GO spectrum shows a large S3 band with low intensity appearing as a shoulder of the 2D band. When the GO is reduced to graphene, as in the case of the G/TiO$_2$ composites, the band S3 (indicated in Figure 38) increases in intensity and is more defined in terms of shape. These changes are more evident in the sample with loading starting from 1% wt.

This reduction, in terms of defects, is accompanied by lower oxygen content in graphene as FTIR suggests.

Three spot analyses have been performed for each sample. Some images were taken and are reported in Figure 39.

a)   b)   c)
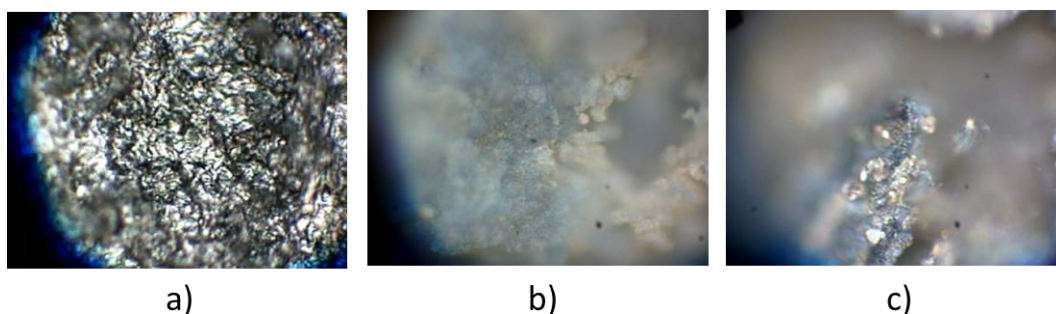
Figure 39. Microscopy images of a) GO, b) 0.5% G/TiO$_2$, and c) 3% G/TiO$_2$ samples.

Figure 39 shows that the composite 0.5% G/TiO$_2$ is less homogeneous with respect to GO sample. This evidence is probably due to the very low graphene loading along with its not complete dispersion. In these samples (blue/grey) the TiO$_2$ and G/TiO$_2$ domains are evident. At higher graphene loadings, higher homogeneity can be observed.

In order to study the effect of the G % wt. loading on the optical properties, DRS spectra were performed. Results are shown in Figure 40. All of the samples present a red shift of the absorption edge compared to bare TiO_2, which shows standard absorption edge at ca. 410 nm, except the sample at lower G loading equal to 0.5%. Probably this G loading is too low to generate a UV light absorption modification on composite. Whilst, 1 wt. % G composite presents an adsorption at ca. 420 nm, which correspond in a red shift of TiO_2 absorption edge equal to 410 nm. This result is in accord with the relevant literature.[176] When, in the G/TiO_2 composites, the G wt. % loading increases at 3% and at 10, the relative absorption edge rises to 440 and 470 nm, respectively. These results indicate that the introduction of graphene causes the narrowing of the band gap, as shown in Figure 40 (intersection between the dashed lines and the wavelength axis) with a consequently catalyst visible light absorption. This narrowing should be attributed to the chemical bonding between TiO_2 and G, by formation of Ti-O-C bond, as previously observed (FTIR analysis, Figure 37) and as suggested by Zhang et al. [176] As a result of the extended photo-responding range a more efficient utilization of the solar spectrum could be achieved, especially under visible light irradiation. The visible light harvesting capability of the 10% G/TiO_2 catalysts is expected to improve its photoactivity.
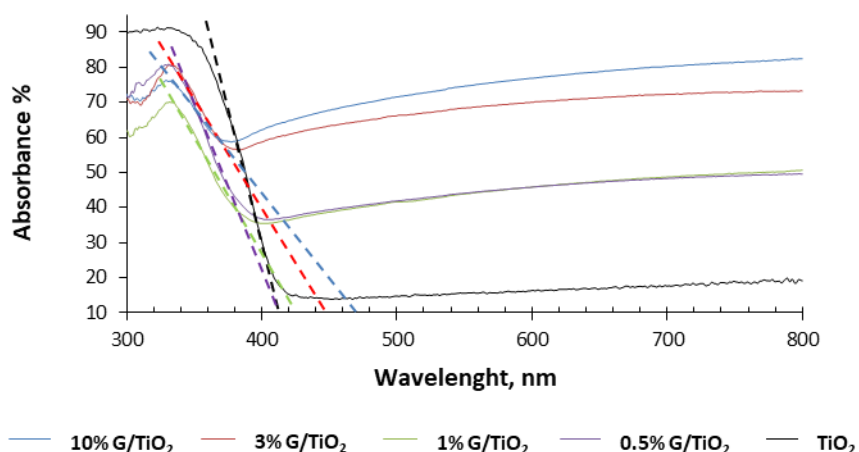
Figure 40. Diffuse Reflectance spectra recorded for all G/TiO_2 composites.

Table 11 summarises the media of specific surface area (SSA) of the samples in desorption and adsorption of N_2. The SSA is higher than that of TiO_2 for samples at

high graphene content (3 and 10%) whilst is lower than TiO_2 at low graphene content (0.5% and 1% G/TiO_2). This effect is probably due to the inhomogeneity of samples at low wt. % (0.5 and 1% of G) where the G particle are not well dispersed thus blocking the access to TiO_2 channels. On the other hand, in the sample at 3 and 10 % G/TiO_2, G is well dispersed in the composite and the SSA of the material (TiO_2) increases making easier the adsorption of the reagent.

Table 11. Specific Surface Area (SSA) obtained by a single point measurements of desorption and adsorption of N_2.

SSA, m^2g^{-1}	10% G/TiO_2	3% G/TiO_2	1% G/TiO_2	0.5% G/TiO_2	TiO_2
A $_{media}$	58	57	45	46	52

3.2.3 Photocatalytic activity of G/TiO_2 samples

The photocatalytic tests for CO_2 reduction were performed in a gas phase batch photoreactor under the conditions detailed in section 3.1.1, in the presence and in the absence of CO_2, cleaning by N_2 under irradiation prior to CO_2 feeding. The same products were qualitatively detected during 6 hours of irradiation by using the G/TiO_2 photocatalysts, but with a different amount depending on the graphene loading. In particular, the amount of CO_2 reduction products increased by increasing irradiation time. The G/TiO_2 composites produced methane (Figure 41) and methanol (Figure 42) as the major products, and in some cases also acetaldehyde and carbon monoxide were detected.

In particular, the 1% G/TiO_2 sample exhibited the best CO_2 photoreduction capability reaching a methane concentration of ca. 1000 μMg^{-1}, corresponding to a methane production rate of 5 $\mu mol\ g^{-1}\ h^{-1}$. This result is in accord with that reported by Tu and coworkers which found a methane production rate of 7.3 $\mu mol\ g^{-1}\ h^{-1}$ after 4 h of irradiation time (reactor volume: 25 mL).

0.5% and 1% G/TiO_2 composites produced a methane concentration of ca. 200 $\mu M\ g^{-1}$ after 6 h of irradiation. The worst methane production (120 μMg^{-1}) was detected in the presence of 10% G/TiO_2, with the highest G content, showing reactivity at least 4 times lower with respect to that measured for 1%G/TiO_2 catalyst.
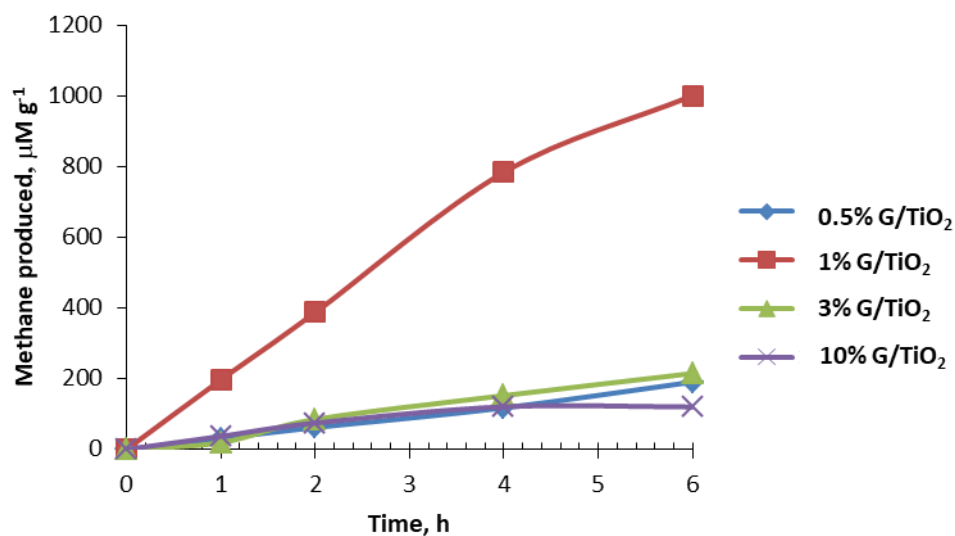
Figure 41. Methane photo-generated versus irradiation time in the presence of G/TiO₂ composites.

As far as the methanol formation is concerned, generally during the first two hours of irradiation its concentration strongly increases and after slows down or decreases. As in the case of methane production, the maximum concentration was obtained in the presence of 1% G/TiO$_2$ which allowed to produce 172 μM g^{-1}, whilst 15 and 43 μM g^{-1} were detected in the presence of 0.5% G/TiO$_2$ and 3% G/TiO$_2$ catalysts, respectively. (Figure 42)

In addition, in this case, the 10% G/TiO$_2$ sample exhibited the worst photoactivity and methanol produced in the first hours of irradiation was degraded during the following irradiation.
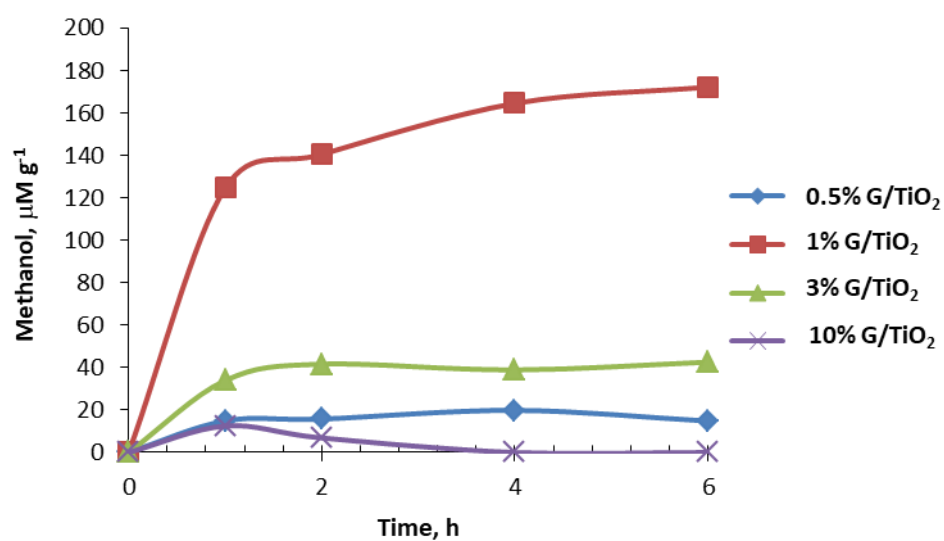
Figure 42.Methanol photo-generated versus irradiation time in the presence of G/TiO$_2$ composites.

As shown in Figure 43, only the samples 1% and 10% G/TiO$_2$ were capable to photoreduce CO$_2$ to carbon monoxide, which reached a concentration of 100 and 90 μM g^{-1}, respectively. In the presence of the other samples, no CO was detected.
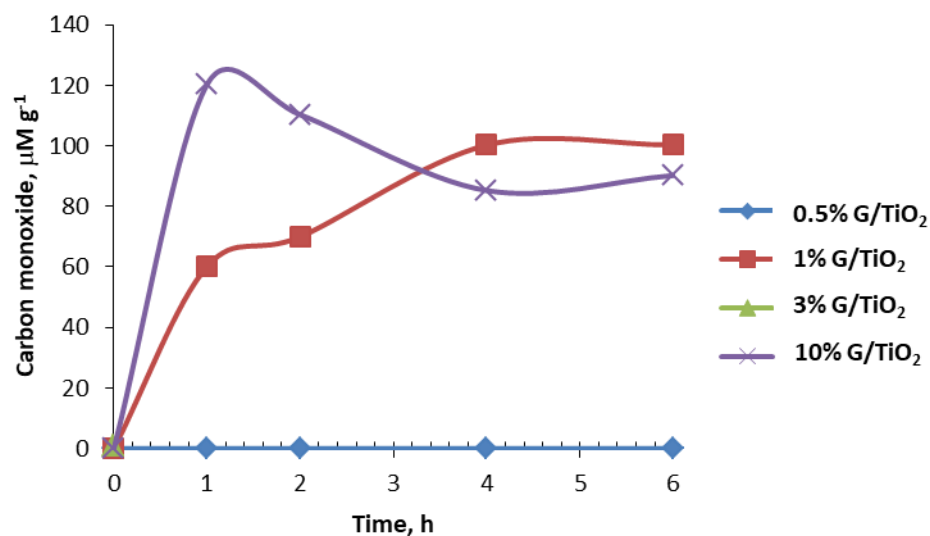
Figure 43. Carbon monoxide photo-generated versus irradiation time in the presence of G/TiO$_2$ composites.

Acetaldehyde was detected only for the samples with low graphene amount (Figure 44). In particular, after 6 h irradiation concentrations of ca. 243 and 12 μM g^{-1} was detected in the presence of 1% G/TiO$_2$ and 0.5% G/TiO$_2$ photocatalysts, respectively.

Notably, the presence of acetaldehyde as a CO_2 photoreduction product has been never observed before in other reports in the presence of graphene modified TiO_2.
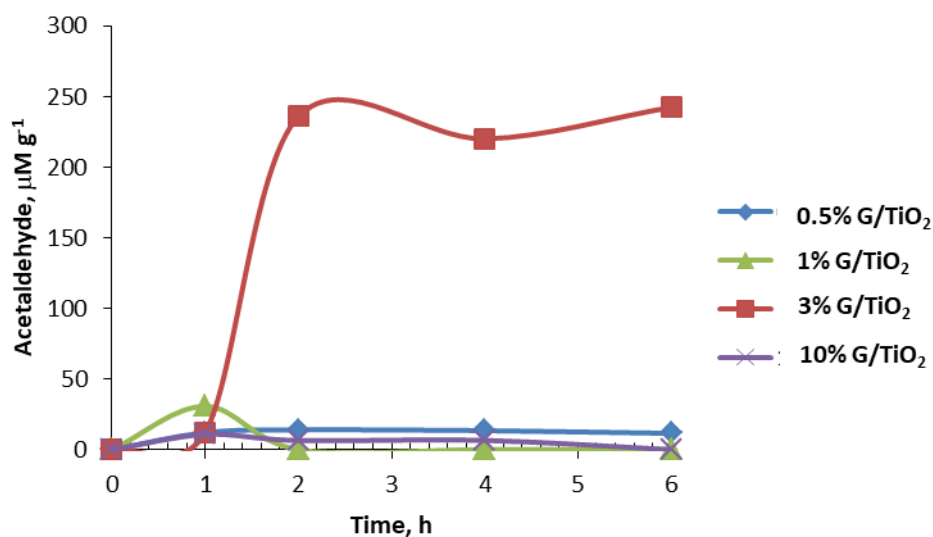
Figure 44. Acetaldehyde photo-generated versus irradiation time in the presence of G/TiO₂ composites.

In order to evaluate the CO_2 photoreduction improvement, due to the graphene loading, TiO_2 alone was also tested under the same experimental conditions. In these experiments, no products were detected highlighting the scarce reduction capability of pure commercial TiO_2 with respect to the composites. This is also evident from the values of total carbon converted which are reported in Figure 45. In detail, a loading of 0.5 % wt of G increases the total carbon converted (Eq. 17 section 3.1.3) from 0 to 5.7 μmol g^{-1}. Further increasing the amount of G from 0.5 to 1% wt in the composite results in an important improvement of the amount of total carbon converted, which reaches a value of 44 μmol g^{-1} (ca. 9 times more just by doubling the graphene content). This result is in accord with the literature studies previously summarized in Table 4. When the amount of G in the composite rises from 1 % to 3 wt %, the photoreduction capability of the material drastically falls from 44 to 7.2 μmol g^{-1} h^{-1} (in terms of total carbon converted). As Figure 45 shows, further increments of graphene loading up to 10% wt, decreases the photoreactivity of material to values comparable with those retrieved for 0.5% G/TiO$_2$. The existence of an optimum graphene content has been already highlighted in literature.[181] However, by comparing the best results obtained with the 1% G/TiO$_2$ catalyst in this

dissertation with those reported in literature, the carbon-converted values hereby reported are the highest ever reported in the presence of metal free photocatalysts.
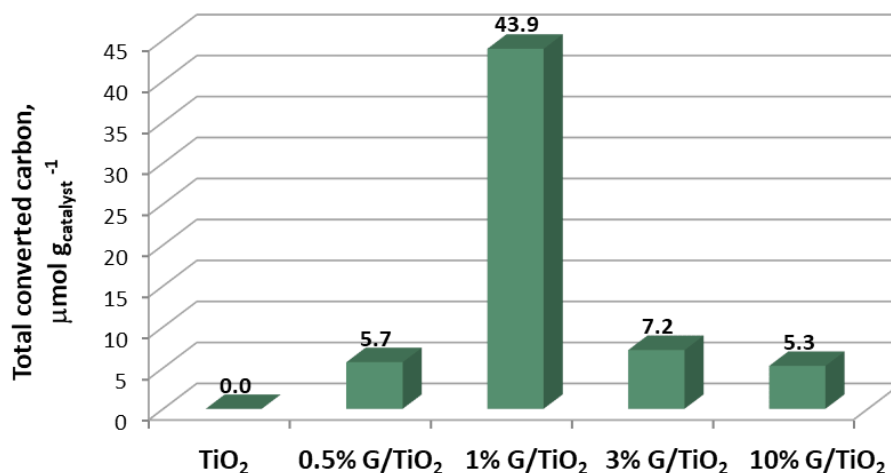
Figure 45. Total carbon converted after 6 h of irradiation time in the presence of G/TiO$_2$ composites.

Even if 1% G/TiO$_2$ photocatalyst shows the best photoreduction capability in terms of CO$_2$ conversion, it shows the lowest selectivity (Eq. 18) towards methane with respect to the other composites tested (Figure 46).

$$Selectivity_i = \frac{i-species\ produced}{\sum_i^n species\ produced}, \quad -$$

Eq. 18
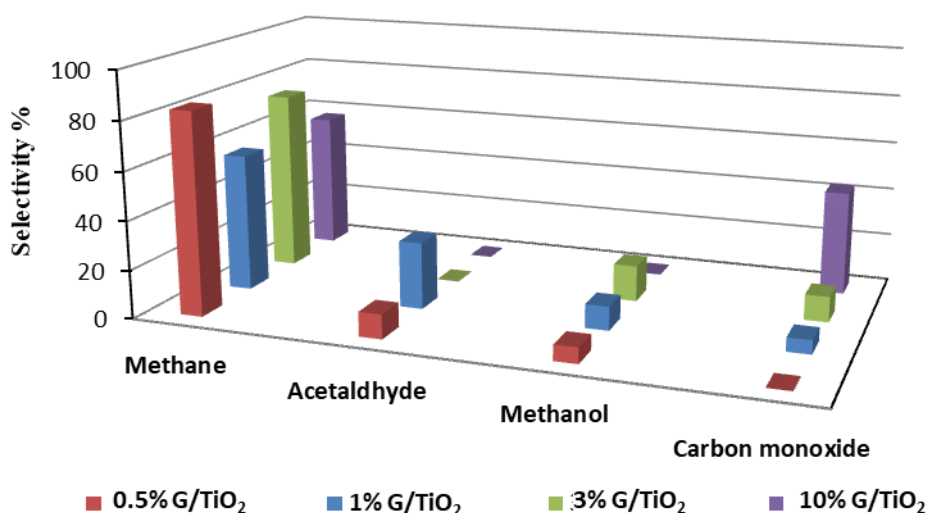
Figure 46. Selectivity of methane, carbon monoxide, acetaldehyde and methanol photogenerated after 6 h of irradiation in the presence of G/TiO$_2$ composites.

