Innovative photocatalysts integrated in flow photoreactor systems for direct CO_2 and H_2O conversion into solar fuels

Deliverable 2.1

List of potential 2D porous materials for the simultaneous photocatalytic conversion of CO2 and H2O into syngas

Collaborative project within H2020-LC-SC3-2020-NZE-RES-CC

Grant agreement No. 101022202

Start date of the project: 01/07/2021

Duration of the project: 48 months

WP	WP2	Photocatalytic Flow Reactor (PCFR1) for syngas formation

Dissemination level[1]	PU	Due delivery date	31/06/2022
Nature[2]	R	Actual delivery date	03/08/2022

Lead beneficiary	UBU
Contributing beneficiaries	all

Project partners:

LEITAT – NUIG – PKU – UBU – CHEM – SOCAR – ICIQ – FUNDITEC – UMICH – STRATA

Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU)

[2] Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other

[3] Creation, modification, final version for evaluation, revised version following evaluation, final

Document history

Version	Issue date	Author	Partner	e-mail address	Comments[3]
1	Alfredo Bol Santiago Aparicio Elizabeth Escamilla-Roa	Alfredo Bol Santiago Aparicio Elizabeth Escamilla-Roa	UBU	alf_bol@ubu.es	Alfredo Bol Santiago Aparicio Elizabeth Escamilla-Roa
2	27/06/2022	Oriol Angurell	LEITAT	Oangurell@leitat.org	Modification
3	28/06/2022	Alfredo Bol Santiago Aparicio Elizabeth Escamilla-Roa	UBU		Modification
4	27/07/2022	Alfredo Bol Santiago Aparicio Elizabeth Escamilla-Roa	UBU	alf_bol@ubu.es	Modification
5	03/07/2022	Oriol Angurell	LEITAT	oangurell@leitat.org	Final

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LIST OF ACRONYMS AND ABBREVIATIONS

A&B Manager:	Administrative and Budgetary Manager
CA:	Consortium Agreement
DoA:	Description of Action
EC:	European Commission
GA:	Grant Agreement
E&IM:	Exploitation & Innovation Manager
IPR:	Intellectual Property Rights
MC:	Management Committee
SC:	Scientific Committee
TM:	Technical Manager
S&T:	Scientific and Technical Manager
WP:	Work Package
WPLs:	Work Package Leaders

1. Introduction

The photocatalytic processes have a wide range of applications such as environmental decontamination treatments (water, urban air or soil) or synthesis of new materials of technological interest for solar energy devices. In relation to the greenhouse effect, this method has been applied for carbon dioxide reduction.[1] In photocatalysis, the catalyst produces electrons and holes (not specifically nearby). For this reason, the ability of these materials to promote charge carrier mobility from areas where electrons are generated to these where holes appear is a desired characteristic. From the point of view of conductivity properties, at least, semiconductors character is a key feature.

Upon light irradiation, the photo excitation is produced in energy levels close to the band gap of the material. The band gap is defined as the energy distance from the top of valence band (VB) to the bottom of vacant conduction band (CB). Photoexcitation enables the promotion of ground state electrons in VB to higher energy CB. This phenomenon is also known as band gap photo excitation: the photon absorption energy needs to be equal or greater than the band gap energy. As a result, photo-excited electrons are promoted to higher energy CB states, and, simultaneously, creating a hole in the lower energy VB state[2].

Covalent organic frameworks (COFs) have been designed and successfully applied for environmental applications,[3] gas storage,[4] CO_2 capture,[5] pharmacological applications as drug delivery agents,[6] catalysis[7] and photocatalysis.[8] COFs are 2D or 3D crystalline porous materials formed by organic groups connected through strong covalent bonds.[9,10] The proper selection of suitable building units leads to well-defined and predictable COF crystalline structures, and thus, task-specific COFs

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designed for several applications can be produced.[11] Therefore, this bottom-up approach for COFs design confers this group of materials a large flexibility thus leading to a platform[12] allowing to find suitable solutions for a plethora of technologies and applications.[13,14,15]

2. Objective

In this part of the project, the main objective is the bibliographic search of the potential candidates to develop 2D porous materials for the simultaneous photocatalytic conversion of CO_2 and H_2O into syngas. Once the suitable photocatalytic materials have been determined, 2D COFs will be proposed using theoretical models which will be further used in the experimental process. On the other hand, considering the feedback of the experimental results about the proposed materials, modifications of the COF will be considered.

