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DELIVERABLE 2.4

Report on the identificaiton of the optimal synthesis methods, combinaton and propportions of materials

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Deliverable D2.4

Report on the identification of the optimal synthesis methods, combination, and proportions of materials

SUN2CHEM

Organisation: CNRS
Main authors: Valérie KELLER

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DELIVERABLE 2.4 – VERSION 1
WORK PACKAGE N° 2

Nature of the deliverable		
R	Document, report (excluding the periodic and final reports)	X
DEM	Demonstrator, pilot, prototype, plan designs	
DEC	Websites, patents filing, press & media actions, videos, etc.	
OTHER	Software, technical diagram, etc.	

Dissemination Level		
PU	Public, fully open, e.g. web	X
CO	Confidential, restricted under conditions set out in Model Grant Agreement	
CI	Classified, information as referred to in Commission Decision 2001/844/EC	

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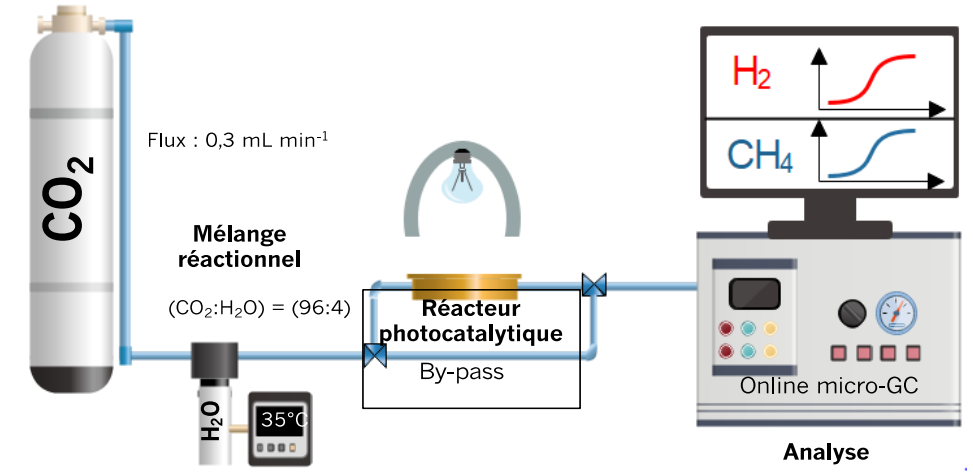
More information on the project can be found at https://sun2chem.eu

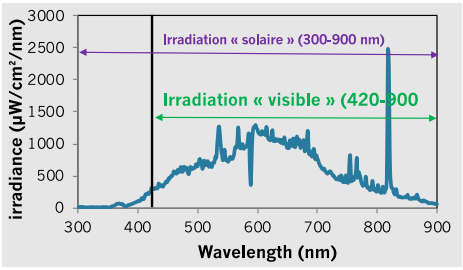
Executive summary

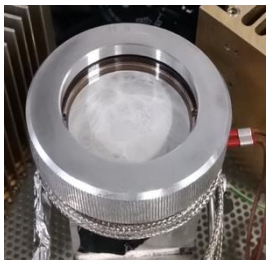
Gas-phase CO_2 photoreduction has been established as one of the key performance indicators to assess photocatalytic behaviour of the different SC1-SC2-(MOFs) and M1-M2/SC1-SC2 or M1-M2/SC-(MOF)s materials in order to identify the optimal synthetic method, combination and proportions of materials. This photocatalytic evaluation is carried out in the frame of Task 2.4 (T_0+9-T_o+18) "Photocatalytic activity evaluation".

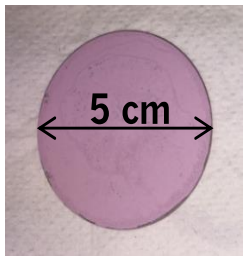
1. Introduction

Gas-phase photocatalytic CO_2 reduction in presence of water vapor has been performed under continuous CO_2 flow in the set-up schematized in Fig. 1, allowing to follow kinetics of CO_2 reduction and products formation under artificial solar-light activation.