In detail, 0.5% G/TiO_2 shows the best selectivity to methane (83.5%). An interesting trend is observable with respect to the methanol selectivity, which increases with increasing the graphene loading and reaches the highest value (14 %) in the presence of 3% G/TiO_2.

10% G/TiO_2 catalyst converts CO_2 only to two products, i.e., methane and CO. In particular, it shows the best selectivity (43%) towards CO. Notably, the selectivity values decrease with decreasing the graphene loading for all of the composites.

3.2.4 Conclusion

The hydrothermal technique was used to prepare G/TiO_2 hybrid materials at different G loading from GO as the precursor. Characterization results highlighted chemical interaction between G and TiO_2 particles through Ti-O-C bonding formation. The electrons photogenerated by excitation of the TiO_2 nanoparticles can transfer through graphene thus reducing losses related to charge recombination. Furthermore, the higher electron availability enables photoreduction of CO_2 into hydrocarbon fuel.

Notably, products deriving from multi-electron transfer processes, such as methane, are preferentially formed. This is due to the less endergonic nature of these processes (-0.24 V vs SHE at pH 7) with respect to the mono-electron transfer one (-1.9 V vs SHE at pH7) , and to the synergistic effect of TiO_2 and G. In fact, the latter efficiently conducts the photogenerated electrons, thus reducing charges recombination and enhancing the electron availability. The highest methane production (1000 $\mu M\ g^{-1}$) was observed for the 1% G/TiO_2 composite and it is the highest ever reported for similar systems in the presence of metal free photocatalysts. This research may open a new doorway for new significant application of graphene for the selective production of methane and methanol as a promising material in membrane photocatalytic continuous reactor. However further investigation is needed.

3.3 O-doped and pristine C_3N_4: structural changes after use for CO_2 photoreduction

The results presented in this chapter give the following manuscript

3.3.1 Photocatalytic test conditions

Photocatalytic tests were performed in a stainless steel T-shaped reactor, composed of UHV vacuum parts (Swagelok and Kurt J. Lesker) with an internal volume of 120 mL. The reactor was fitted with a quartz window to allow irradiation of the catalyst (Figure 47).
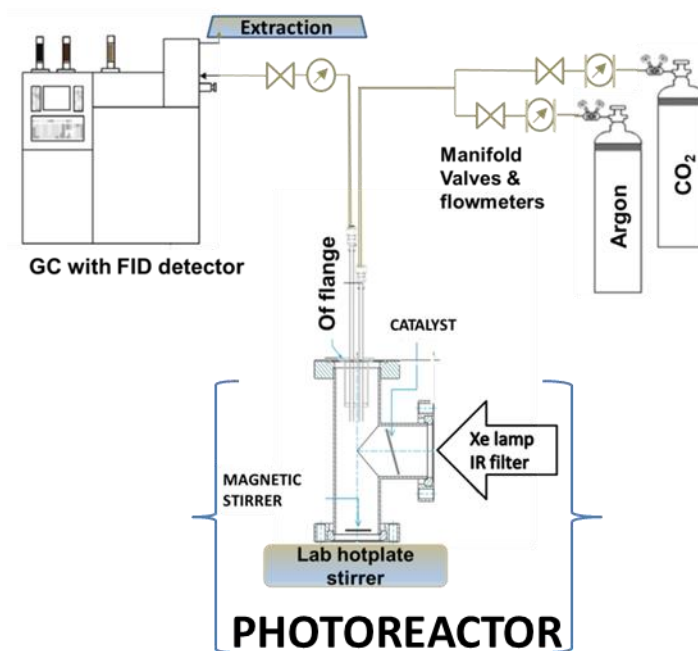
Figure 47. Batch photoreactor scheme equipped with a mass flow controller and light source reported from Cortes et al.[300] The system is on line connected with a GC-FID/TCD.

The catalyst-coated plate was placed inside the reactor facing the quartz window. High purity water (1 mL, Merck, SupraSolv 7732-18-5) was added to the bottom of the reactor at the start of each experiment. The reactor was purged for 10 min with 20% CO_2 (BOC, UN1013, 99.99% purity) in Ar (BOC, UN1006, 99.998% purity) before sealing at a pressure of 2 bar. For the control tests in the absence of CO_2, the reactor was instead purged for 10 min with Ar, and 1 mL of heated water was added to the reactor.[300] The temperature of the reactor was maintained with thermal tape at 70°C for all tests. The light source was a 100 W Xe lamp (LOT Oriel) equipped with an IR filter. The resulting light intensity is reported in Figure 48.
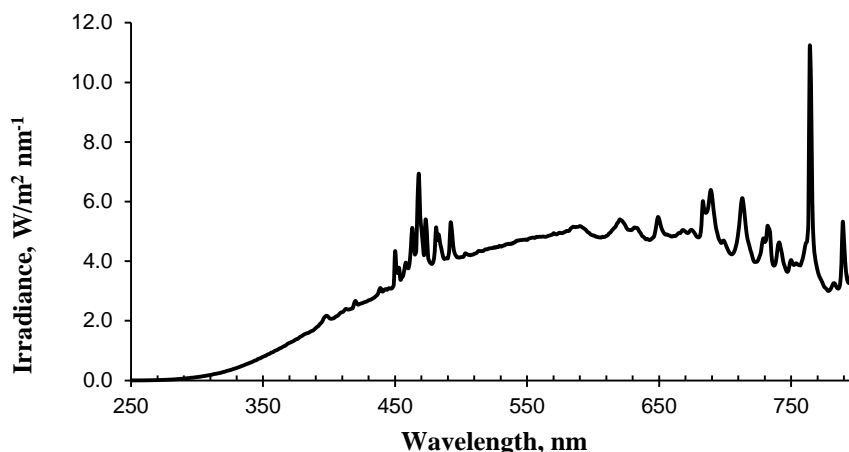
Figure 48. Measured irradiance from 100 W Xe lamp with IR filter.

The gaseous products obtained following irradiation were analyzed by gas chromatography (GC) with a flame ionization detector (FID) and the using Helium (BOC, UN1046, 99.999% purity) as the carrier gas. The GC (Agilent Technologies 7890B) was connected directly to the reactor and samples were analyzed every 30 min leading to a decrease in pressure inside the reactor (0.20 bar) each time a measurement was performed. Tests were replicated to determine the reusability of the material and were named $RnCO_2$ (where R means the replicate runs and n is the number cycles of CO_2 reduction testing performed). The control test in the absence of CO_2 was carried out with the same sampling time points as the other tests and was designated as RnAr. To investigate the effect of surface contaminants some of the samples were exposed to photocatalytic cleaning in the presence of oxygen prior to testing under standard CO_2 reduction conditions.

3.3.2 Characterisations of pure and O doped C_3N_4 materials

Analysis of the g-C_3N_4 and O_R-C_3N_4 was undertaken using FTIR, XRD, and UV-Vis reflectance techniques. The FTIR analysis correlates to previous reports on g-C_3N_4 [204-206, 301-306]. The finger printing from 807 to 1650 cm^{-1} and from 3100 to 3500 cm^{-1} by FTIR analysis demonstrates that the materials synthesized (section 2.2.4) are C_3N_4 structure type (Figure 49). The peaks at 807 cm^{-1} are due to the

characteristic breathing mode of the s-triazine ring system. The peaks at ca. 1242, 1322, 1412, 1563, and 1634 cm^{-1} are typical stretching vibration modes of C=N and C-N heterocycles. In addition, the broad peak between 3600 and 3000 cm^{-1} is caused by the NH and OH stretches. However C-O and C=O bonds are difficult to distinguish in O doped g-C$_3$N$_4$ by FT-IR, as the C-N, C-C and C-O bonds have very similar force constants.[307] Due to this constraint and the limited amount of O expected to be incorporated in the O$_R$-C$_3$N$_4$, no appreciable changes were observed when comparing it with the g-C$_3$N$_4$ catalyst by FTIR.
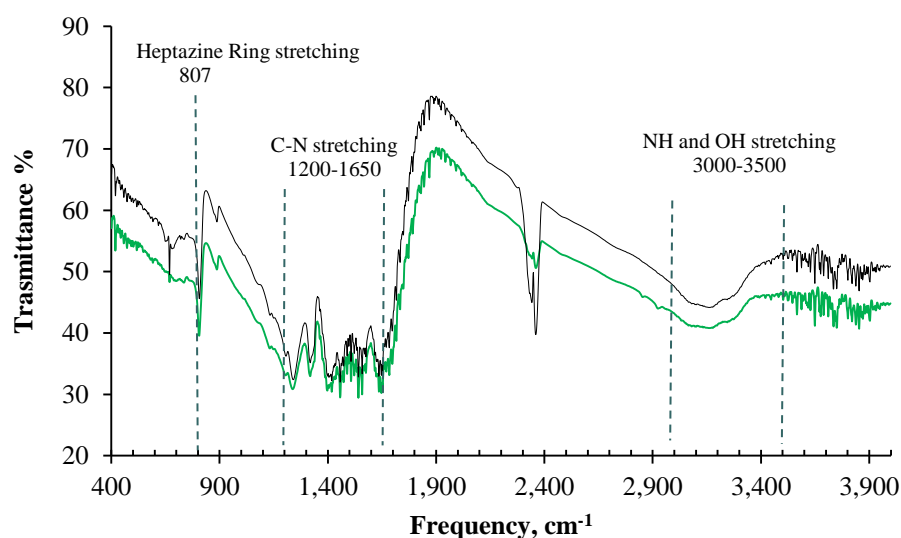
Figure 49. FTIR spectra of as synthesized g-C$_3$N$_4$ (green line) and O$_R$-C$_3$N$_4$ (black line) showing characteristic g-C$_3$N$_4$ fingerprint.

XRD analysis of the synthesized material showed a main 2θ peak at 27.4° which has been assigned to the (002) plane of g-C$_3$N$_4$,[195, 308] corresponding to a d-spacing of 0.326 nm. This peak is usually assigned to the distance between the layers of the 2D graphitic material, which undergo a little left-shift in the O doped materials, as reported in the literature.[274] The secondary intense peak at 2θ of 13.0° is attributed to the (100) plane, with a d-spacing of 0.680 nm, which is usually reported as the intralayer d-spacing.[195, 308] From identification of these features in the synthesized g-C$_3$N$_4$ material and comparison to tri-s-triazine spectra from literature, the synthesized materials can be confirmed to be the h-g heptazine phase of C$_3$N$_4$. The XRD spectra of the synthesised materials compared to expected peak positions previously reported by Fina et al.[308] are shown in Figure 50.
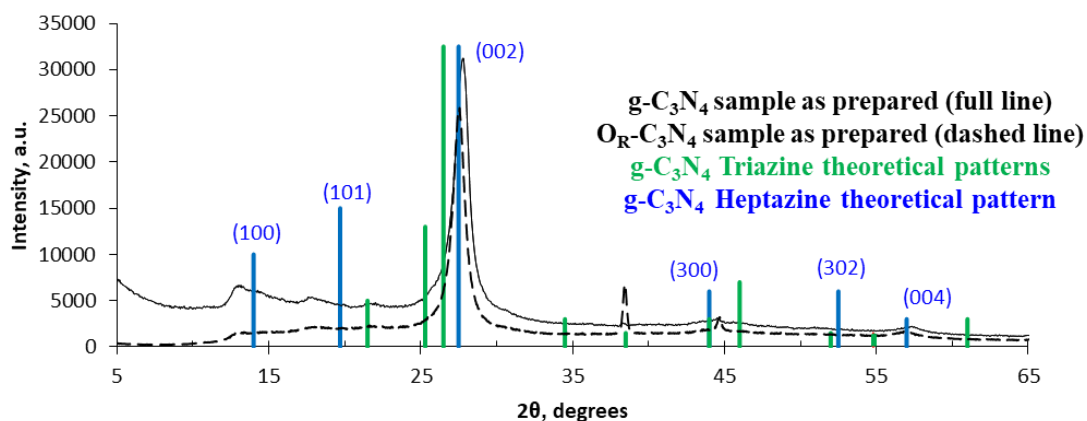
Figure 50. XRD patterns of pure g-C₃N₄ and O_R-C₃N₄ as prepared and the peak positions for two phases of g-C₃N₄ reported by Fina et al.[193, 308] *The name reported heptazine (tri-s-triazine) represents the melem unit.*

To discriminate among the different phases of g-C₃N₄ and to estimate the band gap energy of the material, the optical band gap was measured. When a semiconductor absorbs light with suitable wavelength, electrons are excited from VB to CB with the simultaneous formation of holes in the VB. These charges produced by photoexcitation can reduce and oxidize the adsorbed surface species, respectively, or give rise to recombination phenomena. A recent study reports a computational method which allows to correlate the thickness of s-triazine and h-g heptazine C₃N₄ with the band gap energy of the materials.[198] Diffuse reflectance spectroscopy was utilized to determine the band gap of both synthesized g-C₃N₄ catalysts. These analyses are shown in Figure 51. For pure g-C₃N₄ and O_R-C₃N₄ materials optical band gaps of 2.8 and 2.7 eV respectively were estimated. Both values appear consistent with a hexagonally structured h-g-heptazine C₃N₄,[193] and in addition, as expected, the samples O doped showed a red shift of the optical band gap with respect to the pristine materials.[195, 204, 206]
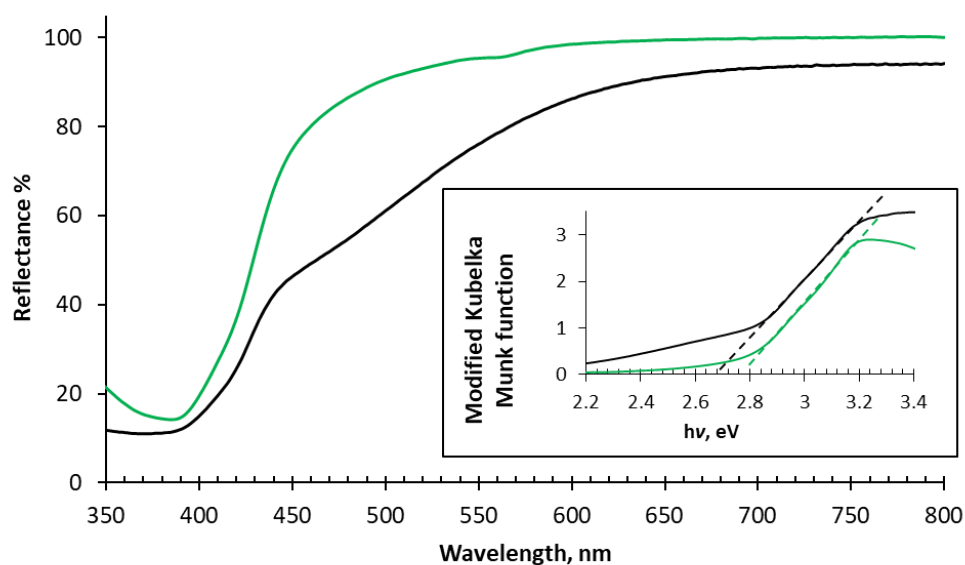
Figure 51. UV-Vis diffuse reflectance spectra of powder of pure g-C₃N₄ (red line) and O$_R$-C₃N₄ (black line) as prepared samples. The inset shows the Kubelka-Munk function vs photon energy, giving the graphic interpolation a band gap energy value equal to 2.8 and 2.7 eV for g-C₃N₄ and O$_R$-C₃N₄, respectively.

3.3.3. Photocatalytic tests

Measurement of photocatalytic activity for CO_2 reduction was performed in a gas phase batch photoreactor testing the g-C_3N_4, O_R-C_3N_4 and O_T-C_3N_4 immobilized samples under the conditions detailed in the section 3.3.1. Chromatographic determination of products from photocatalytic testing yielded only CO, within the limits of detection. No H_2, O_2 (from water splitting reactions), methane or other hydrocarbons were observed. A typical graph of CO production vs time using g-C_3N_4 is shown in Figure 52.
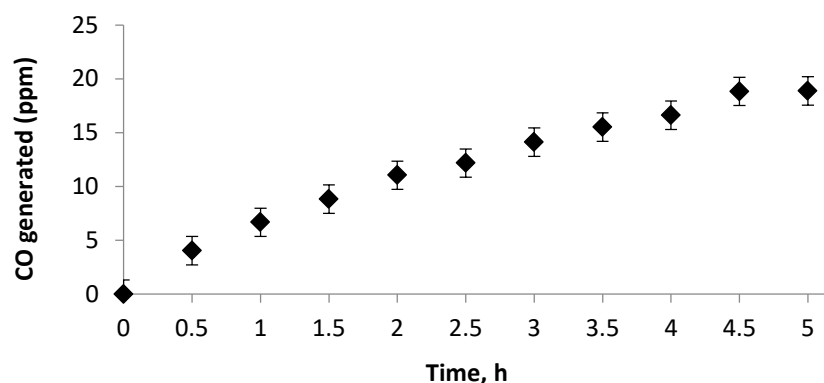
Figure 52. Concentration of CO versus irradiation time in the presence of CO_2 using g-C_3N_4 material.

Having the amount of CO produced with irradiation time, samples were retested to investigate their stability. Reuse of samples showed a decline in the CO concentration (Figure 53) with replicates (R1CO_2 and R2CO_2).

Control runs in the absence of CO_2 were undertaken. In the absence of CO_2, CO was still observed as a product, and a similar trend of lower CO generation on reuse was detected (Figure 53- R1-R3Ar runs).
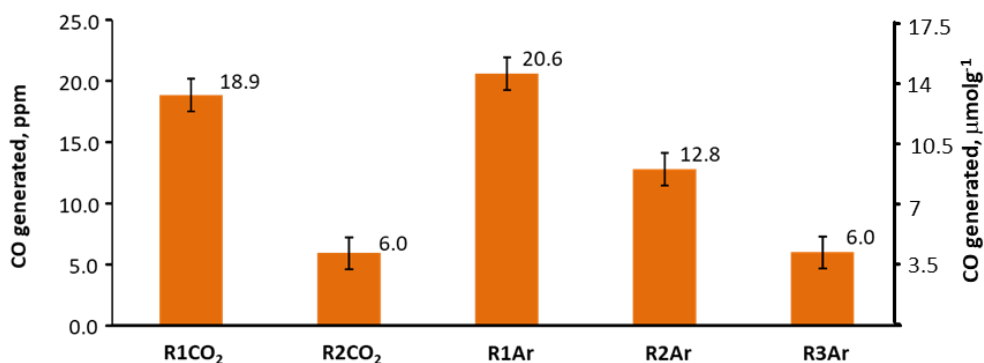
Figure 53. CO concentration obtained after 5 h of irradiation time in the presence (RnCO_2) and in the absence (RnAr) of CO_2 with g-C_3N_4.

