



**Evaluation Report of the Doctoral Thesis titled  
"Photocatalytic reduction of carbon dioxide in hybrid systems"**

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The thesis consists of 152 pages and it is divided in three parts (I-III): **Introduction, Results and Discussion, Conclusion**. Within each part there are different Chapters.

Part I, **Introduction**, is divided in three Chapters: in the first one the candidate gives some general information on CO<sub>2</sub> considered as a chemical feedstock, reporting not only the natural carbon cycle and anthropogenic sources, but also the possibility to activate this molecule, i.e. the electrochemical, biotechnological, photochemical and photocatalytic processes. The section appears exhaustive (with the exception of the photoelectrochemical and photocatalytic processes for which the candidate refers to Chapter 3 of Part I) and the wealth of historical information provided are useful for the readers interested to know details on the evolution of the use of CO<sub>2</sub> and its natural and chemical transformations. Chapter 2 deals with the fundamentals of Heterogeneous Photocatalysis and its applications. The band structures of the semiconductors, the band theory of the solids, some mechanistic aspects and the methods used to sensitize the photocatalysts in order to increase light absorption in the visible light range are reported. The length of the Chapter looks balanced with the rest of the thesis, and it has been brought out clearly, although the literature on heterogeneous photocatalysis used for synthetic purposes could have been wider by taking into account additional recent papers/reviews. In Chapter 3 the photocatalytic transformations of CO<sub>2</sub> are summarized. In particular the evaluator has appreciated the list of some multi-electron transfer processes (with the E° values) to reduce CO<sub>2</sub> to small organic molecules because one should carefully examine what are the steps thermodynamically favored on the surface of the chosen photocatalyst. It is clear that the theoretical E° values can be strongly influenced by many factors as it is reported in the thesis, but they should be an important starting point before discussing on the products experimentally found. The apparently difficult multi-electron transfers could occur more easily under definite experimental conditions (see for instance the formation of methane in which eight electrons should be involved). Moreover also the kinetics factors influenced by the presence of cocatalysts, the presence of mesoporous support for the photocatalysts, the particle size etc, are highlighted in the thesis as they are paramountly important to address CO<sub>2</sub> photoreduction. It is worth noting that in Chapter 3 some non-TiO<sub>2</sub> hybrid photocatalysts are described (Table 3.1) and they are important as the presence of heterojunctions (improving the photoproduced e<sup>-</sup>/h<sup>+</sup> separation) and/or complexes (working as sensitizers) on the surface



has been proposed by many authors as a tool to facilitate the CO<sub>2</sub> photo-activation. The formation of C-C bonds is very difficult and sometimes questioned in the literature. A detailed experimental work with <sup>13</sup>CO<sub>2</sub> is suggested, when possible, to demonstrate unambiguously the origin of the product(s). Moreover long time duration protocols by flowing Helium or Argon are needed before carrying out experiments in the presence of CO<sub>2</sub> in order to clean the photocatalyst used. It appears that control experiments were carefully performed by the candidate.

The candidate reports also in Chapter 3 the possibility to reduce CO<sub>2</sub> by indirect photocatalytic-enzymatic processes. Three types of conversion are reported: conversion into C<sub>1</sub> molecules, carboxylation reactions and fixation into sugars as an HCOH unit. These processes are promising, although most of the enzymes are unstable and expensive like the candidate points out.

Part II, **Results and discussion**, is divided in three Chapters (4-6). Chapter 4 reports the photocarboxylation of acetylacetone and 2,3-dihydrofuran, which showed to be very promising substrates, under CO<sub>2</sub> high pressures (7-8 bars). Various photocatalysts were prepared and characterized very thoroughly by optical, structural, spectroscopic and electrochemical methods, i.e. Diffuse Reflectance spectroscopy, X-ray diffractograms, X-ray photoelectron spectroscopy, SEM observations, EPR analysis, FT-IR, Raman, Photoluminescence, NMR, and Cyclic voltammetry measurements. The syntheses of the used photocatalysts are described in detail. ZnS-A and ZnS-B were prepared starting from Na<sub>2</sub>S or NaOH, respectively, and they differ also for the presence of thiourea during the synthesis of ZnS-B. Various amounts of Ru were deposited (starting from ethanolic solutions of RuCl<sub>3</sub> and by reducing with NaBH<sub>4</sub>) on the synthesized powders and the behaviour of the photocatalysts was compared. The solvents used were carbon tetrachloride and chloroform which facilitated one to perform the spectroscopic analyses (for instance the FT-IR and NMR spectra) before, during and after the irradiation. The main products of acetylacetone carboxylation were identified to be 2-acetyl-3-oxobutanoic acid and 3,5-dioxyhexanoic acid, although other compounds were formed as a result of the decomposition of acetylacetone. The choice of acetylacetone was correctly justified by the ability of this compound to produce allyl radicals which can be stabilized by keto-enol tautomerism. The presence of Ru was essential to detect the main products in the presence of Ru@ZnS-B samples, and 0.5Ru@ZnS-B seemed to be the most photo-active. Other photocatalysts were tested (ZnS and CuI), but they showed to be less photoactive than 0.5Ru@ZnS-B for the formation of 2-acetyl-3-oxobutanoic acid and 3,5-dioxyhexanoic acid. Moreover, the candidate writes that, although one can establish with certainty the formation of COOH groups, it was impossible to determine by NMR what compound was formed (2-acetyl-3-



oxobutanoic acid or 3,5-dioxyhexanoic acid).