3. Methodology

Systematic bibliographic search has been used to achieve the main objective.

Density Functional Theory as implemented in Dmol3 code has been used to establish the periodic 2D COF monolayer model and their properties (in vacuum).

4. Results

The case of 2D COFs consider layer stacked materials which show 2D periodicity as well as column structuring, with both factors determining materials porosity.[16] Different linking molecular units have been considered for the development of stable 2D COFs, such as triazine, imine, imide, olefin or oxazole[17] as well as different topologies.[18] A relevant application of 2D COFs considers their use as photocatalysts

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for CO_2 reduction[19,20] and also their combination with different types of nanoparticles such as Au, Ru, TiO_2, etc. Both characteristics allow CO_2 conversion in thermodynamic and kinetics terms[21] to produce solar fuels. Among the building units used for 2D COFs, perylene[22] and porphyrin[23] have been considered among the literature. A 2D COF based on porphyrin as nodes and perylene as linker was studied by Lin et al.[24] analyzing the ultrafast charge carrier mechanism using a combined experimental and theoretical approach. Moreover, COFs containing perylene and porphyrin as building units show suitable thermal stability[25,26]. Nevertheless, with both units several combinations can be used to develop 2D COFs whose conductivity and electronic properties are suitable for photocatalysis. A list of possible perylene based COF candidates are shown in

Table 1, also including their band gap. As it can be observed in the table, these materials have semiconductor character with band gap ranging from 1.313 to 1.55 eV.[27,28]

Diverse molecules can be linked to porphyrin.[29] Moreover, different metalloporphyrins with Ni, Co, Cu and Zn atoms inserted into the centre of the ring

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have been investigated.[30] The effect of the COF adsorption in an Au support has been also studied.[31] In all cases the band gap justifies their semiconductor behaviour.

Table 1. 2D COFs materials: Electronic properties (band gap eV).

Material (COF)	Electronic properties	Material (COF)
Perylene-dimer	1.43	27
Perylene-ZIF-8	1.313, 1.79	28
Pyridine-porphyrin	1.63	29
Amides-porphyrin	1.75	29
Porphyrin	0.99	30
Zn-Porphyrin	1.23	30
M-Porphyrin (M= Ni, Co, Cu, Zn)	semiconductor	30

As reported before, efficient CO_2 conversion is expected using 2D COFs as photocatalysts specifically when different types of nanoparticles are attached to the COF structure. There are several examples in the literature of photocatalytic systems applied for CO_2 reduction. Combinations of COFs with different materials give rise to a set of composite materials that include Ru, Au and C and oxides such as Ag_3PO_4, Cu_2O, WO_3, TiO_2 among others. In Table 2, a representative set of proposed photocatalysts is shown.

Table 2. Proposed materials to CO_2 reduction process.[1]

[30] Thomas, S.; Li, H.; Dasari, R. R.; Evans, A. M.; Castano, I.; Allen, T. G.; Reid, O. G.; Rumbles, G.; Dichtel, W. R.; Gianneschi, N. C.; Marder, S. R.; Coropceanu, V.; Brédas, J.-L. Design and synthesis of two-dimensional covalent

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Table 1: Representative summary of indirect Z-scheme photocatalytic systems towards CO_2 reduction.[b]