The observation of only CO as gaseous product, the declining CO generation rate (on reuse or extended use), and the observation of CO in the absence of CO_2 suggest that some CO_2 molecules from atmosphere remained strongly adsorbed on the catalyst surface. To confirm this behavior a batch test was carried out in inert

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atmosphere in absence of CO_2 (N_2 humid) at atmospheric pressure and under visible light. This test confirmed a release of CO_2 with the irradiation time as reported in Figure 54.
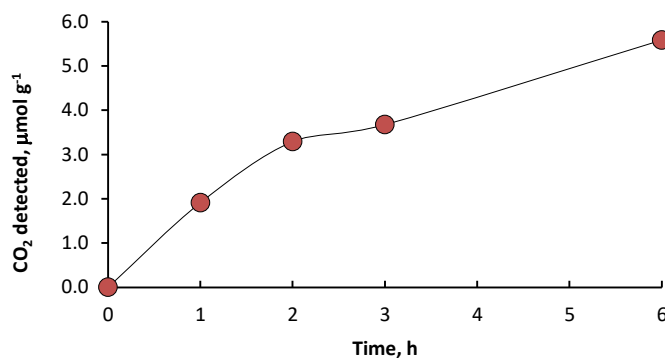
Figure 54. Amount of CO_2 released in a batch reactor under irradiation at ambient pressure and N_2 atmosphere from g-C_3N_4 powder previously cleaned.

Consequently, the adsorbed CO_2 could be responsible for the observed CO. In fact, in the presence of lower CO_2 amounts (just the adsorbed one), a slower catalyst inactivation occurred (***Figure 53***) with respect to the test in presence of higher CO_2 concentration (20% in Ar flow).

To investigate if adsorbed CO_2 or organic fouling was an issue, a twice-used (R2CO_2) sample was photocatalytically cleaned for 3 h in O_2 flow under UV-Vis irradiation. The photocatalytic cleaning with O_2 did not alter the material reactivity within the errors of the analytical system as shown in Figure 55.
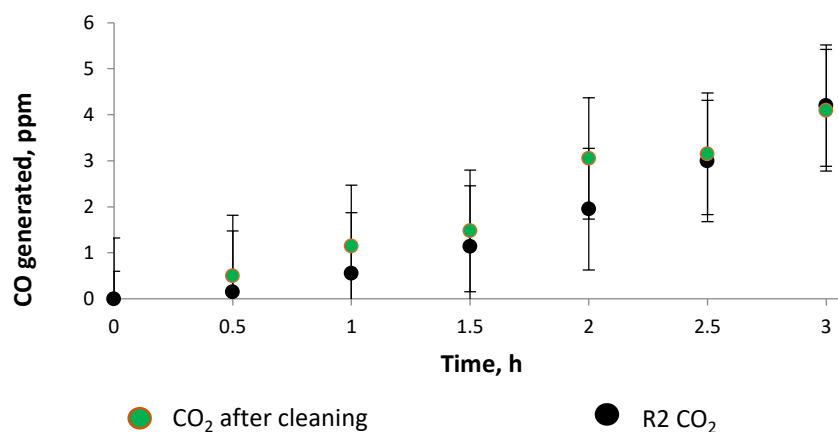
Figure 55. CO photo-generated in the presence of CO_2, before (R2CO$_2$) and after cleaning (CO$_2$ after cleaning) versus irradiation time with g-C$_3$N$_4$ as photocatalyst.

An oxygen doped carbon nitride, O_T-C_3N_4, was also tested for CO_2 reduction using the same methodology as the one utilized in g-C_3N_4 testing. During this experiment, only CO was detected and the CO generated was observed to decrease with reuse. This is a similar trend to that observed in the case of pure g-C_3N_4. Comparison of activity between pure g-C_3N_4 and O_T-C_3N_4 showed that oxygen modification was detrimental for CO formation (Figure 56). O_R-C_3N_4 was also tested under identical experimental conditions and the yield of CO detected was smaller than that found for the thermal oxygen doped and unmodified C_3N_4 samples.
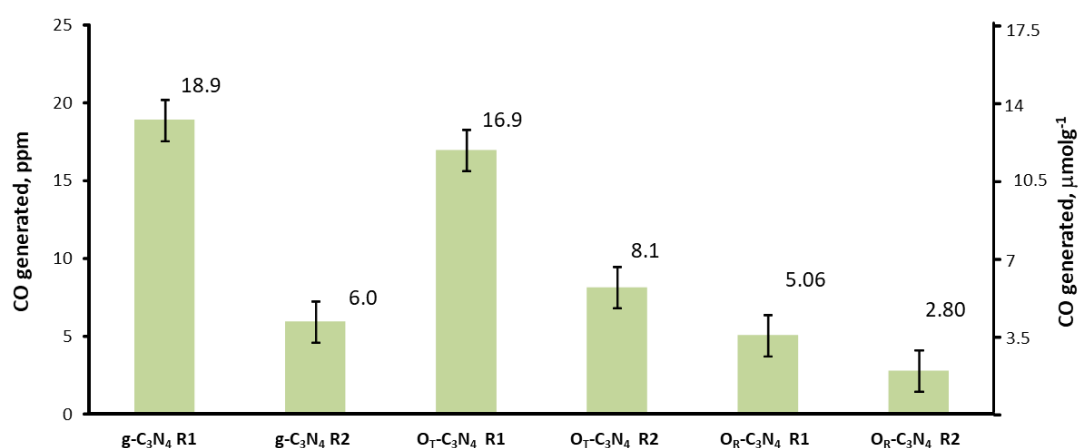
Figure 56. Reproducibly test of CO production in the presence of g-C$_3$N$_4$, O$_R$-C$_3$N$_4$ and O$_T$-C$_3$N$_4$ after 5 h of irradiation time in the presence of CO$_2$.

Table 12 reports the amount of phototogenerated CO expressed in terms of both, ppm and μmol g-1$_{catalyst}$. The apparent Quantum Yield, calculated according to Tan et al.,[309] is also reported. Notably, these figures decrease with reuse for of the catalysts tested, being all correlated.

Table 12. Formal Quantum Yield (QY) and CO generated by all sample used and reused after 5 hours of irradiation time in presence of CO_2 and water.

Catalysts	Ppm	μmol g^{-1}	QY %
C_3N_4 R1	18.9	13.0	0.0132
C_3N_4 R2	6	4.1	0.0042
O_T-C_3N_4 R1	16.9	11.7	0.0118
O_T-C_3N_4 R2	8.1	5.6	0.0057
O_R-C_3N_4R1	5.1	3.5	0.0035
O_R-C_3N_4R2	2.8	1.9	0.0020

Given the limited range of products detected under irradiation, the reduction in product yield with extended use, and the activity decreasing when comparing O_R-C_3N_4 with the O_T-C3N4 and unmodified samples, oxidation of g-C_3N_4 was considered as an alternative source of CO observed. Therefore, samples were analyzed before and after use by XPS and FTIR to determine the degree of oxidation consistent with this hypothesis. The structural and functional groups reported for g-C_3N_4 are given in Table 12. FTIR analysis was used to determine if any changes to the functional groups occur during the photocatalytic tests (Figure 56). All samples showed the finger-printing region characteristic for heptazine subunit and functional groups consistent with expected positions for g-C_3N_4 as detailed in Table 13.

Table 13. Peak positions of structural and functional groups observed by FTIR spectra for g-C_3N_4 and O-C_3N_4 samples.

FTIR analysis		Ref.
Frequency, cm^{-1}	**Functional group**	

1250-1324-1405-1454-1571-1636	C_6N_7 heptazine heterocycle ring	204-206, 301-306
807-813	triazine ring stretching	204-206, 301-306
892	Cross link heptazine deformation	301
1654	N-H deformation	204, 305
1610	C=N	205, 302, 306
3469-3420	NH_2 stretching.	204, 205, 302, 305
3337-3137	asymmetric and symmetric stretching N-H	204, 205, 301, 302, 306
3500-3100, 3350	OH	206, 310, 311

A decrease in the absorbance associated with the g-C_3N_4 functional groups was observed following use in the photoreactor (Figure 57). Such changes were also analyzed by XPS.
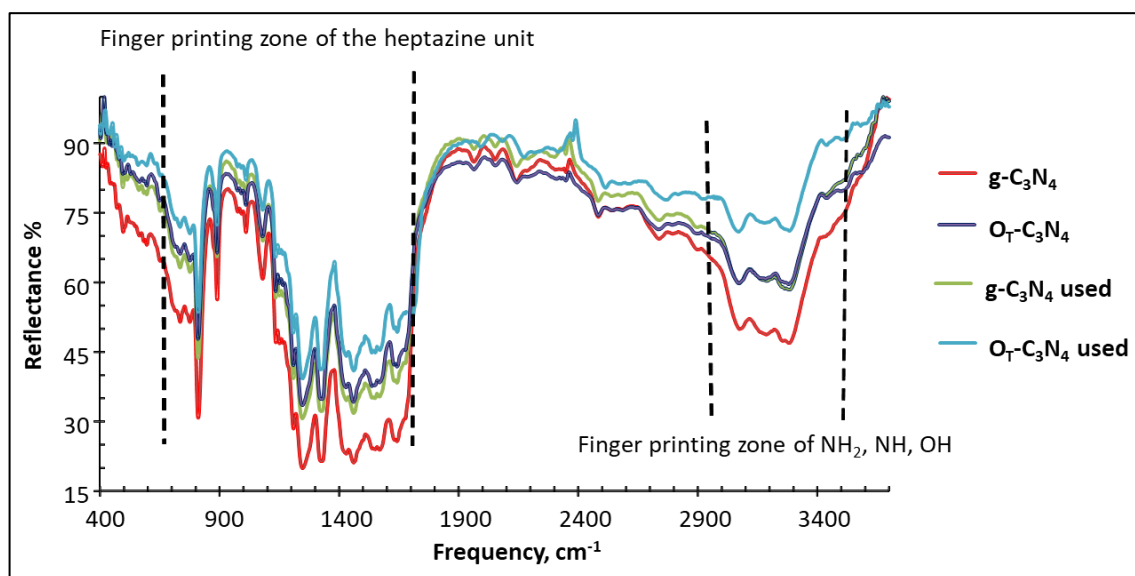
Figure 57. Diffuse FTIR analyses for each sample used and unused.

The XPS elemental profiles and expected position of peaks related to structural and functional groups have previously been reported by researchers investigating g-C_3N_4, as detailed in Table 14. Using this information, in conjunction with analysis

of samples before and after photocatalytic treatment, changes to the photocatalyst surface during CO_2 reduction seem to occur.

Table 14. Structural and peak positions of functional groups which were observed in XPS for g-C_3N_4 and O-C_3N_4

Element	Kind of interaction	Binding energy, eV	Reference
XPS Analysis			
N	400		204-206, 213, 215, 301-306, 310
	N1(N sp^2) C-N=C	398.5	206, 213, 301-306, 310
	N2 (N-H)	399.5	213, 301, 306
	N3 (sp^3) NC$_3$	400.2	206, 213, 301, 302, 304, 305, 310
	N4 (NH$_2$)	401	206, 301, 303, 304, 310
	N-O, or due to O$_2$ and H$_2$O adsorbed	*401.8*	306
	Nπ−π	404.2	213, 301, 305
C	284.8		204-206, 213, 215, 301-306, 310
	C-C	284.6	204, 206, 213, 301, 302, 304, 310
	C-CH$_2$,C-OH, C-O	286.2	204, 213, 301, 303, 310
	C-N	286.2-287.2	206, 301
	C1	288.2	213, 301-304, 310
	C2	288.8	301
	N-C=O	289.8 -288.9	204, 206, 301, 310

	C π–π	293.8	301
O	532.6		204, 206, 213, 215, 301-303, 310
	C=O	530	312
	C-OH, *O-C-N*	*531.9*	199, 204, 206
	H$_2$O adsorbed	532.9	204, 213, 303
	O-N	*533.4*	206

Theoretically, XPS should show a C/N molar ratio of 0.75 for g-C$_3$N$_4$. However, imperfect carbon nitride crystals can lead to changes to this ratio. Investigation of functional groups, particularly carbon oxygen functionalities, that could alter this ratio are detailed in Table 14. To understand the XPS signal, one must consider the differing bonding configurations that both nitrogen and carbon adopt in the g-C$_3$N$_4$ structure (Figure 58). Essentially, as mentioned in the section 1.3.5, carbon has two unique bonding configurations (C1, C2) whilst nitrogen adopts four unique configurations (from N1 to N4) in the carbon nitride structure. This causes a splitting in the XPS signal for each configuration allowing investigation of structure (Figure 58).
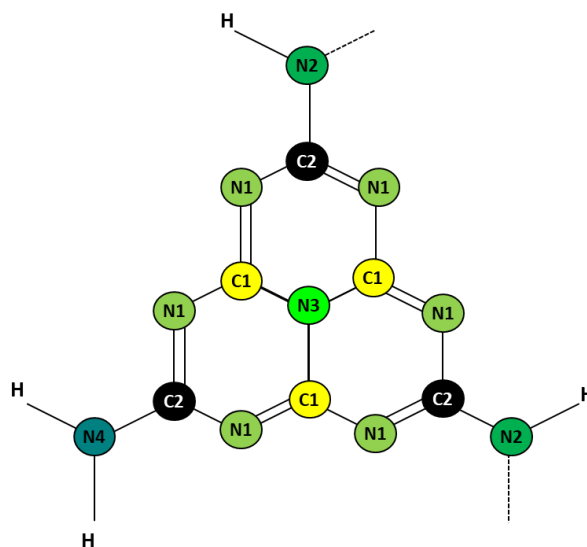
Figure 58. Structure of the repeating heptazine carbon nitride unit with the corresponding atomic assignment according to XPS analysis.

Both elements C and N, in the C_3N_4 graphitic structure, generate the signal due to the π to π* transition (shake-up) at around 293.8 eV and 404.2 eV respectively, as reported in Table 14. In addition to chemical shifts in XPS due to different bonding configurations of carbon and nitrogen in perfect C_3N_4 crystals, the peak positions due to oxygen functionalities characteristic of $O-C_3N_4$ samples are also reported in italic characters in Table 14.

Analysis of elemental composition via XPS was initiated with a wide energy survey, performed in three locations, to look for contamination and estimate differences in the elemental constitution. Only carbon, nitrogen and oxygen peaks of significant magnitude for quantification were observed (Table 15). The value of binding energy for each element observed showed good agreement with literature (Table 14).

This analysis showed that the quantity of oxygen present in the pure as prepared C_3N_4 is the lowest of all the samples. However, for samples that had undergone thermal annealing and/or testing as a photocatalyst, the oxygen content was increased in comparison to untreated material.

Table 15. Survey analysis average of three (wt %) XPS measurements of used g-C_3N_4, unused g-C_3N_4 and $O_R-C_3N_4$ reference.

	O_R-C_3N_4	g-C_3N_4	g-C_3N_4 used	O_T-C_3N_4	O_T-C_3N_4 used
O	5.4	2.0	3.0	2.9	3.6
C	49.6	48.6	49.9	48.5	48.0
N	44.9	49.4	46.8	48.6	48.4

By comparing changes in carbon and nitrogen percentages across sample groups, oxygen inclusion during synthesis of O_R-C_3N_4, thermal treated O_T-C_3N_4 or used g-C_3N_4 data suggests that oxygen incorporated in the structure is likely substituting in one or more of the differing nitrogen positions N1, N2 and N3. In fact, a loss in nitrogen concurrent with increases in oxygen percentage can be observed in Table 14. To discriminate between contributions from strongly adsorbed contaminants and different functional groups, high-resolution scans of N, C and O regions were measured and deconvoluted based on assignments reported in Table 14.

For all samples analyzed, used and unused, a large proportion of the oxygen signal observed came from the water strongly bound to the catalyst. In the as prepared g-C_3N_4 sample, all the oxygen observed was from adsorbed contaminants, H_2O and CO_2. Whilst the used g-C_3N_4 sample, thermally and chemically O-doped samples showed increasing intense contributions from oxygen in lattice (N-C-O-C) and oxygen functionalization of periphery aromatic regions (ArC=O), as detailed in Table 16.

Table 16. Contributions from different oxygen carbon and nitrogen functionalities (Wt %) estimated from deconvolution of XPS each peak centered about at 288.4, 531.5 and 398.9 eV, respectively.

		Wt %				
		O_R-C_3N_4	g-C_3N_4	g-C_3N_4 used	O_T-C_3N_4	O_T-C_3N_4 used
Binding energy, eV	**O Type**	Oxygen				
529.92	O=C Ar	1.37	0.00	0.00	1.35	2.38

Binding energy, eV	N Type	Nitrogen				
531.15	O-C-N in lattice	8.63	0.03	2.34	1.57	2.59
532.28	OH water, CO₂	90.00	99.97	97.66	97.18	95.03
Binding energy, eV	**N Type**	**Nitrogen**				
398.72	N1 edge	68.23	71.34	64.47	65.28	66.88
398.83	N2 external	8.43	3.77	6.83	10.29	7.50
400.08	N3	8.47	9.10	11.12	8.57	10.76
401.08	N4 external	12.79	12.97	14.58	12.90	11.92
404.25	π-π	2.09	2.82	3.01	2.96	2.97
Binding energy, eV	**C Type**	**Carbon**				
284.82	C-C	27.49	22.57	27.58	25.29	25.75
286.4	C-OH	5.43	3.30	3.74	1.81	1.83
288	C1	40.82	40.75	29.11	46.63	35.66
288.6	C2	22.28	28.6	33.81	21.33	30.92
289.64	C=O external	1.27	1.74	2.06	1.00	1.94
293.37	π-π	2.72	3.37	3.71	3.96	3.91

This is suggestive that UV-Vis irradiation of g-C_3N_4 in the presence of water leads to photocorrosion and oxidation of the g-C_3N_4. To understand the changes in the carbon nitride structure, due to increasing oxygenation, the nitrogen and carbon regions were also investigated. In the nitrogen region, due to the bonding in the $C_6N_{10}H_{12}$ heptazine monomer, nitrogen adopts four bonding configurations labeled N1 to N4 in Figure 58, each with a unique binding energy detailed as reported in literature in Table 14 and experimental data found in Table 16. N1 are present on the edges of heptazine base units, N3 are present at the center of a perfect heptazine base, whilst N2 type link heptazine sub units together and N4 represent the groups left upon the termination of polymerization. In a heptazine monomer (Figure 59a) the ratio of N1:N3:N4 is 6:1:3, N2 does not appear in the base unit melem; however as the monomer polymerizes, some N4 type are converted into N2 with the ratio of

N4:N2 groups dependent on the geometry of polymerization (Figure 59c). In the g-h heptazine phase under study here, confirmed by XRD and UV-Vis (see above), heptazine monomers polymerize along parallel zig zag chains linked by single N4 units as illustrated in Figure 59e. Polymerizing in the g-h heptazine structure results in changes in the ratio of N2 to N4 nitrogen, relative to the monomer, as one N4 is replaced with one N2 for every unit extension along the polymerization axis. Illustration of the changes in nitrogen group bonding during polymerization is detailed in Figure 59.
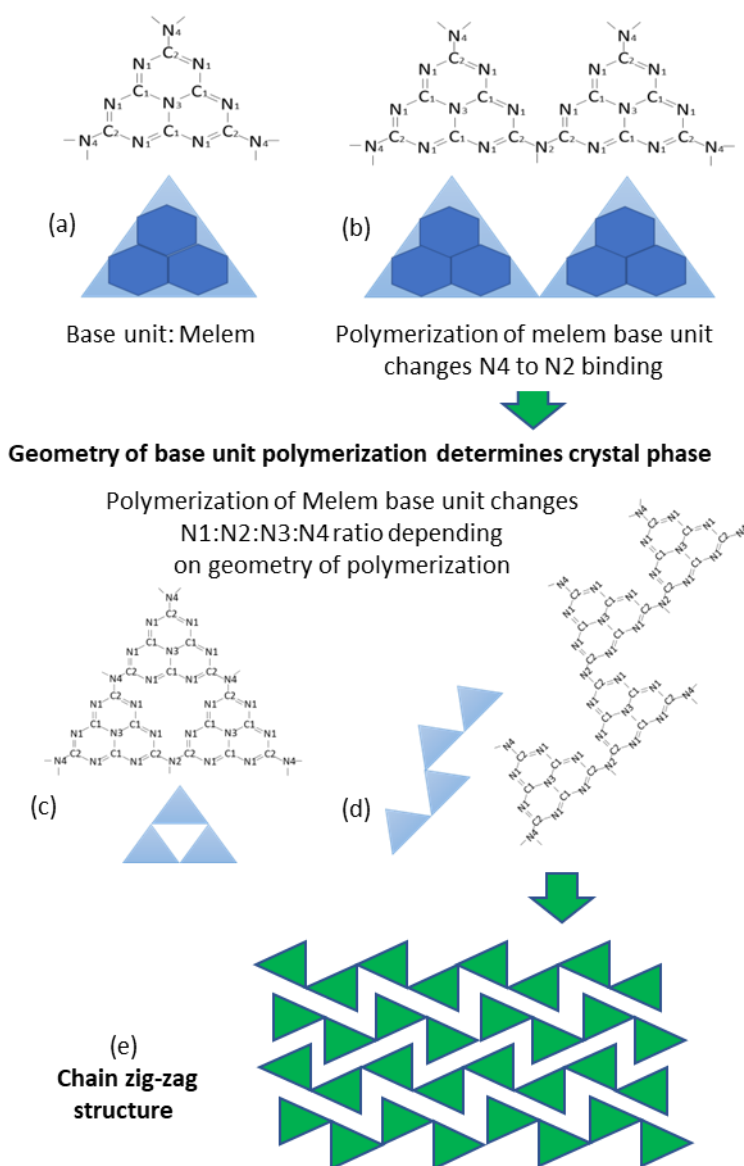
Figure 59. Possible condensation pathway from Melem unit (a) firstly to dimer (b) and then to two different assembling in sheet (c) and linear chains of g-C₃N₄ (d). The chains (d) evolve to g-C₃N₄ zig zag structure (e).

