EXPLORATORY RESEARCH PROJECTS

COD PROIECT: 75/2013

Title of the project:

Self-Assemblies of Nanoparticles of Metal Oxides–Layered Double Hydroxides as Novel Formulations for Photocatalytic Applications

Executive summary of the activities developed inside the research project:

- New knowledge was obtained regarding the self-assemblies procedures of the specific nanocomponents type nanoparticles of metals and/or metal oxides and layered double hydroxides matrices. Further the physical-chemical properties of MeNPs/LDHs and MexOy/LDHs nanorchitectonics were studied. The applications of the novel developed materials in the photocatalytic decomposition of some toxic organic compounds from aqueous solutions, decomposition of CO2 and water splitting processes, were also tested.
- The research activity was developed in a close collaboration with researchers from Chiba University, Japan, (Prof. Yasuo Izumi, group), Antwerp University Belgium, (Prof. Pegie Cool group) and Mexican Institute of Petroleum (Dr. Jaime Valente group).
- 5 young researchers were involved in the project team as Ph.D. students and/or postdocs.

2 Ph.D. thesis were developed and the young researches are co-authors at the publications and the patent that disseminate the project results.

- 11 papers were published in ISI quoted journals (∑F.I.=53.577); these papers are already cited in 47 ISI published papers. 1 patent is under evaluation and 11 presentations were done at international scientific conferences.

Project Leader:

Profesor dr.ing. Gabriela Carja

Brief report of the scientific research activities developed during 2016

2016

OBJECTIVE 4.1. Photocatalytic applications of nanoarchitectural assemblies of MexOy/LDHs and/or Me/LDHAs in processes of "artificial photosynthesis" water decomposition under light action (PWS) and/or decomposition of CO_2 using light energy.

Associated activity. Experimental photocatalytic tests using nanoarchitectural assemblies bassed on MexOy/LDHs si/sau Me/LDHs. Activity developed by international collaboration.

The research activities associated to this objective was developed by international collaboration with Chiba University, Japan (group of Professor Yasuo Izumi) with Instituto Mexicano del Petroleo, Mexico City (Dr. Jaime Sanchez Valente) and University of Antwerpen, Belgium (Professor Pegie Cool). The results obtained by the joined collaboration with the Japanese team regarding the CO_2 reduction using AuNPs/LDHs are already published [1] while the results obtained in the second part of this year by joining collaboration with Mexico and Belgium researchers are just now prepared to be disseminated.

To achieve the aim of this objective we have developed photocatalysts as nanostructures assemblies type AuNPs/layered double hydroxides (LDHs) (Table 1) and AgNPs/LDHs [1]. Gold nanoparticles (AuNPs) have received increasing attentions in catalysis AuNPs supported on solids with high surface area are used for a large variety of catalytic reactions, e.g. photocatalysis, cross coupling, sequential oxidative addition, benzylation of aromatics, oxidative C–C coupling, amination, and nucleophilic addition. The support materials play not only the role of stabilizing AuNPs at different oxidation state ($Au^{\delta+}$, Au^{+}, or Au^{3+}) or controlling their dispersion level (nanoparticle size) but also might act as a buffer for the electron transfer to AuNPs, and thus to reduce the charge-carrier recombination during the photo-responsive processes.

(1) the particle size-dependent photoresponsive characteristics of AuNPs, e.g. surface plasmon resonance (SPR) response, (2) the photo-functionality of the support, and (3) the charge–transfer characteristics from AuNPs to support materials are the recent key issues in designing efficient nano-gold composites as solar-responsive photocatalysts.