Irradiance total : 5100 w.m^{-2}

Irradiance (315-400 nm) : 45,2 w.m^{-2}

- Drop-casting, 25 g m^{-2}

Fig. 1. *(Top) Scheme of the experimental set-up for gas-phase CO_2 photoreduction in presence of water vapor. (Bottom) Emission spectra of the lamp, photocatalytic reactor with drop-casted photocatalytic layer*

2. CO_2 photocatalytic reduction performance

The photocatalytic synthetized composites listed below have been evaluated and compared:

- gC_3N_4-TiO_2 and CeO_2-TiO_2 nanocomposites (CNRS, INSTM)
- $BiVO_4$-TiO_2, BiVO4, CuO, $BIVO_4$-gC_3N_4 (CNRS, ULEI, INAM)
- SC1-SC2/MOF (UiO-66, UiO-66-NH_2, ZiF8, ZIF67) (CNRS)

Only a selection of the photocatalytic results has been given below. **Figs. 2, 3 and 4** compare the impact of the different strategies investigated towards gas-phase CO_2 photoreduction, in terms of CH_4 and H_2 production rate and selectivity.

2.1. Influence of the nature of metal on 1wt.% (Au, Ag, Cu)/TiO_2 activity

A first series of mono-metallic M(1wt.%)/TiO_2 UV-100 system **(Fig. 2-middle)** has been synthetized by impregnation/reduction method at room temperature for M nanoparticles (NPs) deposition using $HAuCl_4$, $AgNO_3$, $Cu(NO_3)_2$ in presence of $NaHB_4$ as chemical reducing agent. The deposition of M NPs increases considerably photocatalytic reduction of CO_2, compared to the bare TiO_2 support. These mono-metallic/TiO_2 photocatalysts mainly yield to the production of H_2 under artificial solar light irradiation, according to reaction conditions described in **Fig. 1**. Amongst the different M NPs studied, Au NPs leads to the highest production rate.

2.2 Influence of g-C_3N_4 content (wt.%) on gC_3N_4-TiO_2 heterojunction activity

The study of the variation of g-C_3N_4content (ranging from 1 to 5wt.%, **Fig. 2-right**) leads to the conclusion that 3wt.% of gC_3N_4 exhibits the best activity and the best selectivity towards CH_4 formation.