Table 17. Change in nitrogen ratios as a function of chain length for h-g-heptazine structure.

	N1	N2	N3	N4	N1 %	N2 %	N3 %	N4 %
Dimer	12	1	2	4	63.16	5.26	10.52	21.05
Tetramer	12	1	2	3	66.66	5.55	11.11	16.67
Octamer	12	1	2	2.5	68.85	5.71	11.43	14.28
Infinite chain	12	1	2	2	70.58	5.88	11.76	11.76

As reported in Table 17, the short heptazine chains result in N1>N4>N3>N2 ratio, whereas, at the infinite chain lengths, ratios become N1>N4=N3>N2 which is equivalent to a N1:N2:N3:N4 ratio of 12:1:2:2. This corresponds to 70.58:5.88:11.76:11.76 percentage ratios useful when comparing this perfect crystal to the percentages obtained from XPS.

For the synthesized $g-C_3N_4$, the N1:N2:N3:N4 percentage ratio from XPS was 71.34:3.77:9.10:12.97, which is good match for expected N1 % in g-h-heptazine with largely perfect heptazine base units. Considering N4, it suggests long range but not infinite chains consistent with XRD, the excess of N4 percentage may also be due to unreacted precursor / monomer material or some shorter chains. Deviation, a lower % than expected, in N2 suggests crystal imperfections, defects or branching of the chains removing side N2 groups, whilst contemporaneously increasing N4 groups. Likewise, the N3 ratio was lower than expected for perfect crystals, suggesting vacancies in some of the heptazine blocks.

N1:N2:N3:N4 ratios from carbon nitride oxidized during synthesis, thermally or during photocatalysis are compared in Table 16. All treatments were observed to result in significant reduction in N1 side groups, relative to the starting material, suggestive of damage/distortion to the base of the heptazine unit. Deconvolution of the N2 and N4 (edge and terminal groups) in used $g-C_3N_4$ shows an increasing N4

percentages, suggesting a reduction in average chain length. In the O_T-C_3N_4 sample, higher N2 and N4, with lower N1 ratios than expected for a perfect g-h-heptazine structure were observed, presumably due to oxygen disrupting periodicity. Its use as a potential photocatalyst showed further changes in the N1:N2:N3:N4, ratio that is consistent with additional restructuring of the polymer towards a more open arrangement.

Deconvolution of XPS C1s region was also used to look at changes in structure following photocatalysis. In this region, the C-C and C-OH peaks are characteristic of adsorbed species or deviance from heptazine structuring / reformation. Both thermal oxidation and use as a potential photocatalyst increased the C-C peak indicative of a material with less heptazine/g-C_3N_4 present. Likewise, signals due to C=O bonding were observed to increase in both sample sets following use as photocatalysts, which is consistent with increasing counts in the oxygen region observed for the same treatment. C1 and C2 regions represent differing carbon nitrogen bonding. In all cases, it showed decreasing C1 and increasing C2 content following photocatalytic use due to changes in nitrogen content during use.

Intentional oxygen doping and repeated use in CO_2 reduction experiments both led to reduced yields of CO in subsequent tests and simultaneous increases in the oxygen content of the g-C_3N_4 with repeated testing. In addition, UV-Vis irradiation was observed to give rise to changes in the g-C_3N_4 structure (N1:N2:N3:N4 ratios).

Another factor to be considered is the role of N in the structure. In particular, as it can be noticed in Table 15 (XPS survey analysis), the increase of O content from the unused to used g-C_3N_4 sample and to O doped samples (O_T-C_3N_4 to $O_R$$C_3N_4$) corresponds to a decrease of the total content of N. This variation (%), which could be due to a replacement of N with O in the structure, could alter CO_2 adsorption properties adversely.

In photocatalytic, tests carried out in the presence of CO_2 under the experimental conditions used (pressure, temperature, and light intensity); the increase in the O content of the g-C_3N_4 was caused by photocorrosion. It is not easy to determine if H_2O, CO_2 or both are the source(s) of O observed in this work. The photocorrosion means the modification of the C_3N_4 structure, due to the substitution of N with O

during the photoreaction, as shown in Figure 60, as indicated by XPS measurements (Table 14) and reported also by Huang et al. when H_2O_2 was used to dope C_3N_4 with oxygen.[204] The mechanism, which led to the final modified C_3N_4 in these experimental conditions, could give rise to formation of a non-stoichiometric or defective solid. Moreover, the figures related to the percentage of the various N types, shown in Table 15, strongly suggest a rearrangement of the g-C_3N_4 structure following use in photocatalytic testing.

Figure 60. Schematic illustration of N replacement by O in g-C₃N₄ material.

As far as the runs carried out in the absence of CO_2 are concerned, the presence of CO_2 adsorbed on the catalyst surface or as impurity in the system cannot be excluded and it can be compatible with the CO formation.[300]

In current literature, only a few papers report repeat testing and generally they concern runs carried out by using C_3N_4 composite and or bulk materials with low surface area. Qin et al.,[214] observed that in the presence of barbituric acid-g-C_3N_4 composite, the photoreduction of CO_2 to CO and H_2 was quite reproducible, at least after three catalytic consecutive tests. Probably, in that case, the presence of barbituric acid stabilized the g-C_3N_4 structure avoiding the replacement of N by O and consequently no decreasing activity was observed. A similar stabilizing effect due to the presence of ceria can be hypothesized in the case of CeO_2-C_3N_4

composite that showed a constant CH_4 and CO production after 4 runs as reported from Li et al.[313]

In contrast with the present study, Fu et al. found the reproducibly of CO_2 photoreduction tests in the presence of both bulk $g\text{-}C_3N_4$ and $O\text{-}C_3N_4$ tube photocatalyst. However, it is important to notice that the amount of CO_2 photoreduction products observed by Fu et al. was always lower than the lowest one revealed in this study. Moreover, to the best of my knowledge, no structure studies were carried out after the use of $g\text{-}C_3N_4$ photocatalyst used for CO_2 reduction.[206] Interestingly, in that case no CO formation was observed during blank test in the absence of CO_2.

3.3.4 Conclusion

During $g\text{-}C_3N_4$ and oxygen doped $g\text{-}C_3N_4$ photocatalytic tests for CO_2 reduction, the main product detected was CO. No other products were detected. The pure material was observed to be more active than the oxygen modified analogue for CO production. A reduction in the rate of CO generation, under irradiation, was observed during both single runs and repeated test cycles with the same catalyst. During control tests in the absence of CO_2, the production of CO was observed under irradiation, raising questions about the origin of the CO and the stability of $g\text{-}C_3N_4$.

Diffuse reflectance FT-IR analysis showed the expected functional groups characteristic of $g\text{-}C_3N_4$ present in all samples. Functional group peak intensity declined with oxygen doping or photocatalytic use. Given the qualitative nature of FTIR, samples were further investigated with XPS to quantify the changes in the functional groups during photocatalytic use or intentional oxidation.

Both analyses, the diffuse FTIR and XPS, showed that the thermal and the photocatalytic treatments produce similar changes to the functional groups, consistent with oxidation of the C_3N_4 structure. The oxidation of the $g\text{-}C_3N_4$ under UV-Vis irradiation was slightly different to the one obtained with oxygen doping,

but produced the same effect on catalytic behavior, i.e., a reduction in product yield under irradiation.

The XPS data showed an increase in oxygen content, both absolute and bound to carbon, after thermal treatment and after photocatalytic use. This study allowed the examination of where and how oxidation disrupts the material structure, showing changes to the heptazine base units along with changes in bonding between units following oxidation or photocatalytic use.

This research points that under the adopted reactor conditions, the photoexcitation actually leads to oxidation of C_3N_4 rather than water splitting, leading to a loss of photocatalytic activity i.e., photocorrosion. Given that the valence band edge of g-C_3N_4 is close to the water oxidation potential, this material has limited over-potential to drive water oxidation and as such, may accumulate intermediate ROS species that may oxidize the catalyst, changing its activity as observed here. C_3N_4 may still be useful as a photocatalyst; however, the use of a z-scheme or a second co-catalyst material on which to run the oxidation reaction may be necessary to avoid g-C_3N_4 oxidation observed in this work. As aforementioned, many researchers use a z-scheme consisting of g-C_3N_4 in composite materials such as g-C_3N_4-TiO_2 where the latter material performs the water oxidations steps, reducing the opportunity of g-C_3N_4 oxidation.[7]

3.4 Photocatalytic CO_2 reduction in continuous membrane reactor: C_3N_4 Nafion membrane

The results presented in this chapter have been published:

F. R. Pomilla, A. Brunetti, G. Marcì, E. I. Garcia-Lopez, E. Fontananova, L. Palmisano, G. Barbieri. CO_2 to Liquid Fuels: Photocatalytic Conversion in a Continuous Membrane Reactor. *ACS Sustainable Chemistry and Engineering*, **2018**, 6(7), 8743-8753

3.4.1 C_3N_4 powder

3.4.1.1 Powder characterisation

Figure 61 shows XRD analysis of C_3N_4 powder in which two characteristic peaks at 27.3° and 13.1° are clearly defined, in good agreement with patterns reported in the open literature.[213] The higher angle peak at 27.3° is characteristic of an interlayer stacking of conjugated aromatic systems, which is indexed to the (002) plane corresponding to the average interlayer distance of 0.326 nm.[216, 314] The lower diffraction peak at 13.1° is indexed to the (100) plane and assigned to the in-plane structural packing of aromatic systems with an average distance of 0.675 nm, characteristic of heptazine heterocyclic ring (C_6N_7) units.[216]

Figure 61. XRD patterns of C₃N₄ (red line) measured for powder and (black line) as reported by Wen et al. [195]

The chemical structure is also confirmed by FT-IR whose peaks (Figure 62) at 890, 1250, 1324, 1405, 1454, 1571, and 1636 cm^{-1} correspond to the typical stretching vibration modes of heptazine heterocyclic ring units.[315] The peak at 804 cm^{-1} belongs to the characteristic breathing mode of triazine units representing the condensed CN heterocycles.[316]

Figure 62. FT-IR spectrum of C₃N₄ powder (red line) and (black line) as reported by Liao et al.[315]

The SEM images (Figure 63a and 63b) show the graphitic structure and the partial exfoliation of C_3N_4 powder caused by the second thermal treatment to which it was subjected.

a   b

Figure 63. SEM image of C_3N_4 powder at two different magnitude, at a) 5 μm and at b) 30 μm, respectively.

The diffuse reflectance spectra were recorded for investigating the electronic band structure of the C_3N_4 sample, which was determined by the intersection (red spot) of the tangent lines (Figure 64, blue lines) of the Kubelka−Munck modified function, $[F(R'\infty)h\nu]^{1/2}$ versus the energy of the exciting light. The band gap identified as 2.8 eV (Figure 64) falls in the region of visible light absorption of the photocatalyst corresponding at ca. 443 nm. The discrepancy with the theoretical value of 2.7 eV of the bulk materials is ascribable to the intrinsic superiority of 2D structures of the exfoliated C_3N_4.[198]

Figure 64. Kubelka-Munck modified function vs. the energy irradiating the C₃N₄ sample.

The BET analysis of the bulk g- C_3N_4 shows a low specific surface area (7 m^2 g^{-1}) as reported by Krivtsov et al.[317] On the contrary the exfoliated powder sample gave a specific surface area of 154 m^2 g^{-1}, in agreement to Zhang et al.[318] that measured a specific surface area of exfoliated g- C_3N_4 equal to 160 m^2 g^{-1}. This relatively high value can be attributed to the two thermal treatments undergone by the melamine, in agreement with Papailias et al.[319] who stated that structural and optical properties highly depend on the process temperature and, thus, poly-condensation degree.[175]

3.4.1.2 Preliminary powder photocatalytic test condition and results

For evaluation of the photocatalytic activity, the photocatalytic CO_2 reduction was previously carried out by using powdered C_3N_4 in a batch reactor, which is shown in Figure 26 (section 3.1.1). In detail, 350 mg of C_3N_4 sample was placed in a cylindrical Pirex batch reactor with total volume of 130 mL. As before described (section 3.1.1), the photocatalyst insight the reactor was first cleaned under light with humid He,[114] and subsequently under dark conditions, CO_2 was fluxed for 30 min in the reactor. A 48 µL of distillate water was introduced into the reactor by

means of a syringe. Afterward, the batch reactor was placed in a solar box (1500 W, Xe lamp), and the experiments were carried out for 6 h. The concentration of the species was analysed by a Shimadzu gas chromatograph equipped with FID and a Hewlett-Packard GC with TCD, injecting in each a 250 μL sample by means of gas-tight syringe.

During 6 h of irradiation time, the batch reactor conversion was followed for an initial H_2O/CO_2 feed molar ratio equal to 0.5, obtaining 0.6 μmol $g_{catalyst}^{-1}$ h^{-1} of converted carbon. The most abundant products were CH_4 and CO, accordingly to the literature data of gas-phase CO_2 photoreduction.[320, 321]

3.4.2 Photocatalytic membrane test conditions

Photocatalytic membrane was utilized for CO_2 photoreduction with H_2O as reducing agent. Before the characterization and the photoreduction measurements, the membrane prepared was cleaned. In this procedure carried out by using the membrane reactor set up described above, all the membranes underwent "blank reaction" measurements. An argon stream together with H_2O, instead of CO_2, was fed continuously for 8-24 h into the reaction module, under the same operating conditions, which were chosen to carry out the photocatalytic experiments including the UV-Vis irradiation. The aim of this procedure was to clean the membrane from any residuals of solvent and other low molecular weight organics eventually present in the polymer solution that could be released during the reaction measurements invalidating the results.

The reactor was equipped with a medium–high mercury vapour pressure lamp (Zs lamp, Helios Ital quartz, Milan) with emittance from 360 nm (UV-Vis) to 600 nm which was used to irradiate the membrane. The flat sheet membrane was assembled in a stainless steel module where a quartz window allowed the UV-Vis irradiation of the catalytic membrane surface.

Once placed in the UV-Vis exposure chamber, the membrane module was continuously fed with CO_2 and H_2O by means of a mass flow controller and an HPLC pump, respectively. Figure 65 shows the experimental apparatus set up. The

membrane reactor mainly consists of three parts: the feed/retentate chamber, the permeate chamber and the catalyst loaded membrane. The two reactor chambers can be considered as lumped parameter systems since reaction takes place in the membrane layer and no concentration gradient of any chemical species is expected, also owing to the low conversion occurring in this specific reaction. Thus, the composition of these two volumes is the same as the related reactor exiting streams, which are retentate and permeate. The module was placed in vertical position to facilitate permeate and retentate sampling, as well as avoiding stagnant zones.

Figure 65. Scheme of Photocatalytic membrane reactor setup.[322]

Table 18 summarizes the operating conditions explored. The trans-membrane pressure difference of 2 bar was regulated by a back pressure controller. The gaseous fraction of retentate and permeate flows was measured by bubble soap flow-meters, after cooling streams outgoing from the reactor with apposite ice traps. The composition of these streams was measured by an Agilent Technologies 7890A gas chromatograph with TCD (HP-PLOT and Molsieve columns). The condensate fraction of the retentate and permeate, periodically sampled, was analysed by an Agilent 6890N gas chromatograph with FID and an HP-5 column.

It has to be highlighted that all the reaction measurements, lasting 25-30 h, were performed in steady state conditions, which were reached within 5 h for all of the species obtained.

The catalytic membrane was used in the continuous photocatalytic membrane reactor for some weeks changing feed molar ratio and feed flow rate as reported in Table 18. During the whole period, C_3N_4 piling out was not evident since no loss in reactor performance and/or selectivity was measured.

Table 18. Operating conditions for C_3N_4 photocatalytic membrane reaction measurements.

CO_2 flow rate, mL(STP[*]) min^{-1}	11-107
H_2O/CO_2 feed molar ratio	0.5; 2; 5
Feed Pressure, bar	2
Permeate Pressure, bar	1
Contact time, s	2; 9.8; 18.7

*STP: standard temperature and pressure, 0°C and 1 bar.

Particular attention was devoted to analysing the effect of contact time on membrane reactor performance. It was defined as the ratio of the catalyst weight dispersed in the membrane to CO_2 feed flow rate, considered as the limiting reagent (Eq. 19).