Among the numerous materials of large surface area, layered double hydroxides (LDHs) exhibits unique features not found in other solid supports if used as support materials for AuNPs, thus making AuNPs/LDHs composites specific catalysts [2]. The flexibility of the LDHs composition, their semiconducting characteristics, and their high adsorption capacity enables to tune the electronic density at the interface between AuNPs and LDHs. Furthermore, LDHs own a unique self-repairing property to reconstruct its layered structure, after being transformed through calcination into mixtures of metal oxides by the calcination, utilizing its structural "memory effect" to restore original layered structure from mixed oxides. Utilizing the structural memory effect of LDHs, we recently reported a simple, one-step route to fabricate AuNPs directly on Zn–Al–Ce LDHs and Zn–Ga LDHs. This method used the capability of LDH matrix to form self-supported AuNPs on LDHs, by exploiting the property of LDHs to restore its original layered structure in the aqueous solutions of gold salts, e.g. $AuCl_3$ and $Au(CH_3COO)_3$, without using any organic additives as surfactant and/or stabilizer for AuNPs.

Table 1
Characteristics of the tested Au/ZnGaAl-LDH samples [1].

Entry	Sample name	Au						S_{BET} (m^2 g^{-1})[e]	E_g (eV)	Photocatalytic rates (μmol L^{-1} h^{-1})
		Contents (wt%)	Au^0 : Au^{3+}	Particle size distribution (nm)	Mean size (nm)		Exposed Au^0 (μmol g_{cat}^{-1}) [d]			
				TEM	TEM	EXAFS				
a	ZnGaAl-LDH	——	——	——	——	——	——	97	5.7	25
b	Au/Zn_2Al-Rec-1[c]	4.8	0 : 100	1.1–13.6	4.7 (±2.4)		0	81	3.1	125
c	Au/Zn_2Al-Rec-2	16	0 : 100	1.8–18.0	4.9 (±2.1)		0	59	2.5	47
d	Au/Zn_2Al-Rec-3-Light[a,c]	4.8	65 : 35	1.9–25.4	8.5 (±3.6)	2.5	27	79	2.6	199
e	Au/Zn_2Al-Imp-$NaBH_4$[c]	2.2	85 : 15	2.2–7.7	4.1 (±1.0)	4.8	31	54	——[f]	42
f	Au/Zn_2Al-Imp-Lysine[c]	1.9	100 : 0	3.9–14.0	7.3 (±2.0)	5.3	19	67	——[f]	43
g	Au/Zn_2Al-Light[c]	4.8						-	——[f]	68

[a] Irradiated by Solar light simulator during LDH the reconstruction for 20 min for Au/Zn_2Al-Rec-1.
[b] Evaluated from XANES edge jump values.
[c] For Au/Zn_2Al-Rec-1, Au/ZnAl-Rec-3, Au/ZnAl-Imp-$NaBH_4$, Au/Zn_2Al-Imp-Lysine, and Au/Zn_2Al-Light the amount of gold introduced during the sample preparation compared to the amount of support material was the same (5:100).
[d] Estimated based on Au content in catalyst, Au^0:Au^{3+} ratio, mean Au size by TEM, and the correlation between dispersion and diameter of fcc cubo-octahedron particles [41].
[e] BET surface area evaluated for samples after photocatalytic phenol decomposition tests for 5 h.
[f] It was difficult to determine the absorption edge due to the overlap of broad SPR peaks.

The relatively wide band gap was advantageous to set the conduction band (CB) minimum enough negative for these LDHs compared to the reduction reaction potentials of

1. Photolysis of water to yield hydrogen fuel or photocatalytic water splitting (PWS) described as:

(1) $H_2O \longrightarrow H_2 + 1/2\ O_2$, ΔG^0 (298 K) =+237 kJ/mol;

2. Photocatalytic reduction of CO_2 yielding single-carbon molecules such as CO, CH_4, CH_3OH, formaldehyde and formic acid.

(2) $CO_2 + H_2O \longrightarrow CH_3OH + 3/2O_2$, ΔG^0 (298 K) =+698.7 kJ/mol;

versus standard hydrogen electrode (SHE). It is essential to utilize visible light, 97% of the spectrum of solar radiation [2], while utilizing the enough negative potential of CB minimum.