The photocatalytic transformations of 2,3-dihydrofuran was carried out in the presence of 1%Ru@ZnS-A photocatalyst and no products of CO<sub>2</sub> fixation were found. Some small amounts of methanol were found, probably by an effect of a multielectron CO<sub>2</sub> reduction. Differently from what observed in the presence of 1%Ru@ZnS-A, 2,3-dihydrofuran-3-carboxylic acid (product of 2,3-dihydrofuran carboxylation), tetrahydrofuran and cyclopropanecarboxaldehyde were found as the main products in the presence of 1%Ru@ZnS-B. Also in this case small amounts of methanol were detected.

The photocarboxylation of 2,3-dihydrofuran was carried out also in methanol, as this solvent can donate protons. <sup>13</sup>C-NMR in addition to GC-MS analysis was used and it was established that some of the products formed in the absence of CO<sub>2</sub>, but 2,3-dihydrofuran-3-carboxylic acid was found in the presence of CO<sub>2</sub> both in chloroform and methanol. The conclusion was that both 1%Ru@ZnS-B and 1%Ru@ZnS-A photocatalysts were effective for the carboxylation of dihydrofuran, but the selectivity and the efficiency of the reaction were low.

In Chapter 4 the mechanism of the photocatalytic carboxylation is reported with the help of EPR study. The EPR study allowed to detect signals attributable to DMPO·CO<sub>2</sub> adduct at the surface of Ru modified photocatalysts. Moreover also a DMPO·SO<sub>3</sub> adduct was detected, indicating some photocorrosion process involving ZnS. As far as the oxidative step is concerned, a study performed by cyclic voltammetry with an acetonitrile solution of acetylacetone, demonstrated that the photoinduced oxidation of acetylacetone is thermodynamically possible. By concluding this Chapter the candidate reports that Ru can be considered as a co-catalyst with a multiple role: to improve the adsorption of CO<sub>2</sub>, to promote the charge separation, to lower the energy barriers. The claim that the prepared materials can enable CO<sub>2</sub> formation also in water is intriguing, but it should take into account the increased photocorrosion phenomena to which ZnS is generally subjected in the presence of H<sub>2</sub>O.

In Chapter 5 the candidate presents other photocatalysts, in particular p-semiconductors like NiO, CuI and CuS, because they could be more suitable for CO<sub>2</sub> reduction by considering the low potentials of their conduction bands (for instance -2.1 V for CuI). These materials were home prepared and thoroughly characterized by bulk, spectroscopic and electrochemical methods. The photocatalytic tests carried out in water or in chloroform afforded mainly HCOOH, CO and CH<sub>4</sub>, although other compounds as CH<sub>3</sub>OH and H<sub>2</sub> were sometimes found. The compounds found depended on the catalyst and the experimental conditions used. For instance, interestingly, NiO annealed at 1050°C was selective for CO<sub>2</sub> reduction to CO, whereas the amount of HCOOH was significant in the presence of home prepared CuI, with respect



to a commercial sample. In this Chapter the study of some parameters, as type of organic (isopropanol) and inorganic (iron(II) sulphate) electron donors and polarity of the solvent to optimize the photocatalytic reduction of  $\text{CO}_2$  is reported. The conclusion is that such materials (p-type semiconductors) could be more suitable than  $\text{TiO}_2$  because of the negative potential of their conduction band favouring the electron transfer to  $\text{CO}_2$ .

In Chapter 6 the candidate reports in brief (i) the enzymatic reduction of  $\text{CO}_2$  to a fuel (in water and under ambient conditions) by using the reduced form of the coenzyme NADH with *in situ* regeneration of NADH in the presence of a semiconductor with and without any electron mediator and glycerol, (ii) the enzymatic reduction catalysed by formate dehydrogenase, formaldehyde dehydrogenase and alcohol dehydrogenase, by using energy from NADH. Many unmodified and modified semiconductors were studied, and among them ZnS doped with iron or cobalt, surface modified  $\text{TiO}_2$  ( $(\text{NH}_4)_2[\text{CrF}_5(\text{H}_2\text{O})]@\text{TiO}_2$ ,  $\text{rutin}@\text{TiO}_2$ ),  $\text{Cu}_2\text{O}$ ,  $\text{InVO}_4$  were particularly interesting. The possibility to absorb visible light and different mechanisms of sensitization are reported. The mechanism of the overall photocatalytic process consists in the transfer of the photoinduced electrons to the surface reactive sites with a subsequent reduction of the sensitizer which transfers hydrogen and electrons to  $\text{NAD}^+$ .

Part III, **Conclusion** appears well written and it allows the readers to understand the main aims of the work carried out during the thesis along with the findings presented. The comments by the candidate are honest and they reflect often the difficulty to perform the photoactivation of  $\text{CO}_2$ .

As final judgement by the evaluator, I like to say that the thesis is inspired from both the theoretical and methodological point of views. The aims and the methods are clearly described and the candidate represents the ideas, the knowledge and the results with a good theoretical background. The results obtained are worth of mention as they are scientifically relevant.

I am convinced that this thesis meets all the requisites for obtaining the PhD degree.

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