No difference in CO_2 exiting the reactor from the feed one could be measured practically; therefore, CO_2 conversion did not represent an appreciable value to be considered significant in order to evaluate the reactor performance. Instead, it was evaluated through the produced species flow rate/catalyst weight (Eq. 20), the total converted carbon/catalyst weight ratio (Eq. 21), and reaction selectivity (Eq. 22).

$$Contact\ time = \frac{C_3N_4\ catalyst\ weight\ embedded\ in\ the\ membrane}{CO_2\ feed\ flow\ rate}, s \qquad \text{Eq. 19}$$

$$\frac{Produced\ Species\ flow\ rate}{C_3N_4\ catalyst\ weight} = \frac{Compound\ flow\ rate}{Amount\ of\ catalyst\ dispersed\ in\ membrane}, \frac{\mu mol}{h\ g_{catalyst}} \qquad \text{Eq. 20}$$

$$\frac{Converted\ carbon}{C_3N_4\ catalyst\ weight} = \frac{\sum Carbon\ flow\ rate\ for\ each\ produced\ species}{Amount\ of\ catalyst\ dispersed\ in\ membrane}, \frac{\mu mol}{h\ g_{catalyst}} \qquad \text{Eq. 21}$$

$$Selectivity_i = \frac{i-species\ flow\ rate}{\sum_i^n species\ flow\ rate},\ -$$

<div align="right">Eq. 22</div>

3.4.3 Characterisations of C_3N_4-Nafion membrane

Figure 66a shows FTIR/ATR representative spectra relative to the photocatalytic membrane for both air-facing and casting plate-facing surfaces. Firstly, the analyses confirmed the presence of C_3N_4 catalyst in the membrane matrix as the characteristic chemical structure was maintained by peak presence between ca. 1630 and 1320 cm^{-1}, in agreement with FTIR analysis of C_3N_4 powder (Figure 62). All the signals in the range between 970 and 1400 cm^{-1} belong to the Nafion structure. In particular, the bands appearing at 970-983 cm^{-1} are attributed to C−O− C stretching vibrations; the band at ca. 1066 cm^{-1} can be related to the symmetric stretching of $-SO_3-$. In the range between 1400 and 1100 cm^{-1} the asymmetric stretching bands of $-SO_3-$ should be found, but they are covered by the more intense bands of $-CF_2$ stretching, visible in the spectra.[323] Moreover, interactions between the Nafion matrix and the loaded C_3N_4 occur as already reported in the literature by Wu et al.[324] The C_3N_4 nanosheets consist of a two-dimensional material that through ammine groups establishes crosslinking interactions with the hydrophilic -SO_3- groups present in the Nafion matrix. FT-IR/ATR analysis of C_3N_4 Nafion membrane shows, with respect to Nafion membrane, a blue-shift of - SO_3- characteristic asymmetric vibration from 1054 cm^{-1} to 1063 cm^{-1} (Figure 66a, inset). The g-C_3N_4 nanosheets incorporated in the membrane during membrane formation turns the Nafion original "spherical structure" into a new "lamellar structure" increasing the amorphous phase.[324]

Figure 66. a) FT-IR (ATR) spectra of (black line) air-facing and (red line) casting plate-facing membrane surfaces of C_3N_4–loaded Nafion membrane (in the inset, the blue shift of -SO$_3$-groups in the Nafion owing to the presence of the catalyst). SEM of (b) air-facing (magnification 5kX), (c) casting plate-facing surfaces (5 kX), (d) cross-section (3 kX), (e) detail (15 kX), of cross section of C_3N_4–loaded Nafion membrane.

OH band intensity of the casting plate-facing surface spectrum was higher than the air-facing surface one, most likely owing to the higher catalyst concentration related to its segregation on this membrane side, as also confirmed by SEM images. Indeed, from the perusal of Figure 66b), the air-facing surface of the C_3N_4-loaded Nafion membrane appears dense in agreement with the expectations for a membrane prepared by solvent evaporation method. On the contrary, the casting plate-facing surface presents some porosities owing to the slow solvent evaporation from the most inner layers of the cast solution that can give rise to local phase separation processes (Figure 66c). Moreover, the SEM image of the casting plate-facing surface highlights a partial segregation of the C_3N_4 partially deposited on the bottom part of the membrane. The SEM images of the cross section (Figure 66d and 66e) confirmed the dense nature of the membrane and the formation of catalyst

micro-aggregates, present in the whole cross section, but more concentrated in the bottom part of the same.

The integrity of catalyst when embedded in membrane matrix was also confirmed by UV–Vis diffuse reflectance spectroscopy analyses that showed a band gap of 2.8 eV for the membranes in dry and wet conditions as for C_3N_4 catalyst powder. Moreover, Nafion matrix was proved to be transparent to UV-visible radiation, as the spectrum was recorded analysing the air-side membrane surface.

3.4.4 Results and discussions

The tests carried out in absence of CO_2 are shown in Figure 67 for both photocatalytic and pure Nafion membrane plotting the species distribution as a function of time on stream. MeOH, EtOH, HCHO and C_3H_6O (acetone) were found in the first sample after 2 h testing at the reactor exit. Their flow rate suddenly decreased along with the time and after 7 h no species were detected at the reactor outlet. This treatment was further continued up to 10-12 h. The continuous operating mode of the membrane reactor, implied a continuous removal of residual species from reactor volume, therefore their decreasing trend confirmed their nature as residues.

The zero values reached by each species profile clearly indicated that the membranes did not longer contain any compound; therefore, the species measured in reaction experiments could only be the result of the photocatalytic activity of the C_3N_4-Nafion membrane. The presence of the same compounds (Figure 67, right side) in a bare Nafion membrane confirms the previous hypothesis. The difference in the profile evolution along with time could be attributed to the different membrane thickness and the filler (catalyst) presence.

Figure 67. Membrane cleaning (removal of any residuals potentially present) before reaction. C_3N_4 loaded Nafion membrane (active area and thickness respectively 20.4 cm^2 and 65.8 ± 3.7 μm) and bare Nafion membrane (active area and thickness respectively 4.1 cm^2 and 81.3 ± 4.3 μm).[322]

As aforementioned, photocatalytic reaction measurements were carried out in presence of H_2O/CO_2 feed analysing the effect of the feed molar ratio and contact time (Eq. 19) on the membrane reactor performance. At a contact time of 2 s, MeOH and EtOH flow rates increased with H_2O/CO_2 feed molar ratio (Figure 68), reaching 17.9 and 14.9 μmol $g_{catalyst}^{-1}$ h^{-1}, respectively, at a feed molar ratio equal to 5 against 4 and 1.7 μmol $g_{catalyst}^{-1}$ h^{-1} obtained at a feed molar ratio of 0.5. Contrarily, to the water defect corresponds a larger HCHO production; therefore, at H_2O/CO_2 feed molar ratio of 0.5, HCHO was the most abundant product, reaching a flow rate of 27 μmol $g_{catalyst}^{-1}$ h^{-1} (Figure 68).

Figure 68. Flow rate/catalyst weight of the various species formed as a function of H_2O/CO_2 feed molar ratio at a contact time of 2 s.

This trend can be explained through the reactions stoichiometry (Eqs 23-25).

$$CO_2 + 2\ H_2O = CH_3OH + 3/2\ O_2 \qquad\qquad Eq.\ 23$$

$$2\ CO_2 + 3\ H_2O = CH_3CH_2OH + 3\ O_2 \qquad\qquad Eq.\ 24$$

$$CO_2 + H_2O = HCHO + O_2 \qquad\qquad Eq.\ 25$$

A water excess (as in the case of H_2O/CO_2 feed molar ratio=5) leads to MeOH and EtOH as the main products whereas a water defect (as in the case of H_2O/CO_2 feed molar ratio=0.5) leads to HCHO as the main one. Traces of acetone were also found at a feed molar ratio of 0.5, most probably owing to the occurrence of secondary reactions of intermediates not desorbed from the catalytic site, as reported in the literature.[325, 326]

Similar trends were obtained at a contact time of 9.8 s (Figure 69), where MeOH and EtOH were again the favoured products at a high H_2O/CO_2 feed molar ratio, even though their flow rates were ca. half of that obtained at a contact time of 2 s.

Figure 69. Flow rate/catalyst weight of the various species formed as a function of H₂O/CO₂ feed molar ratio at a contact time of 9.8 s.

This effect can be attributed to the time that the reacting species remain in contact with the catalyst under UV-Vis light. The high contact time, or, in other terms, the slower removal of the reaction mixture from reaction volume can induce MeOH and EtOH to be partially oxidized producing formaldehyde (Eq. 26) or fully oxidized to CO_2 as reaction product. On the contrary, a low contact time implies a fast removal of products from the reaction volume exposed to UV light and, thus, less promotion of secondary reactions.

$$CH_3OH + 1/2\ O_2 = HCHO + H_2O \qquad\qquad Eq.26$$

Analogously, at a feed molar ratio of 0.5, HCHO flow rate/catalyst weight decreased from 27 (at 2 s) to 9 μmol $g_{catalyst}^{-1}$ h^{-1} (at 9.8 s) reaching zero at a feed molar ratio equal to 5. Acetone production instead increased as a function of the feed molar ratio up to stable value of ca. 2 μmol $g_{catalyst}^{-1}$ h^{-1}.

Figure 70 and Figure 71 show the effect of the contact time. MeOH and EtOH were preferential products at the lowest value of contact time.

Figure 70. Flow rate/catalyst weight of the various species formed as a function of C_3N_4 weight/CO_2 feed flow rate at H_2O/CO_2 feed molar ratio equal to 2.

As it increased, their flow rate decreased down to a constant value, whereas HCHO and acetone increased as a result of oxidation reaction and secondary reaction between intermediates, respectively. At a feed molar ratio of 5, which means in a water excess, no HCHO was detected (Figure 71). In these conditions, even though MeOH and EtOH decreased along with contact time, they remained the most abundant products in the whole range of contact time considered in the experiments.

Figure 71. Flow rate/catalyst weight of the various species formed as a function of C_3N_4 weight/CO_2 feed flow rate at H_2O/CO_2 feed molar ratio equal to 5.

The reaction selectivity (Eq. 22) is an important parameter to define the products distribution.

The highest selectivity in alcohols production was observed at low value of contact time and high H_2O/CO_2 feed molar ratio (Figure 72). The best MeOH and EtOH selectivity 54.6% and 45.4 % respectively, were in fact observed at H_2O/CO_2 feed molar ratio equal to 5 and contact time of 2 s, representing 100% of carbon-containing products. Globally, alcohols selectivity tended to increase with feed molar ratio.

Figure 72. Reaction selectivity as a function of C₃N₄ weight/CO₂ feed flow rate (left side) and H₂O/CO₂ feed molar ratio (right side).

This behaviour in the CO_2 reduction reaction was previously explained as usual outcome when in the presence of water excess (Eqs. 24-25). Instead, it followed a decreasing trend with contact time, confirming how the slow removal of products from the reaction volume promoted secondary reactions, favouring HCHO and acetone formation.

The capability of the system to convert CO_2 into other carbon-containing species was quantified in terms of total converted carbon/catalyst weight (Eq. 21) and the results are summarized in Figure 73. The highest conversion (47.6 μmol $g_{catalyst}^{-1}$ h^{-1}) occurred at the highest H_2O/CO_2 feed molar ratio and lowest contact time, with an amount of converted carbon 8 times greater than that measured in the worst conditions (H_2O/CO_2 feed molar ratio=5 and contact time=18.7 s). Comparing the results obtained by the photocatalytic membrane reactor operated in continuous mode with that of the batch system, the membrane reactor converted at least 10 times more carbon than the batch, also in unfavourable conditions. The dispersion in the Nafion matrix increases the active surface of the catalyst implying an easier achievement of the catalytic sites by light and reagents. Moreover, the continuous removals of products from the reaction volume not only favours the reaction, but also promotes the species desorption and the restore of active sites, making them available for further conversion.

Figure 73. Total Converted Carbon as function of H_2O/CO_2 feed molar ratio and contact time.

Table 19 compares the photocatalytic membrane reactor performance with other results available for C_3N_4 in the literature or obtained by using a continuous reactor. Notably, the MeOH flow rate/catalyst weight of the photocatalytic membrane reactor presented in this work is, under some experimental conditions, significantly higher than the ones obtained with other reaction systems. In comparison with result obtained by Sellaro et .[268] where a TiO_2-based catalyst was embedded in a Nafion matrix, a wider products distribution resulted, with comparable MeOH production. By comparing this work with the data reported for batch systems, the advantage offered by the continuous system is confirmed. The MeOH production is, in fact, higher than most of the ones obtained by using simple C_3N_4 as catalyst and higher or, at least, comparable when it is used as co-catalyst in batch conditions. Moreover, it is worth noticing that, as already observed[268] and differently from what can be found in most of the literature for batch reactors, neither CH_4 nor CO were detected, alcohols being the main products. The synergic effect of the use of a photocatalytic membrane and a continuous flow mode reactor allows the substrate to undergo a lower degree of reduction as fresh CO_2 is continuously fed into the system and the produced species are continuously removed from the catalytic sites, reducing the possibility of having over-oxidation.[110]

Remarks on possible reactions involved are above reported.

A pioneering work of Inoue et al.[105] reported the following reduction reactions:

$$CO_2 + 2H^+ + 2\ e^- = HCOOH \qquad\qquad\qquad \text{Eq. 27}$$

$$HCOOH + 2H^+ + 2\ e^- = HCHO + H_2O \qquad\qquad \text{Eq. 28}$$

$$HCHO + 2H^+ + 2\ e^- = CH_3OH \qquad\qquad\qquad \text{Eq. 29}$$

$$CH_3OH + 2H^+ + 2\ e^- = CH_4 + H_2O \qquad\qquad \text{Eq. 30}$$

and, the oxidation reaction:

$$H_2O + 2h^+ = \tfrac{1}{2}\ O_2 + 2\ H^+ \qquad\qquad\qquad \text{Eq. 31}$$

Each of the hypothesized reduction reactions involves two electrons and the various reactions occur in sequence; thus, 8-electrons are required per each CO_2 molecule to obtain CH_4.

Ethanol and acetone, also experimentally detected in this work, were not included among the above reactions. For ethanol, the below reactions could occur:

$$CH_3OH + HCHO + 2H^+ + 2\ e^- = C_2H_5OH + H_2O \qquad \text{Eq. 32}$$

$$CH_4 + CH_3OH = C_2H_5OH + 2H^+ + 2\ e^- \qquad\qquad \text{Eq. 33}$$

$$CH_4 + HCHO = C_2H_5OH \qquad\qquad\qquad\qquad \text{Eq. 34}$$

To obtain ethanol, two more electrons are needed (12 electrons in total for the reduction of two CO_2 molecules, 6 of which are necessary to obtain one molecule of CH_3OH, 4 for one molecule of $HCHO$ and 2 electrons in Eq. 32 or the presence of CH_4 (Eq. 33). However in this system, no CH_4 was detected; therefore, the first hypothesis is more likely.

Similarly for acetone, the reactions which could occur on the irradiated catalyst surface are:

$$C_2H_5OH + CH_3OH = CH_3COCH_3 + H_2O + 2\ H^+ + 2\ e^- \qquad \text{Eq. 35}$$

$$C_2H_5OH + HCHO = CH_3COCH_3 + H_2O \qquad\qquad \text{Eq. 36}$$
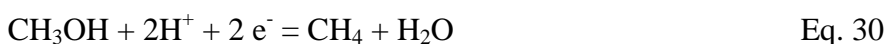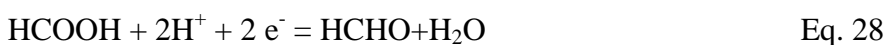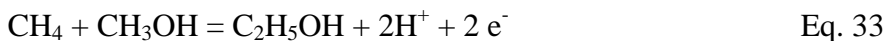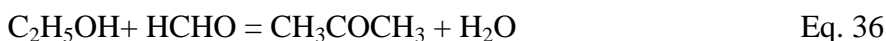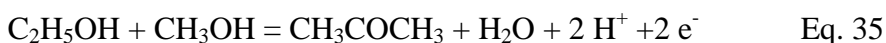
Equations 35 and 36 do not need any additional electrons. Other solutions can be hypothesized and, in addition, mechanisms based on elementary steps would be useful for understanding the reaction path and then the species produced.

However, it is worth to tentatively correlate the Inoue schemes with some variables used in the present work such as residence time and feed molar ratio.

During CO_2 reduction, the chemical species move from one (feed) membrane face to the permeate one. Along this path, accordingly to the schemes of Inoue et al.[105] and the others reported above, CO_2 conversion to HCOOH, HCOOH to HCHO, HCHO to CH_3OH, CH_3OH and HCHO to C_2H_5OH and acetone take place. CO_2 is always inside the membrane, independently from the feed molar ratio; thus, the first, 2-electrons step, could occur everywhere in the catalytic membrane, although no HCOOH was detected in the exiting stream.

The lower water content (low feed molar ratio) does not favour the oxidative reaction (Eq. 31) and hence the H^+ production is low. Therefore, the schemes implying four electrons are favoured also for the small availability of this ion (Figure 6, HCHO production). The higher feed molar ratio favours the larger-electrons schemes leading, e.g., to MeOH formation owing to H^+ large availability.

The feed molar ratio plays a significant role: its lower value favours the low-electrons schemes (e.g., HCHO production, four-electrons), whilst a higher value leads to high-electrons scheme (e.g., MeOH, six-electrons). Therefore, the whole process is a combination of the reactions (2, 4, 6, etc. electrons) since these schemes describe a set of reactions in series and as such, at the end, all the reactants and products of each reaction are in principle expected in the exiting stream.

Table 19. Comparison with results reported in literature

Catalyst	Reactor configuration	Flow rate/catalyst weight, μmol $g_{catalyst}^{-1}$ h^{-1}							Ref.
		MeOH	EtOH	HCHO	Acetone	HCOOH	CH_4	CO	
C_3N_4 catalyst embedded in a Nafion membrane	Continuous	0.9-17.9	0.3-14.9	0-27	0-1.8	0	0	0	[322] This chapter
C_3N_4	Batch						5		[327]
C_3N_{4*}	Batch	25				1250			[303]
C_3N_4 catalyst placed in glass fiber	Continuous						0.5	5.2	[328]
C_3N_4 nanotubes	Batch	0.28							[329]
C_3N_4	Batch						0.62-1		[330]
C_3N_4	Batch	0.26					Traces		[331]
C_3N_4	Batch	10	12						[332]
C_3N_4	Continuous	Traces							[333]
3 MEA-C_3N_4	Batch	0.28					0.34		[331]
AgBr/C_3N_4	Batch				2		21		[327]
C_3N_4 3%Cu/TiO_{2*}	Batch	102				1118			[303]
2 Au-C_3N_4 catalyst placed in glass fiber	Continuous						4.3	6.5	[328]
C_3N_4/ZIF 8 (nanocluster on C_3N_4 nanotubes)	Batch	0.75							[329]
CdIn$_2$S$_4$/C_3N_4 20% wt.	Continuous	42.7							[333]
6 SO/0.12B-0.2P-C_3N_4	Batch						6.25-7.5		[330]
Ag-N doped C_3N_4-G-50	Batch	20	50						[332]
TiO_2 catalyst embedded in a Nafion membrane	Continuous	12.6-45	0	0	0	traces	0	0	[268]
TiO_2 nanoparticles in porous cavities of commercial Nafion membranes	Continuous	56 (supercritical CO_2 as feed)				38			[266]
Membrane microreactor	Continuous	111							[334]
TiO_2/Y-zeolite anchored on Vycor glass	Batch	5					8		[335]
Ti-mesoporous zeolite	Batch	3.5					7.5		[130]

Ti-b(OH) and Ti-b(F)	Batch	5.9						1		[336]
TiO$_2$ and 2% Cu/TiO$_2$ in NaOH solution	Batch	0.78								[337]
Cu/TiO$_2$ film supported on optical-fiber	Continuous	0.45								[338]
Cu/TiO$_2$ and Ag/TiO$_2$ film supported on optical-fiber	Continuous	4.12								[339]
TiO$_2$ anatase	Batch	0.075						0.40		[340]
TiO$_2$ polymorphs	Continuous						3.15	2.13		[341]
TiO$_2$ polymorphs	Continuous						2.1			[342]
phtalocyanines /TiO$_2$	Batch						26			[343]

*under UV light

3.4.5 Conclusion

In this work, photocatalytic CO_2 conversion was carried out, as yet not in the literature, in a continuous photocatalytic reactor with an exfoliated C_3N_4-based membrane irradiated by UV light. The effect of H_2O/CO_2 feed molar ratio and contact time on species production, reaction selectivity and converted carbon were investigated.