The nanosized characteristics of the self-assemblies Au/LDHs were studied by HRTEM and some characteristics are described in Figure 1 [1]. As-synthesized and preheated samples of LDHs were tested for the photocatalytic conversion of CO_2 and H_2O splitting. The tests were conducted in a closed circulating system (171 mL) equipped with a photoreaction quartz cell that had a flat bottom (23.8 cm^2). 100 mg of the LDH catalyst was uniformly spread in the photoreaction cell and was evacuated by rotary and diffusion pumps (10^{-6} Pa) at 290 K for 2 h until the desorbed gas was detected by an online gas chromatograph (GC). 2.3 kPa of CO_2 (0.177 mmol) and 21.7 kPa of H_2 (1.67 mmol) were introduced to both intact and pretreated LDH photocatalysts [1]. The photocatalyst was then irradiated with UV–visible light from the 500-W xenon arc lamp (Ushio, Model UI-502Q) from downward through the flat bottom of the quartz reactor for 5 h. The distance between the bottom of the reactor and the lamp house exit window was set to 20 mm. The temperature was within the range 305–313 K at the catalyst position during the illumination for 5 h. Products and reactants were analyzed using packed columns of molecular sieve 13X-S and polyethylene glycol (PEG-6000) supported on Flusin P (GL Sciences) set in the online GC equipped with a thermal conductivity detector (Shimadzu, Model GC-8A).The special transfer of electrons between the nanoparticles of Me or MexOy (e.g. AuNPs and/or AgNPs or silver oxides NPs) to the matrices of LDHs were studied by EXAFS analysis. Figure 2 [1] presents the EXAFs spectra of some catalytic samples before being tested for CO_2 reduction under solar irradiation.

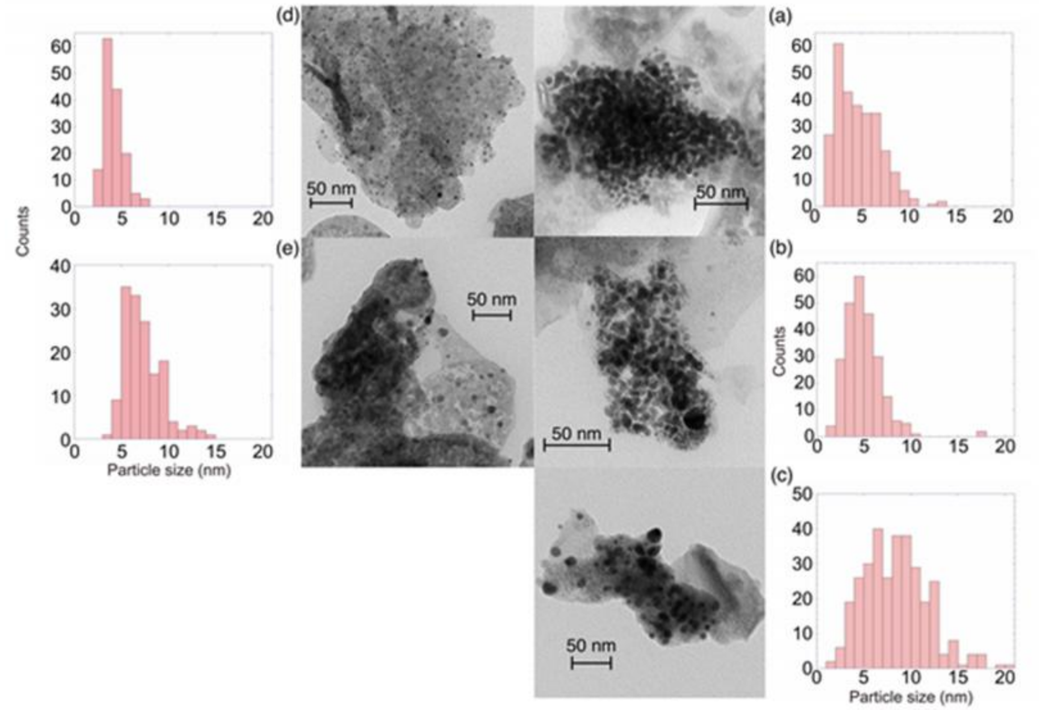


Figure 1. TEM images and analysis for Au/Zn_2Al-Rec-1 (a), Au/Zn_2Al-Rec-2 (b), Au/Zn_2Al-Rec-3-Light (c), Au/Zn_2Al-Imp-$NaBH_4$ (d), and Au/Zn_2Al-Imp-Lysine (e).