Composite	CO_2 reduction catalyst	Electron mediator	O_2 evolution catalyst	Synthesis method	Reaction medium	Light source	Activity ($\mu mol\ g^{-1}\ h^{-1}$)	AQY (%) (wavelength)	Stability	Ref.
$g\text{-}C_3N_4/Bi_4O_5I_2$	$g\text{-}C_3N_4$	I_3^-/I^-	$Bi_4O_5I_2$	simple mixing method	H_2O	300 W xenon lamp ($\lambda > 400$ nm)	CO: 45.6 CH_4: 5.6 H_2: 2.2 O_2: 9	N/A	> 25 h	[85]
[Ru-dpbpy]-$(CuGa)_{1-x}Zn_{2x}S_2$/$BiVO_4$	[Ru-(dpbpy)][9]-$(CuGa)_{1-x}Zn_{2x}S_2$	$[Co(tpy)_2]^{2+/3+}$	$BiVO_4$	simple mixing method	H_2O	500 W xenon lamp ($\lambda > 390$ nm)	CO: 0.103 $CHOO^-$: 0.023 H_2: 0.122	N/A	N/A	[84]
$Ag_3PO_4/g\text{-}C_3N_4$	$g\text{-}C_3N_4$	Ag	Ag_3PO_4	simple mixing method	H_2O	500 W xenon lamp	CO: 39.8 CH_3OH: 8.8 CH_4: 4	N/A	> 24 h	[86]
CdS/RGO/TiO_2	CdS	RGO[68]	TiO_2	kinetics-controlled coating method	H_2O	300 W xenon lamp	CH_4: 0.113	N/A	> 20 h	[87]
$Fe_2V_4O_{13}$/RGO/CdS	$Fe_2V_4O_{13}$	RGO	CdS	chemical vapour deposition method	H_2O	300 W xenon lamp	CH_4: 3.85 O_2: 2.26	N/A	N/A	[88]
$g\text{-}C_3N_4$/BiOBr	$g\text{-}C_3N_4$	Au	BiOBr	deposition–precipitation method	H_2O	300 W xenon lamp ($\lambda > 380$ nm)	CO: 6.67 CH_4: 0.92	N/A	N/A	[89]
WO_3/Au/In_2S_3	In_2S_3	Au	WO_3	deposition and calcination method	H_2O	300 W xenon lamp ($\lambda > 420$ nm)	CH_4: 0.42	N/A	N/A	[90]
TiO_2/RGO/$CuGaS_2$	$CuGaS_2$	RGO	TiO_2	photoreduction and simple mixing method	H_2O	300 W xenon lamp ($\lambda > 330$ nm)	CO: 1.5 H_2: 288 O_2: 112	N/A	N/A	[91]
Bi_2WO_6/Au/CdS	CdS	Au	Bi_2WO_6	bath deposition method	H_2O	300 W xenon lamp	CH_4: 2.02	0.012 (430 nm)	> 8 h	[92]
Bi_2WO_6/RGO/$g\text{-}C_3N_4$	$g\text{-}C_3N_4$	RGO	Bi_2WO_6	two-step hydrothermal method	H_2O	300 W xenon lamp ($\lambda > 420$ nm)	CO: 16 CH_4: 2.5 H_2: 2.25 O_2: 10.5	0.75 (400 nm)	> 20 h	[93]
$BiVO_4$/C/Cu_2O	Cu_2O	C	$BiVO_4$	ionic-layer adsorption reaction method	H_2O	300 W xenon lamp ($\lambda > 420$ nm)	CO: 3.01	N/A	> 20 h	[94]
ZnV_2O_6/RGO/$g\text{-}C_3N_4$	$g\text{-}C_3N_4$	RGO	ZnV_2O_6	solvothermal method	H_2O	35 W xenon lamp	CH_3OH: 542.92	0.283 (450 nm)	> 32 h	[95]
UiO-66-NH_2/RGO/O-ZnO	UiO-66-NH_2	RGO	O-ZnO[94]	solvothermal method	H_2O	300 W xenon lamp ($\lambda > 420$ nm)	CH_3OH: 34.83 HCOOH: 6.41	N/A	> 36 h	[96]
CoZnAl-LDH/RGO/$g\text{-}C_3N_4$	$g\text{-}C_3N_4$	RGO	CoZnAl-LDH	hydrothermal method	H_2O	300 W xenon lamp	CO: 10.11 CH_4: 0.45	0.45 (385 nm)	> 15 h	[97]

The previous experimental and theoretical results suggest that perylene and porphyrin are suitable semiconductor units to build a COF structure.
With all these information, some theoretical models have been developed and reported in the periodic project meetings.
A preliminary 2D COF material based in both units has been designed including Zn atoms at the center of perylene ring to increase the catalytic properties. So, a COF model with 2D perylene-Zn-porphyrin-COF has been stablished. Moreover, different functionalization of perylene units with propanethiol and butanoic acid as an anchoring points the Zn-COF to the reactor wall have been proposed.
Finally, functionalization with the propanethiol has been proposed for stabilization of the catalytic nanoparticles.

5. Conclusions and next steps

The preliminary COF model could be modified and improved, specifically, perylene functionalization, increasing the length of the anchoring thiol group from 2, 3 and 4 C atoms. This can be the beginning of the study of the stacking effect. In the same way, the modeling of the interaction of the Au and RuO_2 nanoparticles on the full COF model (2x2x1 unit cell) will be studied. Also, the study of the effect of different metal atoms at the center of the perylene ring, such as Sn, could be a suitable method to increase semiconductor properties.

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