Total converted carbon per gram of catalyst varied between 5 to 47.6 µmol $g_{catalyst}^{-1}$ h^{-1}, with the latter value obtained at an H_2O/CO_2 feed molar ratio of 5 and 2 s as contact time with alcohols as prevailing products. The membrane reactor converted at least 10 times more carbon than the batch system, as a result of the better dispersion of catalyst which is embedded in the Nafion matrix.

Overall, alcohols production was promoted by a low contact time as a result of the fast removal of the reaction mixture from the reaction volume exposed to UV light and, thus, with less promotion of oxidation and/or secondary reactions. On the contrary, the slow removal caused a partial oxidation of MeOH and EtOH, favouring HCHO production. In all the cases, a water defect corresponded to a larger HCHO production, reaching a flow rate of 27 µmol $g_{catalyst}^{-1}$ h^{-1} at an H_2O/CO_2 feed molar ratio equal to 0.5.

The highest MeOH and EtOH selectivities were 54.6% and 45.4 % respectively, at H_2O/CO_2 feed molar ratio equal to 5 and contact time of 2 s, representing 100% carbon-containing products.

A good alcohols production rate of 32.8 µmol $g_{catalyst}^{-1}$ h^{-1} was obtained at the best operating conditions.

3.5 Photocatalytic CO_2 reduction in continuous membrane reactor: C_3N_4-TiO_2/Nafion membrane

The results presented in this chapter will be partially reported in a paper under submission to *Submission to Energy & Environmental Science*.

3.5.1 C_3N_4-TiO_2 powder

3.5.1.1 Powder characterization

The diffuse reflectance spectra of C_3N_4, TiO_2 and C_3N_4-TiO_2 samples were recorded in order to investigate their band gap energy (Figure 74). In particular, the band gap of the C_3N_4-TiO_2 was determined by the intersection (green spot) of the tangent lines indicated in the inset Figure 74.
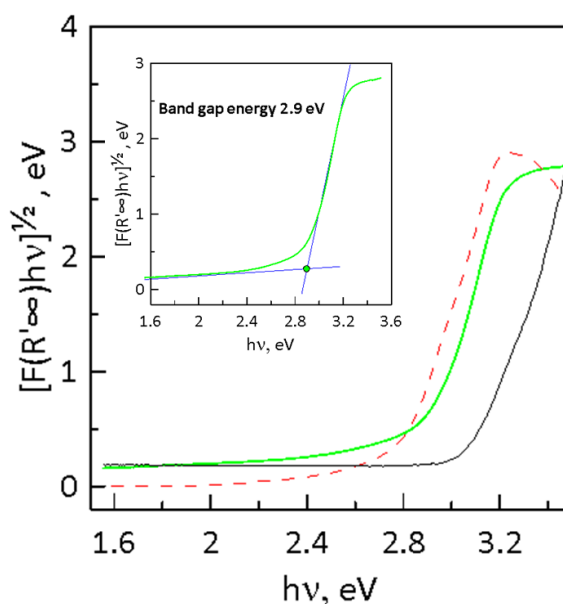
Figure 74. Kubelka-Munck modified function vs. energy for C_3N_4 (dashed red line), TiO_2 (black line) and C_3N_4-TiO_2 (green line) samples. The C_3N_4-TiO_2 band gap energy is reported in the inset.

The band gap of the C_3N_4-TiO_2 sample is 2.9 eV (inset of Figure 74) which falls in the region of visible light absorption and corresponds to ca. 428 nm. Probably due to the

very close band gaps value of the bare samples and the instrumental resolution, in the composite spectrum only one band gap energy was observed instead of two. Thus, by comparing the pure TiO_2 and C_3N_4 reflectance spectra, Li et al. report only one band gap energy for the C_3N_4-TiO_2 sample with an absorption in the visible range accompanying a red shift in the absorption edge, due to the synergistic effect between TiO_2 and C_3N_4.[344]. The discrepancy with the value of 2.8 eV of the pure C_3N_4 materials, previously found, is ascribable to the presence of TiO_2 which shows a typical band gap energy value of 3.1 eV (black line, Figure 74).

Figure 75 shows the FTIR spectra of TiO_2, C_3N_4 and C_3N_4-TiO_2 samples. According to literature data, the spectrum of the composite material shows the characteristic bands of C_3N_4 and TiO_2.[221, 345] In particular, as far as C_3N_4 is concerned, the absorption peak at 1644 cm^{-1} can be ascribed to the sp^2 C=N stretching vibration modes, while the strong peaks at 1248, 1320, and 1416 cm^{-1} to the sp^3 C–N heterocycle stretching. Besides, the band at ca. 810 cm^{-1} is attributed to the typical breathing mode of the tri-s-triazine units.[207, 209] All of these peaks are representative of the unchanged melem unit structure of C_3N_4 arising after the composite preparation as clearly evidenced by comparing the spectrum of C_3N_4 (red line- Figure75) with that of the composite (green line-Figure75). The spectra between ca. 1250-1650 cm^{-1} were less defined in the composite with respect to the bare C_3N_4, due to high amount of TiO_2 (75% TiO_2 and 25% C_3N_4). Furthermore, a strong wide band from 400 to 900 cm^{-1} is due to the TiO_2 presence in the composite C_3N_4-TiO_2, which corresponds to Ti–O and Ti–O–Ti stretching vibration modes.[221, 345]
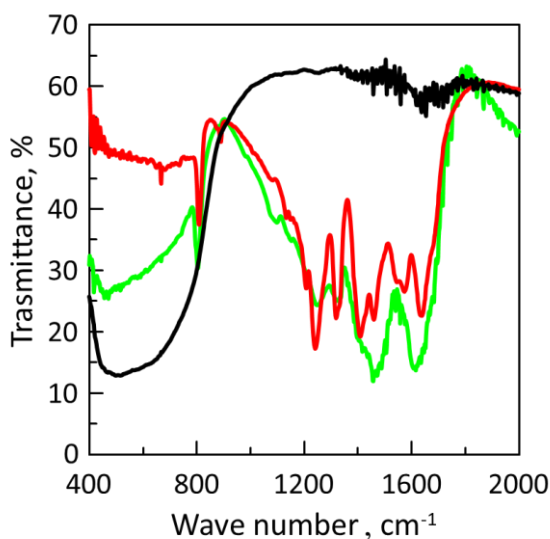
Figure 75. FT-IR spectrum of C₃N₄ powder (red line), TiO₂ (black line) and C₃N₄-TiO₂ composite (green line).

XRD diffractograms of the C_3N_4 based materials along with the bare TiO_2 and C_3N_4 samples are shown in Figure 76. The pattern of C_3N_4-TiO_2 composite (red line) shows three main peaks at 13.1°, 25° and 27.3° due to the presence of C_3N_4 and TiO_2 materials. In fact, as in the case of C_3N_4, C_3N_4-TiO_2 composite shows two characteristic peaks at 27.3° and 13.1° clearly defined, in good agreement with the patterns reported in the relevant literature and already described in the paragraph 3.4.1.1. The presence of TiO_2 in the composite is confirmed by the intense peak at 25° corresponding to the anatase crystal phase (black line), although the less intense peaks of Anatase phase at 45° and 65° are absent in the composite.
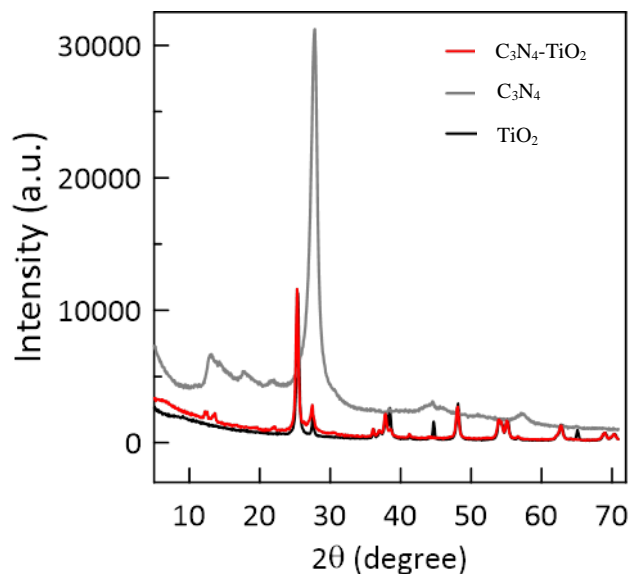
Figure 76. XRD spectra of TiO₂, C₃N₄ and C₃N₄-TiO₂ samples.

3.5.1.2 Preliminary photocatalytic tests: experimental conditions and results by using C₃N₄-TiO₂ photocatalyst

The preliminary CO_2 photoreduction tests were carried out by using a batch reactor in Pyrex with a volume of 140 mL and equipped with a septum to permit sampling (Figure 26 section 3.1.1). 0.35g of photocatalyst were dispersed in the bottom of the photoreactor and N_2 was flushed for 2 h inside the system under irradiation in order to photo-desorb possible impurities and/or carbon residues from the catalyst surface. Subsequently, the photoreactor was saturated with CO_2 containing the vapour pressure of water at 25 °C. To start the experiment in the presence of humid CO_2, the stream of CO_2 was continuously flushed for at least 1 h inside the reactor after bubbling in a water containing flask. In order to evaluate the effect of the amount of water on the CO_2 photoreduction in batch reactor, two tests were preliminary performed by injecting through a syringe 3.6 and 50 μL distilled water, respectively, in the reactor. Then the reactor was closed and irradiated by simulated solar light produced by a SOLARBOX apparatus (CO·FO.ME·GRA) equipped with a 1500W high-pressure Xenon lamp.

The possible presence of products deriving from C impurities was checked by previously irradiating the photocatalysts before the photoactivity experiments in the

presence of CO_2 under a flow of humid He according to Strunk et al.[114] This procedure allowed also to clean the surface of the photocatalyst. Notably, no organic species were observed during this treatment.

Aliquots of the gaseous reaction mixture were withdrawn at fixed irradiation times by using a gas-tight micro syringe. The evolution of the formed organic products was followed by a GC-2010 Shimadzu equipped with a Phenomenex Zebron Wax-plus column by using He as the carrier gas and a FID. CO was analysed by a HP 6890 GC equipped with a packed column GC 60/80 Carboxen-1000 and a TCD. The latter analysis was also useful to check that the system was effectively sealed by monitoring the constant amount of N_2 inside the reactor (no air penetrated inside the reactor).

The CO_2 conversion was followed in the presence of two different amounts of H_2O (reductant agent) equal to 3.6 and 50 µL converting 0.26 and 5.27 µmol $g_{catalyst}^{-1}$ of carbon, respectively (Table 20). In particular, at lower content of H_2O, the only product was CH_4, while at higher content of water, the most abundant products detected were CH_4, MeOH and acetaldehyde with traces of CO. According to the literature data reported in Table 6 (section 1.3.5), the addition of TiO_2 to C_3N_4, increases the photo-converted CO_2 as it is evident by comparing the total carbon converted of test II carried out in the presence of the composite (Table 20) with the results of the test reported in the section 3.4.1.1 in the presence of C_3N_4 sample (0.6 µmol g^{-1} h^{-1}) carried out under the same experimental conditions.

Table 20. Carbon conversion rate and photogenerated products and total carbon converted after 6 h of irradiation time in batch reactor in the presence of CO_2 and H_2O by using C_3N_4-TiO_2 photocatalyst.

I test: Amount of H_2O equal to 3.6 µL		II test: Amount of H_2O equal to 50 µL	
Carbon conversion rate, µmol g^{-1} h^{-1}			
0.04		0.9	
Products	µmol g^{-1}	Products	µmol g^{-1}
CH_4	0.26	CH_4	1.33

		CO	0.1
		Acetaldehyde	1.48
		MeOH	2.36

3.5.2 Photocatalytic membrane test conditions

A photocatalytic membrane was utilized for CO_2 photoreduction with H_2O as the reducing agent. Prior to the characterization and the photoreduction tests, the prepared membrane was cleaned. The cleaning procedure, carried out by using the membrane reactor set up above described, consists in a "blank reaction" where, together with H_2O, an argon stream was fed into the reaction module instead of CO_2, in continuous regime for 8-24 h, at the same operating conditions chosen for the catalytic experiments (under UV-Vis irradiation). The aim of this procedure was to clean the membrane from any residuals of solvent and other low molecular weight organics, possibly present in the polymer solution, that could be released during the reaction measurements thus affecting the results.

The reactor set up used has been described in section 3.4.2 (Figure 65), while the operating conditions applied are summarised in Table 21.

Table 21. Operating conditions for C_3N_4-TiO_2 photocatalytic membrane reaction measurements.

CO_2 flow rate, mL (STP[*]) min^{-1}	
H_2O/CO_2 feed molar ratio	0.5; 2; 5
Feed Pressure, bar	3;5
Permeate Pressure, bar	1
Contact time, s	2; 3.5

[*]STP: standard temperature and pressure, 0°C and 1 bar.

In detail, the trans-membrane pressure difference (3 and 5 bar) was regulated by a back-pressure controller. The gaseous fraction of the retentate and permeate flows, previously cooled down by means of opportune ice traps, was measured by bubble soap flow-meters. The composition of these streams was measured by an Agilent Technologies 7890A gas chromatograph with TCD (HP-PLOT and Molsieve columns). The retentate and permeate condensate fractions were periodically sampled and analysed by an Agilent 6890N gas chromatograph equipped with FID detector and an HP-5 column. All of the tests, lasting 16-20 h, were performed in steady state conditions, which were reached within 5 h for all of the species.

The catalytic membrane was used in the continuous photocatalytic membrane reactor for some weeks changing feed molar ratio, feed pressure, feed flow rate, etc. During the whole period, piling out of C_3N_4-TiO_2 was not evident since no loss in reactor performance and/or selectivity was observed.

Particular attention was devoted to the analysis of the effect of contact time (Eq. 19 section 3.4.2), feed molar ratio and pressure on the membrane reactor performance.

No difference of CO_2 concentration between the feed and the output could be practically measured. Therefore, CO_2 conversion did not represent a significant parameter to be considered to evaluate the reactor performance. Instead, the efficiency of the reaction was evaluated on the basis of produced species by considering the ratios (i) produced species flow rate/catalyst weight (Eq. 20 section 3.4.2), (ii) total converted carbon/catalyst weight ratio (Eq. 21 section 3.4.2), and (iii) the reaction selectivity (Eq. 22 section 3.4.2).

3.5.3 Characterisation of C_3N_4-TiO_2/Nafion membrane

Figure 77a shows two FTIR/ATR representative spectra of the same photocatalytic membrane by considering the air-facing (red spectrum) and casting plate-facing (black spectrum) surfaces. The black spectrum confirmed the presence of C_3N_4-TiO_2 catalyst in the membrane matrix. In fact, the characteristic chemical structure is testified by the bands between ca. 1630 and 1320 cm^{-1}, in agreement with the FTIR analysis of C_3N_4-TiO_2 powder (Figure 75). However, these signals are not evident in the spectrum of the air facing surface of the membrane (red spectrum in Figure 77) due to the catalyst segregation at the bottom of the membrane during the membrane preparation process. In both spectra, all of the signals in the range between 970 and 1400 cm^{-1} are due to the Nafion structure. In particular, the bands at 970-983 cm^{-1} are attributed to C−O−C stretching vibrations and the band at ca. 1066 cm^{-1} can be related to the symmetric stretching of −SO_3−. The asymmetric stretching bands of −SO_3− should occur between 1400 and 1100 cm^{-1}, but they are masked by the more intense bands of −CF_2 stretching.[323] In this region, the casting plate facing surface spectrum (black line) shows higher intensity than the red spectrum due to the TiO_2 band between 400-900 cm^{-1}, which corresponds to Ti–O and Ti–O–Ti stretching vibration modes as previously described (see Figure 75).
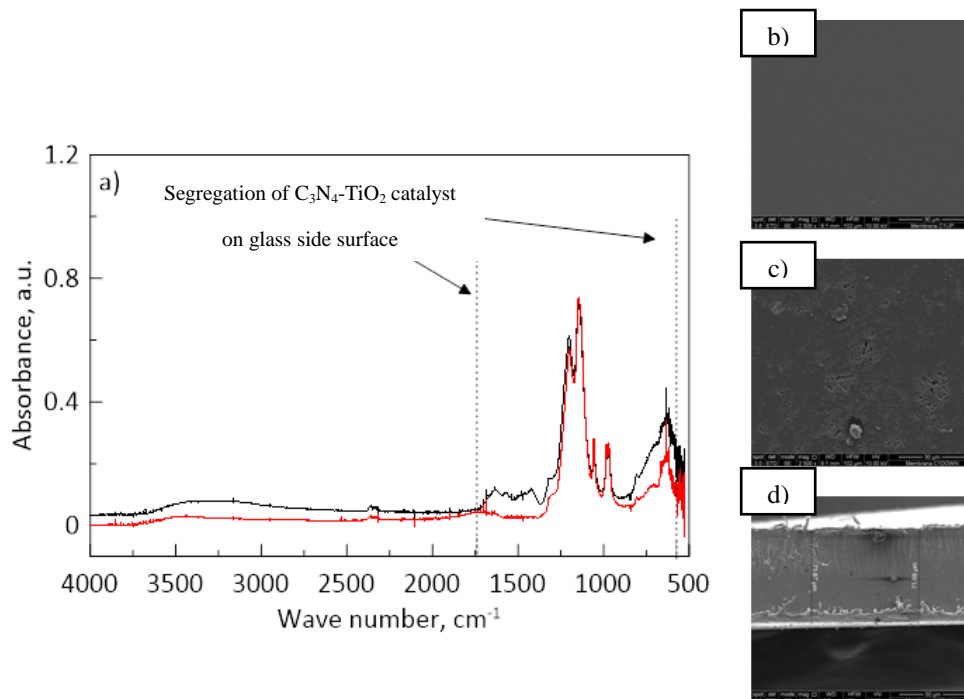
Figure 77. (a) FT-IR (ATR) spectra of (black line) casting plate-facing and (red line) air facing membrane surfaces of C_3N_4-TiO_2 loaded Nafion membrane. SEM of (b) air-facing (magnification 2.5 kX), (c) casting plate-facing surfaces (2.5 kX), (d) cross-section (1.5 kX) of C_3N_4-TiO_2/loaded Nafion membrane.

The difference between the casting plate and the air facing surfaces is confirmed by SEM analyses. Indeed, the air-facing surface of the C_3N_4-TiO_2/loaded Nafion membrane shown in Figure 77b appears dense in agreement with the expectations for a membrane prepared by solvent evaporation method. On the contrary, the casting plate-facing surface presents some porosities owing to the slow solvent evaporation from the most internal layers of the cast solution that can give rise to local phase separation processes (Figure 77c). Moreover, the SEM image of the casting plate-facing surface highlights a segregation of the C_3N_4 partially deposited on the bottom part of the membrane confirming the FTIR/ATR analysis. The SEM image of the cross section (Figure 77d) confirmed the dense nature of the membrane and the formation of catalyst micro-aggregates, present in the bottom side.