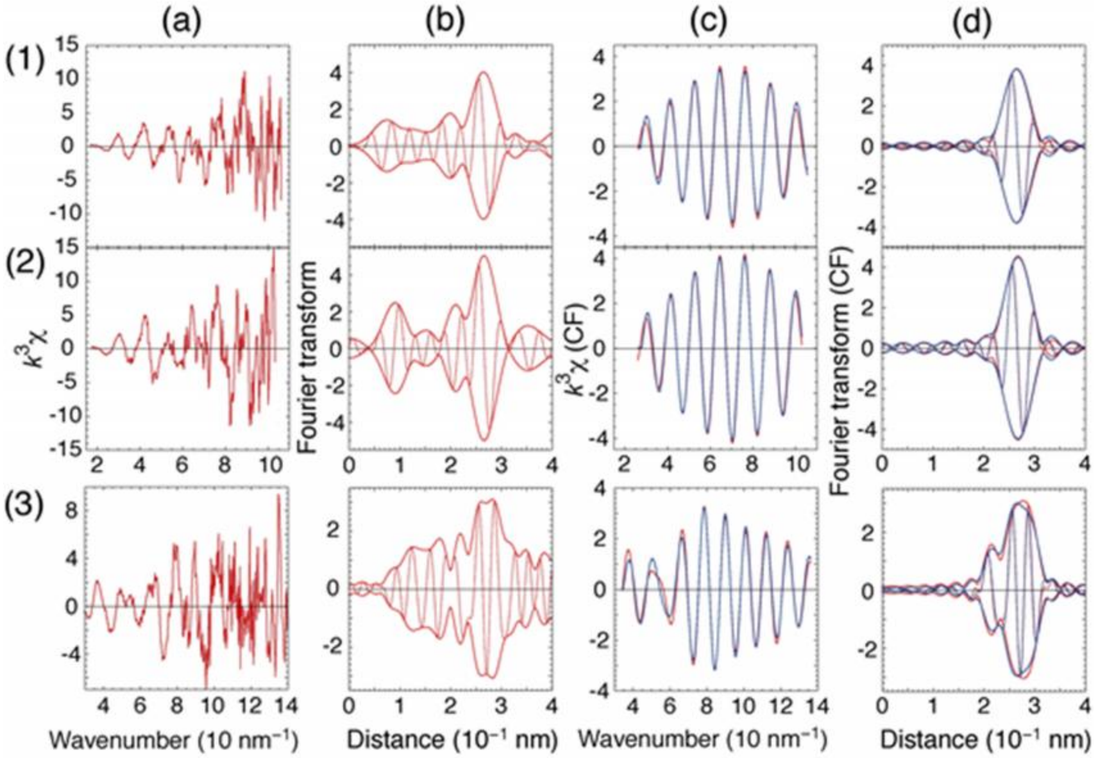


Figure 2. Ag K-edge EXAFS for Ag/Zn_3Ga|CO_3-IE373-15 (1) and Ag/Zn_3Ga|CO_3-IE373-180 (2) and Au K-edge EXAFS for Au/Zn_3Ga|CO_3-IE (3). k^3-weighted EXAFS oscillation (a), its associated Fourier transform (b), and best-fit results in k-space (c) and R-space (d).