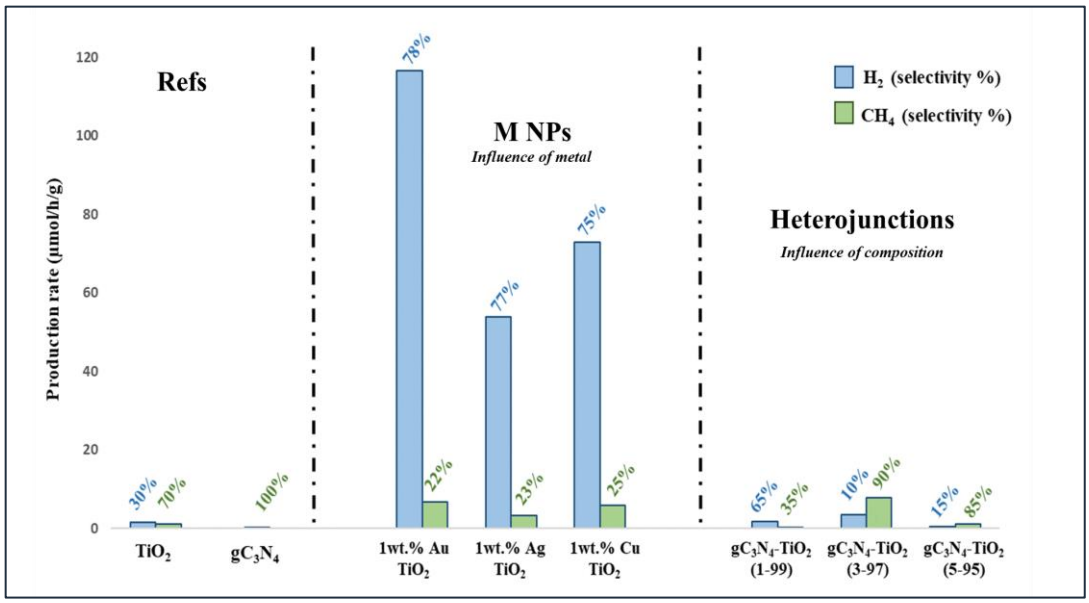


Fig. 2. *CO_2 photoconversion reaction rate and CH_4, H_2 electronic selectivity on* ***(Left)*** *Bare TiO_2-UV100 and g-C_3N_4* photocatalysts. **(Middle)** 1wt.% M(Au, Ag, Cu)/ *TiO_2-UV100* photocatalysts. **(Right)** gC_3N_4-TiO_2 UV-100 heterojunctions.

2.3. Influence of the nature of metal, of the composition and of the deposition method on 1wt.% M1M2(Ag, Cu, Au)/TiO_2 activity

From **Fig. 3-left** showing the impact of Ag-Cu composition (varying from 10-90 to 90-10) on the activity of CO_2 photoreduction of 1wt.% AgCu/TiO_2 UV-100 photocatalysts, it can be observed that $Ag_{10}Cu_{90}$ composition results in the highest activity with the most important selectivity towards H_2 production. One can mention that applying a thermal reduction (TR) at 600°C (**Fig. 3-middle left**) is beneficial for increasing the selectivity towards CH_4 formation, even if the total

reaction rates remain low. The influence of the nature of the 1 wt.% Ag-M2(Au, Cu)/TiO_2 UV-100 (**Fig. 3-middle right**) reveals that the presence of Au in the bi-metallic system results in increasing both the activity and selectivity towards CH_4 production. One can also mention that the tri-metallic AuAgCu system yields the increase in H_2 production. Moreover, deposition of Ag NPs (impregnation/reduction) via thermal reduction of the Ag-based precursor at 600°C, followed by chemical reduction of Cu-based precursor (**Fig. 3-right**) leads to the best yield of CH_4 formation.