The integrity of the catalyst, when embedded in the membrane matrix, was also confirmed by UV–vis diffuse reflectance spectroscopy analyses that showed a band gap of 2.9 eV for the membranes in dry and wet conditions as for C_3N_4-TiO_2 catalyst powder. Moreover, Nafion matrix was proved to be transparent to UV-visible radiation, as the spectrum was recorded analysing the air-side membrane surface.

3.5.4 Results and discussions

Figure 78 shows the results obtained in the tests carried out in the absence of CO_2 (Ar/H_2O stream) by using photocatalytic and pure Nafion membrane plotting the species distribution as a function of time on stream.
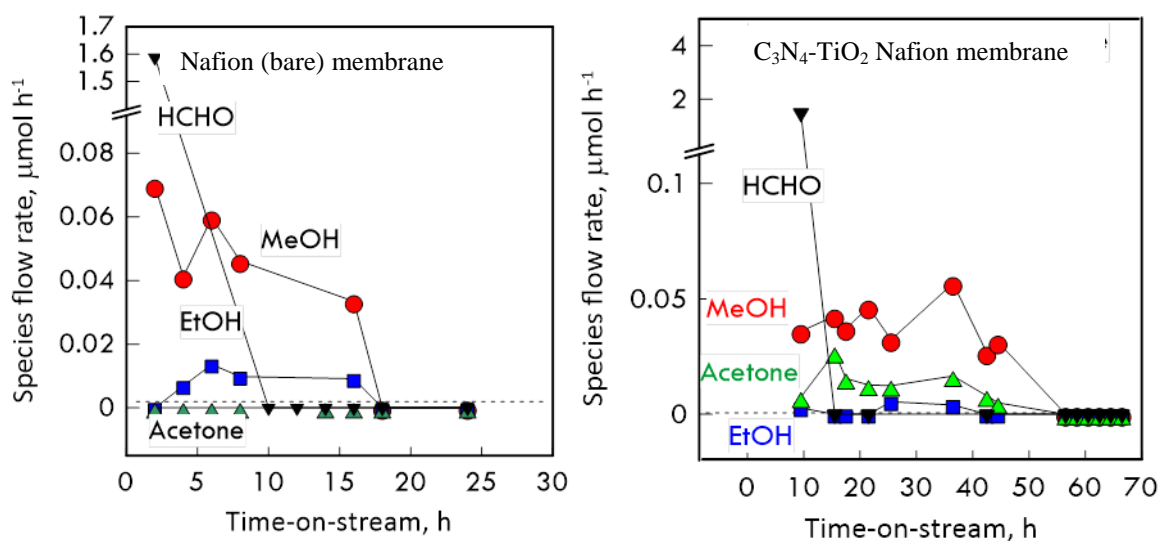
Figure 78. Membrane cleaning (removal of any residuals potentially present) before reaction. C₃N₄-TiO₂ loaded Nafion membrane (active area and thickness respectively 4.1 cm² and 65.8 ± 3.7 μm) and bare Nafion membrane (active area and thickness respectively 4.1 cm² and 78.3 ± 7.8 μm).[322]

MeOH, EtOH, HCHO and C_3H_6O (acetone) were found in the first sample after 2 h of irradiation. In both membrane tests, all of the species flow rate, and especially the HCHO one, decreased with the time until no species could be detected exiting the reactor after 15 and 54 h for the Nafion bare and photocatalytic membrane, respectively. This cleaning treatment was continued up to further 8-12 h. The continuous operating mode of the membrane reactor, implied a continuous removal of residual species from the reactor volume; therefore, their decreasing trend confirms their nature of residues. The zero values reached by each species profile clearly indicates that the membranes did not longer contain residual compound; therefore, the species detected in the reaction experiments in the presence of CO_2 could only be the result of the photocatalytic activity of the C₃N₄-TiO₂-Nafion membrane. The presence of the same compounds in a

bare Nafion membrane (Figure 78) confirms the previous hypothesis. The difference in the profile evolution along with time could be attributed to the different membrane thickness and the filler (catalyst) presence.

When in the Ar-H_2O feed, the Ar is switched to CO_2, the photocatalytic membrane was tested in the reactor (Figure 65) at different feed molar ratios H_2O/CO_2 (0.5, 2 and 5) and contact time (2 and 3.5 s) as reported in Table 21. As previously mentioned, also the pressure effect on the membrane photoreactor performance was evaluated by carrying out CO_2 photoreduction at the pressure of 3 and 5 bar. Generally, these experiments gave MeOH, EtOH, HCHO and acetone as products.

Figure 79 shows both species flow rate and converted carbon obtained in the experiments performed at lower contact time (2 s) as a function of H_2O/CO_2 feed molar ratio. In detail, MeOH and EtOH species flow rate increased reaching 45 and 5 μmol g^{-1} h^{-1}, respectively, by increasing the feed molar ratio from 0.5 to 5. On the other hand, acetone production firstly raised up to 8 μmol g^{-1} h^{-1} at H_2O/CO_2 feed molar ratio equal to 2 and then decreased to zero at H_2O/CO_2 molar ratio of 5. The MeOH and EtOH trends, as previously reported in the section 3.4.4, are due to the feed molar ratio effect on the products distribution. In fact, by considering the stoichiometric ratio of the alcohol formation from CO_2 and H_2O (Eq. 23-24) the alcohol production is favoured by a water excess. Instead, acetone (C3) formation probably arises from secondary reactions of intermediates not desorbed from the catalytic site, as reported in the literature.[325, 326]

The total converted carbon/catalyst weight (Eq. 21) was quantified to define the capability of the system to convert CO_2 into other carbon-containing species (Figure 79). MeOH was the main product for all of the feed molar ratio and concurrently the carbon converted increased by increasing the feed molar ratio reaching the highest value of ca. 58 μmol g^{-1} h^{-1}.
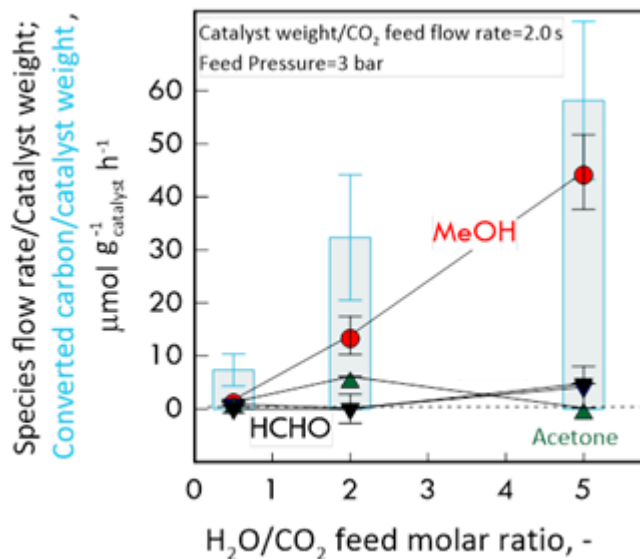
Figure 79. Flow rate/catalyst weight of the various species formed and carbon converted (histogram) as a function of H_2O/CO_2 feed molar ratio at a contact time of 2 s.

Similar trends were obtained at a contact time of 3.5 s (Figure 80), where MeOH was again the favoured product, even though its flow rate was ca. three times less than that obtained at a contact time of 2 s. This lower production is probably due to back reactions (Eq. 26, reported again hereby) oxidizing back to CO_2 the formed MeOH. These reactions are favoured at higher contact times because of the slower removal of O_2 produced in the reactor.

$$CH_3OH + 3/2\ O_2 = CO_2 + 2H_2O \qquad\qquad Eq.26$$

Traces of HCHO were also found at the highest water amount.

Also at a contact time of 3.5 s, the total carbon converted increased with the H_2O/CO_2 molar ratio.

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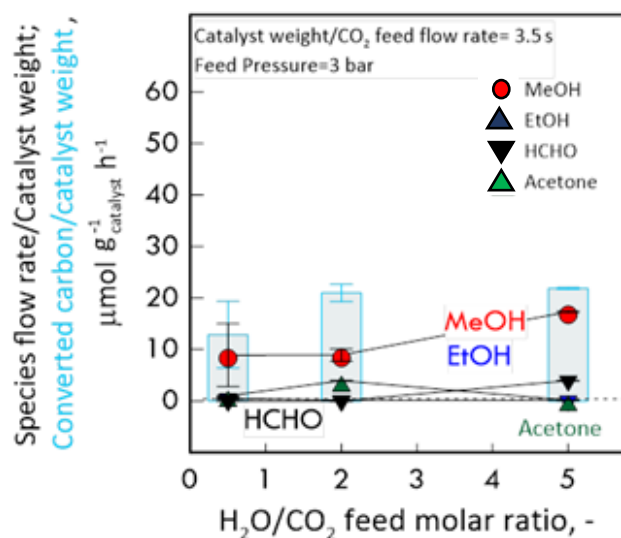
Figure 80. Flow rate/catalyst weight of the various species formed and carbon converted (histogram) as a function of H_2O/CO_2 feed molar ratio at a contact time of 3.5 s.

To define the best membrane reactor performance, Figure 81 shows the total converted carbon/catalyst weight (Eq. 21) obtained in all of the considered experimental conditions. The highest conversion (ca. 58 μmol $g_{catalyst}^{-1}$ h^{-1}) was achieved at the lowest contact time and highest H_2O/CO_2 feed molar ratio, with an amount of converted carbon 7 times greater than that measured in the worst conditions (H_2O/CO_2 feed molar ratio=0.5 and contact time=2 s). By comparing the results obtained by the photocatalytic membrane reactor operating in continuous mode with that of the batch system reported in Table 21, the membrane reactor converted at least 9 times more carbon than the batch, even in the most unfavourable conditions. As previously reported for the C_3N_4-Nafion membrane, the dispersion of the C_3N_4-TiO_2 in the Nafion matrix increases the active surface of the catalyst thus implying that the catalytic sites are more easily reached by light and reagents than when the powder is not embedded in the membrane. Moreover, by comparing the set of data obtained at contact time of 2 s with the ones at 3.5 s, the continuous removal of products from the reaction volume not only favours the reaction, but also promotes the species desorption and the release of active sites, making them available for further reactions. Furthermore, at fixed contact time of 2 s, a linear trend appears by changing the feed molar ratio, thus confirming the previous observations regarding the H_2O/CO_2 feed molar ratio effect. The same trend was detected for contact time of 3.5 s but with a smaller slope value due to a slower removal

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of O_2 produced. In fact, the O_2 presence, as reported in literature, inhibited the photoreduction of CO_2.[346]
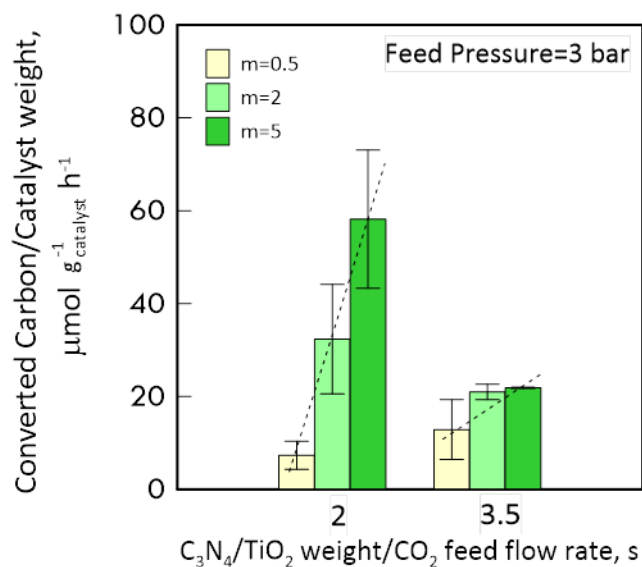
Figure 81. Converted carbon per gram of catalyst as a function of contact time at different H_2O/CO_2 feed molar ratio.

The study presented in this dissertation is hereby again reported to compare, at the best contact time (2 s) and reaction pressure (3 bar) the species flow rate obtained from CO_2 photoreduction experiments carried out in the presence of C_3N_4 and C_3N_4-TiO_2 Nafion membranes at two different feed molar ratios equal to 2 and 5, respectively, in Figure 82.
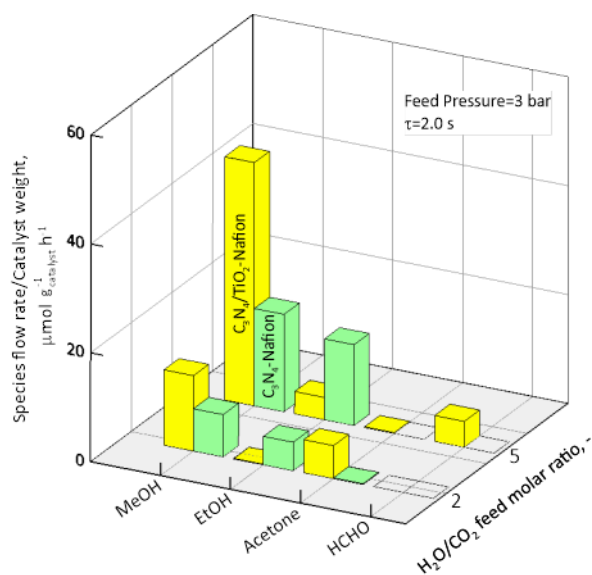
Figure 82. Comparison of the flow rate/catalyst weight of the various species formed at H_2O/CO_2 feed molar ratio of 2 and 5 for C_3N_4-TiO_2-Nafion and C_3N_4-Nafion membranes

The MeOH production was favoured by using the C_3N_4-TiO_2 Nafion membrane, at both feed molar ratios. On the contrary, the C_3N_4-Nafion membrane showed a similar capability in term of MeOH and EtOH production. Nevertheless, at a contact time equal to 2 s, for all of the used catalysts, MeOH was the main product in both feed molar ratio. In fact, by tuning the contact time in order to avoid back reaction, the kinetic favored MeOH production (6 e⁻) compared to the EtOH production (12 e⁻) as shown in equations 12 and 14 as before mentioned in the Chapter 1 (below reported), being in this case the thermodynamic effect negligible.

$$CO_2 + 6\ H^+ + 6\ e^- = CH_3OH + H_2O \qquad E^0_{(V\ vs\ SHE)} = -0.39$$

$$2\ CO_2 + 12\ H^+ + 12\ e^- = C_2H_5OH + 3\ H_2O \qquad E^0_{(V\ vs\ SHE)} = -0.33$$
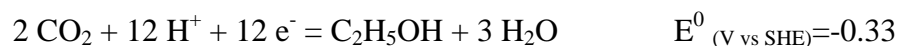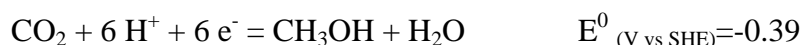
These evidences are confirmed in the total carbon converted values shown in Figure 83. In detail, the performance to transform CO_2 by using C_3N_4-TiO_2 Nafion membrane was higher than C_3N_4 Nafion membrane at all the feed molar ratios and at fixed pressure and contact time. As reported in literature, generally the heterojunction formation between two semiconductors improves the capability of CO_2 photoreduction. The potential of the holes photogenerated in the g-C_3N_4 valence band is not enough positive to oxidize water and O_2 (see Eq. 9 of Chapter 1). Notably, in H_2O oxidation semi-reaction also H^+ ions are formed that are required in the CO_2 reduction. The limitation of C_3N_4 valence band

energy[221] generates lower amounts of H^+, and through these, lower yield for all of the products was achieved. The introduction of TiO_2 in the heterojunction C_3N_4-TiO_2, improved the water oxidation[219, 221] power due to the more positive potential of holes generated in the valence band of TiO_2 [90] (ca. $E^0_{vsSHE} = +2.7$ V) with respect to those generated in C_3N_4 (ca. $E^0_{vsSHE} = +1.2$ V) (see Figure 13 in Chapter 1).

Again, as previously mentioned, increasing the H_2O/CO_2 feed molar ratio results in higher amount of carbon converted, reaching the highest value of ca. 60 μmol g^{-1} h^{-1} by using the C_3N_4-TiO_2 Nafion membrane at molar ratio equal to 5. This value was at least 60 time higher than the carbon converted achieved in the batch test by using the C_3N_4-TiO_2 powder (Figure 83). Even in the worst conditions (0.5 feed molar ratio), the carbon converted in the membrane reactor in the presence of C_3N_4-TiO_2 Nafion membrane was at least 10 times more with respect to the carbon converted values obtained in the batch reactor.
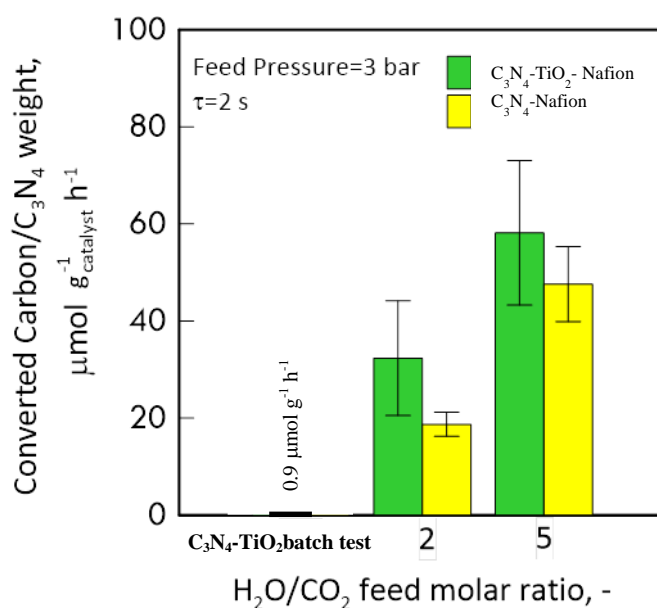
Figure 83. Comparison of converted Carbon/catalyst weight of the various species formed in batch reactor by using C_3N_4-TiO_2 photocatalyst and the photocatalytic membrane as a function of H_2O/CO_2 feed molar ratio.

To evaluate the reaction pressure effect on the photoreduction of CO_2 in the membrane reactor, the C_3N_4-TiO_2 loaded Nafion membrane was tested at reaction pressure of 5 bar.

Figure 84 shows the formed compounds flow rate in the best conditions of fixed feed molar ratio and contact time of 5 and 2 s, respectively at two different feed pressure (3 and 5 bar). The experiment carried out at a feed pressure of 3 bar gave ca. 45, 5 and 6 μmol g^{-1} h^{-1} of MeOH, EtOH and HCHO, respectively, reaching a carbon converted value of ca. 61 μmol g^{-1} h^{-1}. When the feed pressure increased to 5 bar, the alcohol production decreased, in particular the MeOH fell to 33 μmol g^{-1} h^{-1} and no EtOH was produced. On the contrary, when the reaction pressure shifted from 3 to 5, the HCHO raised up from 6 to 28 μmol g^{-1} h^{-1}. These results are probably due to the pressure effect on the removal of the photoproducts due to the CO_2 reduction occurring. The higher pressure could reduce the desorption of O_2 photoproduced so that oxygen is available to initiate back reactions of alcohol either photoproduced to HCHO.
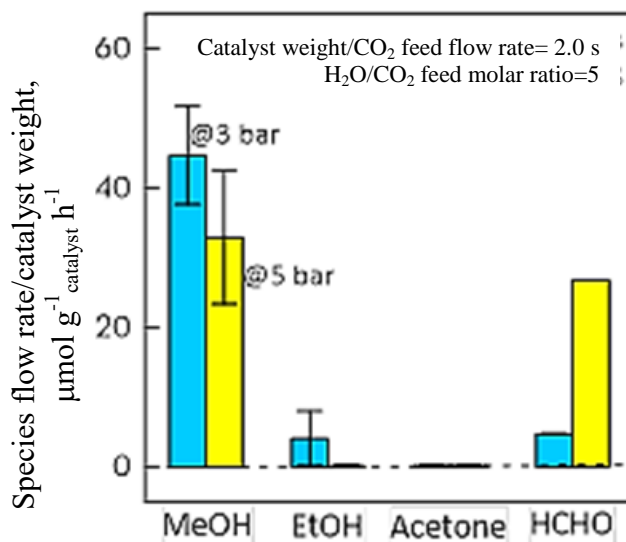
Figure 84. Flow rate/catalyst weight of the various species formed at 3 and 5 bar.

This hypothesis is confirmed by the fact that the carbon converted value obtained at the two reaction pressures did not change (see Table 22). Therefore, the pressure does not influence the photoreduction capability of the photocatalytic membrane but affects the products distribution.

Table 22. Carbon converted at contact time and molar ratio equal to 2s and 5, respectively at 3 and 5 bar as feed pressure by using the C_3N_4-TiO_2 loaded Nafion membrane.

Carbon converted, μmol g^{-1} h^{-1}	
at reaction pressure of 3 bar	at reaction pressure of 5 bar
61	61

Figure 85 shows the selectivity values towards the species formed versus the two reaction pressures investigated of 3 and 5 bar. These results highlighted that at a lower reaction pressure the MeOH is the favored product reaching more than 80% of selectivity.
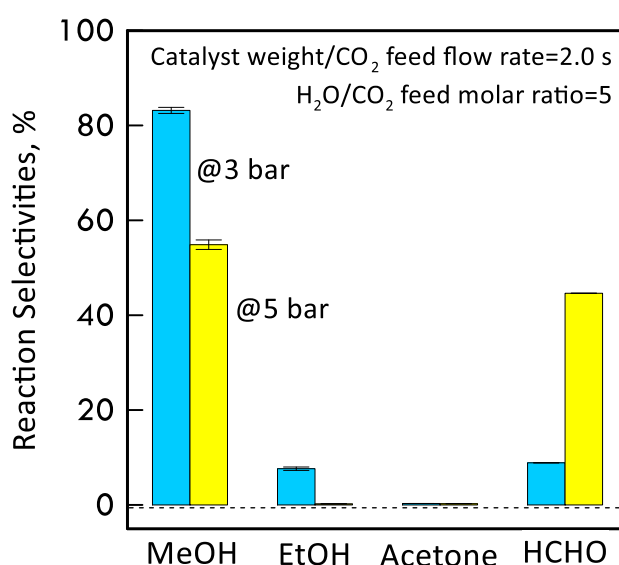
Figure 85. Reaction selectivity of the various species formed at 3 and 5 bar.

Summarizing, the best parameter for both membranes to convert CO_2 to MeOH were lower contact time, higher molar ratio and feed pressure of 3 bar. Figure 86 compares the MeOH selectivity and production rate of the photocatalytic membrane discussed in this dissertation and the results reported from Sellaro et al.[268] which investigated the same reaction under the same experimental conditions (feed molar ratio, feed pressure and contact time) but in the presence of a membrane loaded with bare TiO_2. In this last case methanol was the only product detected.
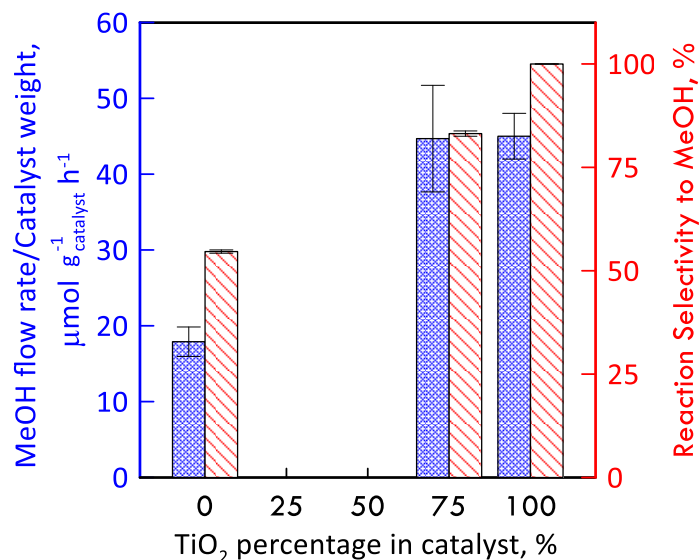
Figure 86. MeOH flow rate per gram of catalyst and relative selectivity as a function of TiO_2 content by comparing literature data.[268]

In the presence of C_3N_4-TiO_2, the MeOH production rate increased more than two times when the TiO_2 content in the photocatalytic membrane increased from 0% to 75%. Also the selectivity toward MeOH production followed the same trend. When the TiO_2 content raised up to 100%, so without C_3N_4, the MeOH production did not change but the selectivity toward MeOH increased from 80% to 100%. These results suggest that the C_3N_4-TiO_2 composite loaded Nafion membrane was more performant in terms of carbon converted with respect to C_3N_4 and TiO_2 Nafion membranes with a little loss in terms of selectivity towards MeOH with respect to the case of TiO_2 loaded membranes.

3.5.5 Conclusion

For the first time the photocatalytic C_3N_4-TiO_2 loaded Nafion membrane was prepared and used to photocatalytic CO_2 conversion in a continuous photocatalytic reactor irradiated by UV-Vis light. The effects of H_2O/CO_2 feed molar ratio, feed pressure and contact time on species production, reaction selectivity and converted carbon were investigated.

Total converted carbon per gram of catalyst varied between 5 and 61 μmol $g_{catalyst}^{-1}$ h^{-1}, with the latter value obtained at an H_2O/CO_2 feed molar ratio of 5, 3 bar as feed pressure and 2 s as contact time with MeOH as prevailing product. The membrane

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reactor converted at least 10 times more carbon in the worst condition setting than the batch system, as a result of the better dispersion of catalyst which is embedded in the Nafion matrix.

Overall alcohols production was promoted by a low contact time and pressure as a result of the fast removal of the reaction mixture from the reaction volume exposed to UV light and, thus, with less promotion of oxidation and/or secondary reactions. On the contrary, the slow removal caused a partial oxidation of MeOH and EtOH, favouring HCHO production.

By comparing the results obtained in this dissertation with those reported in literature value, the C_3N_4-TiO_2 Nafion membrane is more efficient in terms of carbon converted than TiO_2/Nafion membrane. A relationship between the MeOH production and selectivity versus the TiO_2 content in the photocatalyst loaded in polymeric matrix was found.

Conclusions

In the present thesis, promising materials were investigated considering the relationship between physico-chemical features, reactor type, reactor set-up to activity for CO_2 photoreduction by using water as reductant agent.

With the aim to increase the CO_2 photoreduction efficiency were adopted the following different strategies: (i) TiO_2, ZrO_2 based materials were obtained by modifying the bare semiconductors by means of metal and non-metal doping or by coupling them with opportune graphitic materials (such as graphene or graphitic C_3N_4), and (ii) the design of the photocatalytic set-up and the operating parameters influencing the reaction efficiency were tailored by using continuous photocatalytic membrane reactors and different feed molar ratio, residence times and feed pressure.

In particular, the bare semiconductors TiO_2, ZrO_2, and C_3N_4 were obtained by introduction of graphitic materials as C_3N_4 or graphene in TiO_2 composites, or Ce and Er doping in ZrO_2 structure, or again by oxygen doping on C_3N_4.

These materials tested in batch reactors by using water as the reductant showed capability for CO_2 photoreduction. In all the tests, CO_2 photoreduction occurs giving CH_4 and CO or alcohol and acetaldehyde as the main products as a function of catalyst and experimental conditions operated.

The best powder photo-capability in batch reactors was obtained by using 1% G/TiO_2 and 0.5% Er/ZrO_2 materials, giving ca. 44 and 88 μmol g^{-1} of carbon converted after 6 h of irradiation time, respectively. In the first case, the major products obtained during the CO_2 photoreduction was methane whilst in the second case were ethanol and acetaldehyde.

Also flat sheet photocatalytic C_3N_4 and C_3N_4-TiO_2 Nafion membranes were prepared and tested for CO_2 reduction in a continuous photocatalytic membrane reactor using water as reductant.

Alcohol and formaldehyde were found as the main products and their relative amounts were a function of photocatalytic membrane type and experimental

conditions operated such as the feed H_2O/CO_2 molar ratio, contact time and the reaction pressure.

In all experimental conditions and by using both membrane (C_3N_4 and C_3N_4-TiO_2 membrane) the continuous photocatalytic membrane reactor showed a higher photo-capability for CO_2 reduction with respect to all of the batch results obtained. To convert CO_2 the best parameters were found at the highest feed H_2O/CO_2 molar ratio of 5 and at the smallest contact time (2 s) and reaction pressure (3 bar) for both photocatalytic membrane. In these favourite conditions, furthermore a trend was found between the methanol production/selectivity with the TiO_2 content in the photocatalyst loaded Nafion membrane. The best performance was reached by using the C_3N_4-TiO_2 Nafion membrane obtaining ca. 61 μmol g^{-1} h^{-1} of carbon converted with a methanol production equal to ca. 45 μmol g^{-1} h^{-1} (ca. 80 % selectivity).

This *Ph.D* dissertation provided (i) an interesting structural study of C_3N_4 before and after use in the CO_2 photoreduction tests, (ii) a remarkable study of catalyst photoactivity by using oxide and graphitic material in batch reaction, (iii) a promising route for the optimisation of the photocatalytic continuous membrane reactor in terms of feed molar ratio, residence time and reaction pressure.

Appendix A. Publications

PUBBLICAZIONI

1. ZrO_2 Based materials as photocatalysts for 2-propanol oxidation by using UV and solar light irradiation and tests for CO_2 reduction. E. I. Garcìa-Lòpez, G. Marcì, F. R. Pomilla, M. C: Paganini, C. Gionco, E. Giamello, L. Palmisano. *Catalysis Today*, **2018**, 313, 100-105

2. CO_2 to Liquid Fuels: Photocatalytic Conversion in a Continuous Membrane Reactor. F. R. Pomilla, A. Brunetti, G. Marcì, E. I. Garcìa-Lòpez, E. Fontananova, L. Palmisano, G. Barbieri. *ACS Sustainable Chemistry and Engineering*, **2018**, 6(7), 8743-8753

3. Photocatalytic CO_2 valorization by using TiO_2, ZrO_2 and graphitic based semiconductors. F. R. Pomilla, R. Molinari, G. Marcì, E.I. Garcia-Lopez and L. Palmisano. *Research and Technologies for Society and Industry* (IEEE-RTSI), ISBN: CFP18C29-ART, Part Number: 978-1-5386-6286-3, **2018,** 478- 483.

4. Graphitic C_3N_4 physical changes following photocatalytic tests in the presence of CO_2 and water. F. R. Pomilla, M. A. L. R. M. Cortes, J. W. J. Hamilton, R. Molinari, G. Barbieri, G. Marcì, L. Palmisano, P. K. Sharma, A. Brown, J. A. Byrne. *Journal of Physical Chemistry C, 2018*, 122, 28727-28738

5. CO_2 valorisation by using a C_3N_4/TiO_2 Nafion membrane in a photocatalytic membrane reactor: optimisation parameters. *In preparation.*

COMUNICAZIONI A CONGRESSI INTERNAZIONALI

1. ORALE: Photocatalytic CO_2 valorization by using TiO_2, ZrO_2 and graphitic based semiconductors. F. R. Pomilla, R. Molinari, G. Marcì, E.I. Garcia-Lopez and L. Palmisano. Research and Technologies for Society and Industry (RTSI), ISBN: CFP18C29-ART, Part Number: 978-1-5386-6286-3, from pag. 478 to pag. 483, **2018**. 4° International Forum EEEI, RTSI, section Nanomaterials for 4.0, 10-13 Septermber **2018**, Scuola Politecnica of University of Palermo, Palermo, Italy.

2. CO_2 reduction in photocatalytic membrane reactor: products selectivity study. F.R: Pomilla, A. Brunetti, G. Marcì, E. I. Garcia-Lopez, E. Fontananova, L. Palmisano, G. Barbieri. European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA) 10, Almeria, Spain, 4-8 June **2018**. (P15)

3. ZrO_2 base materials: preparation, characterization and photocatalytic activity for 2-propanol oxidation and CO_2 reduction. E. I. Garcia-Lopez, G. Marci, F. R. Pomilla, M. C. Paganini, C. Gionco, E. Giamello and L. Palmisano. 5th European Conference Environmental Applications of Advanced Oxidation Processes- EAAOP5, 25-29th June **2017**, Prague, Czech Republic.

4. Photocatalytic membrane rector for CO_2 conversion, F. R. Pomilla, A. Brunetti, G. Marcì, E. Fontananova, L. Palmisano and G. Barbieri, CO_2 Summit III: Pathways to Carbon Capture, Utilization, and Storage Deployment ECI Cetraro (CS), Italy , May 22-26, **2017**

5. CO_2 conversion in continuous photocatalytic membrane reactor, F.R. Pomilla , A. Brunetti, G. Marcì, E. Fontananova, E. I. Garcia-Lòpez, L. Palmisano and G. Barbieri. 10th Korea-Italy workshop on the "Membrane Technology for Climate Change", page 91, Didimol Plaza KRICT, Daejeon, Republic of Korea, **2017**

COMUNICAZIONI A CONGRESSI NAZIONALI

(INVITED, ORAL O POSTERS)

I.   Foto-reattori a membrana per la valorizzazione del CO_2. <u>F. R. Pomilla</u>, A. Brunetti, G. Marcì, E. I. Garcià –Lopez, E. Fontananova, G. Marcì, L. Palmisano and G. Barbieri. Congresso Società Chimica Italiana congiunto delle sezioni Sicilia e Calabria, Palermo, Italy, 01-02 Marzo **2019**, Oral presentation

II.   Photocatalytic membranes for CO_2 reduction, <u>F. R. Pomilla</u>, A. Brunetti, E. Fontananova, G. Marcì, L. Palmisano and G. Barbieri. Seminar Day, CNR-ITM, Arcavacata di Rende (CS), Italy, 01 Dicember **2016**, Oral presentation

Periodo all'estero.

Periodo di sei mesi all'estero presso i laboratori del NIBEC dell'Università della Ulster, Jordanstown, Belfast sotto la supervisione del prof John Anthony Byrne.

Partecipazioni a progetti all'estero.

Partecipazione, dal 19/09/2016 al 06/10/2016, ad un progetto internazionale dal titolo " Innovative Oxide materials for the solar Photocatalytic degradation" (IOSPEP) all' interno del progetto SFERA nella Piattaforma Solare di Almeria.

Appendix B. Training *Ph.D* school activity

Attività didattica

ELENCO DEI SEMINARI SEGUITI

1) 8/02/2016 (tramite videoconferenza) ore 15:00-16:00 The LCH, Dark Matter and beyond by professor Tomer Volansky of Tel Aviv University (https://physics.tau.ac.il/), 16:30-17:30 Dark Matter from cosmological observations and connection with the searches at colliders by professor Pasquale Serpico of LAPTH-CNRS (https://lapth.cnrs.fr/)

2) 18/05/2016, (ore 10:00-13:30) in Aula Magna dell'Università delle Calabria. Convegno "L'affascinante fisica del neutrino e l'evoluzione cosmica" promosso dal Prof. Marco Schioppa.

3) 18/05/2016, (ore 14:00 – 17:30) Aula Caldora – Università della Calabria. "Approccio sostenibile al recupero delle strutture esistenti"

4) Giovedì 19 (ore 15:00-18:30) e Venerdì 20 (ore 9:00-17:00) Maggio 2016 Aula Magna dell'Università della Calabria. "Pianeta Acqua - La qualità della risorsa idrica in Calabria: stato dell'arte e prospettive".

5) 07/06/2016 (ore 15:30), Cubo 15B aula E, dell'Università della Calabria, tenuta dal professore Salvator Dominguez-Bella dal titolo "Roman raw materials in the Hispania Baetica, the case of the maritime baths mosaic in Baelo Claudia, Cadiz, Spain."

6) 08/06/2016 (ore 9:00), Cubo 15B aula E, dell'Università della Calabria, tenuta dal professore Salvator Dominguez-Bella dal titolo "Archeometric research applications of the mXRF. Same examples in the South Spain."

7) 27 /06/ 2016 (Ore 15:30 - 18:30), Aula PT3, Cubo 45 B, Piano Terra, dell' Università della Calabria, dal titolo "In-situ π-Anchor for Delaying Debonding of U-wrap FRP in Shear Strengthened RC Beams".

8) Mercoledì 29 giugno 2016, ore 15:30, Aula Magna DiBEST, III piano, cubo 15b, dell Università della Calabria, tenuto dal Prof. Josè Arribas, dal titolo "Identification of diagenetic aspects in sandstones: examples and practices".

9) 28-03-2017, Seminario "Intuvo Roadshow", Responsabile Nicola Cimino, Agilent Technologies Italia, Arcavacata di Rende, Università degli studi della Calabria. 8 ore

10) 05/06/2018. Seminario su analisi topografiche dei materiali. Responsabile: Prof.ssa Monica Santamaria. Università degli Studi di Palermo, Dipartimento DICAM, Viale delle Scienze. 8 ore

11) 04/04/2018. Seminario dal titolo" Inside the review process". Responsabile: Prof. Davide Ravasi, Università degli Studi di Palermo, aula Capitò, ed. 7, Viale delle Scienze. 10 ore

ATTIVITA' FORMATIVE GENERALI EFFETTUATE

1) Scienza e tecnologia delle membrane – Preparazione di membrane. ITM-CNR 19-22/04/2016. Docenti: L. Giorno, A. Figoli, A. Gugliuzza (4CFU).

2) Analytical techniques for environmental studies. 24, 26 Maggio - 7,13,14 Giugno 2016 presso le aule e i laboratori dei cubo 15A /B e 14 A /B. Docenti: Donatella Barca, Paola Donato, Fabio Scarciglia (4CFU).

3) Scienza e tecnologia delle membrane – Applicazione di membrane. ITM-CNR 9,14,15,16 Giugno 2016. Docenti: E. Drioli, A. Criscuoli, G. Di Profio, G. Barbieri (4CFU).

4) Writing a scientific paper: Guidelines and Tips. Docente: Alessio Caravella (4 CFU). 27/06-01/07 2016.

5) Scienza e tecnologia delle membrane – Caratterizzazione di membrane. ITM-CNR 01-07/07/2016. Docenti: A. Figoli, A. Gugliuzza (4CFU)

6) Corsi LIO presso il Laison Office dell'Università della Calabria. (4 CFU)

7) Corso di "Calcolo scientifico", Responsabile Prof. Pantano, Università degli studi della Calabria. Dal 13/03 al 22/05/2017. (4 CFU)

8) Corso di "Materiali per la catalisi eterogenea". Responsabile Prof. Giuseppe Marcì, Università degli studi di Palermo. Dal 26-09 al 15-12-2017. (6CFU)

9) Corso: Corso: English for everyday life. Responsabile: Prof. Deborah Cully. Ulster University, Jordanstown, Belfast, Northem Ireland. Da Agosto a Dicembre 2017. 1 semestre.

10) Corso: Accademic writing. Responsabile: Prof. Deborah Cully. Ulster University, Jordanstown, Belfast, Northem Ireland. Da Agosto a Dicembre 2017. 1 semestre.

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