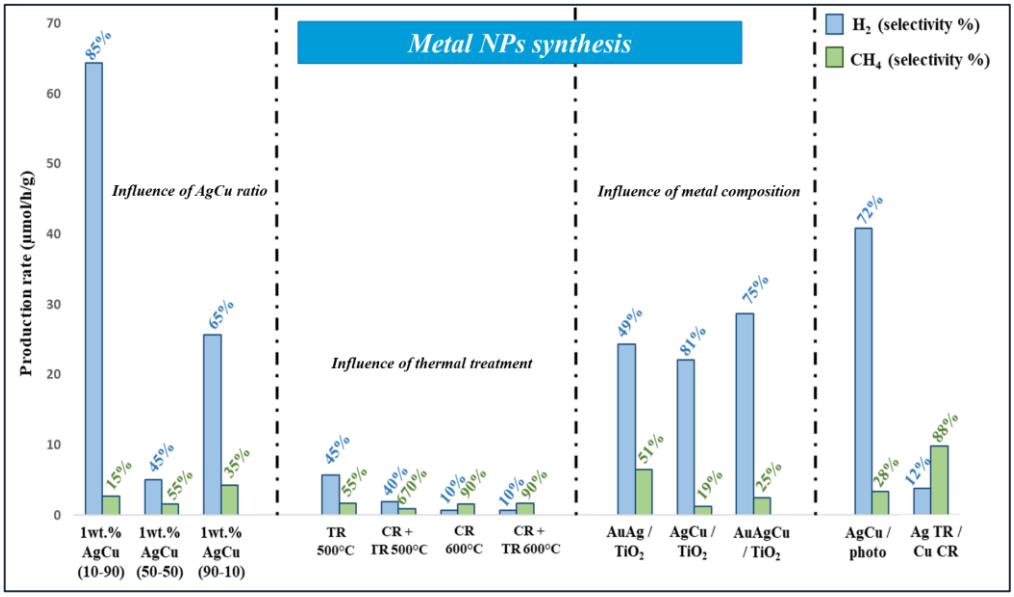


Fig. 3. *CO_2 photoconversion reaction rate and CH_4, H_2 electronic selectivity on* ***(Left)*** *1wt.% Ag(1-x)Cu(x)/ TiO_2-UV100* photocatalysts. **(Middle-left)** 1wt.% Ag(90)Cu(10)/*TiO_2-UV100* photocatalysts, depending on chemical reduction (CR) and/or thermal reduction (TR) post-deposition treatment. **(Middle-right)** 1wt.% AgM2(Au, Cu)/*TiO_2-UV100*. ***(Right)*** *AgCu/TiO_2-UV100 photocatalyst depending on photodeposition or thermal/chemical post-deposition reduction treatment.*

2.4. Influence of the ZIF8-ZIF67-TiO_2 heterojunction

From **Fig. 4-middle**, one can observe that 10 wt.% ZIF-67 yields to almost total selectivity towards CH_4 formation. The nature of ZIF material associated with TiO_2 strongly impacts the reaction rate and H2 production selectivity, accompanied with low CH_4 formation yields.

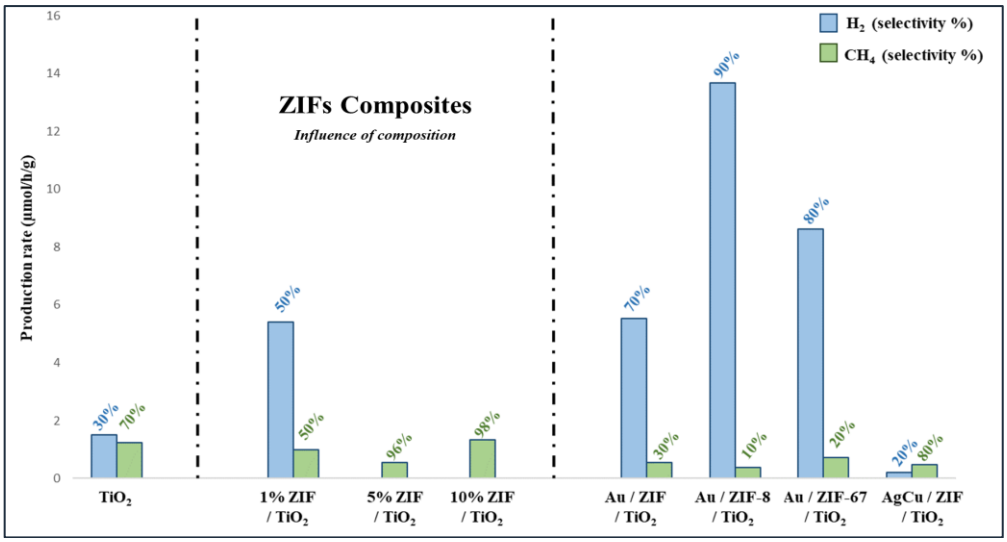


Fig. 4. *CO_2 photoconversion reaction rate and CH_4, H_2 electronic selectivity on* ***(Left)*** *Bare TiO_2-UV100 support*. **(Middle-left)** x(1, 5, 10) wt.% ZIF-67)/*TiO_2-UV100* photocatalysts. d*UV100*. ***(Right)*** *1wt.% Au/ZIF/TiO_2-UV100 photocatalysts.*