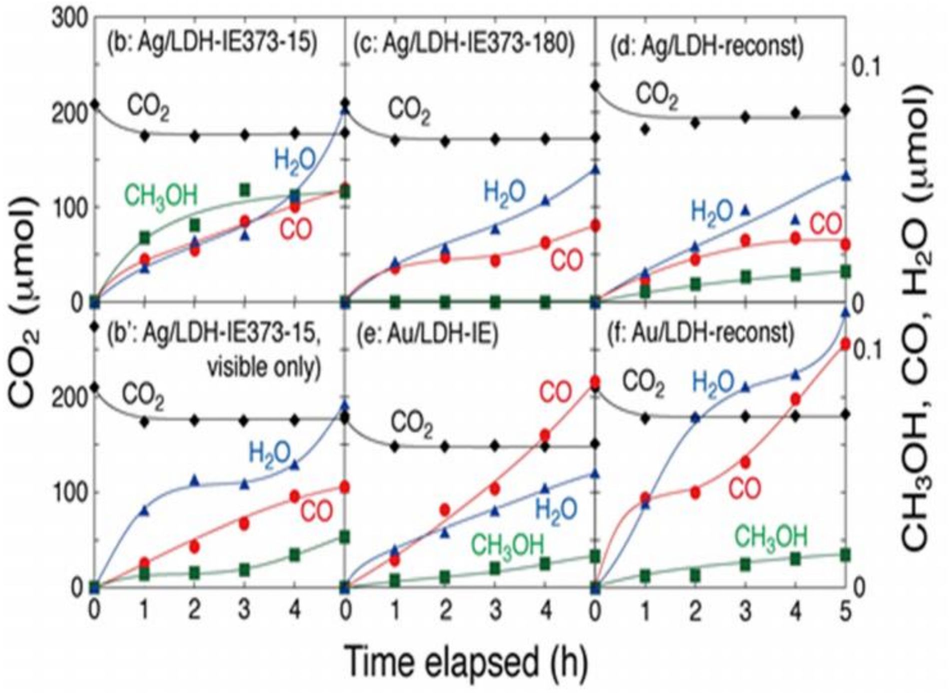
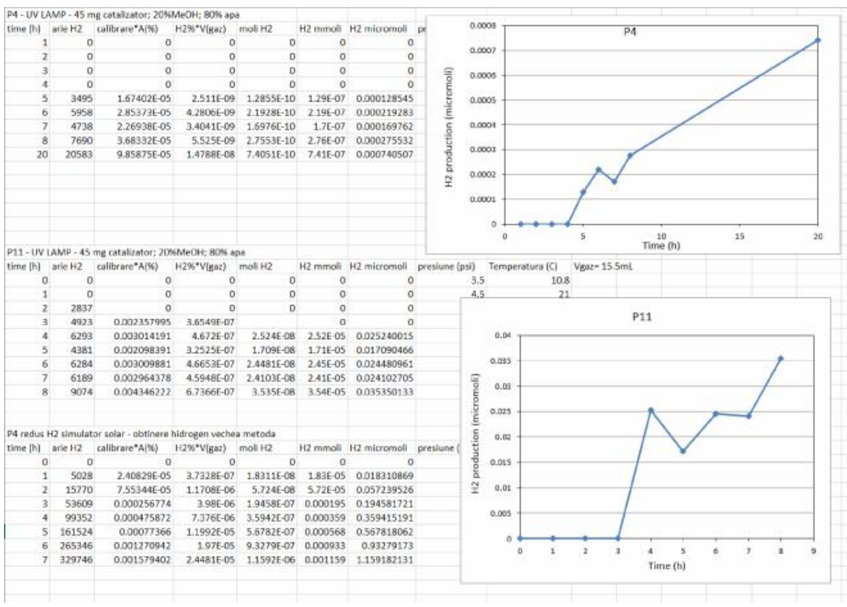


Figure 3 [2]. Time course of photocatalytic tests under CO_2 (2.3 kPa) and H_2 (21.7 kPa) using UV-visible light and Ag/Zn_3Ga|CO_3-IE373-15 (b), Ag/Zn_3Ga|CO_3-IE373-180 (c), Ag/Zn_3Ga|CO_3-reconst (d), Au/Zn_3Ga|CO_3-IE (e), and Au/Zn_3Ga|CO_3-reconst (f). Time course of comparison tests under CO_2 (2.3 kPa) and H_2 (21.7 kPa) using visible light (λ > 420 nm) and Ag/Zn_3Ga|CO_3-IE373-15 (b'). CO_2 (◆; diamond), H_2O (▲; triangle), CH_3OH (▪; square), and CO (●; circle).

Some of the preliminary results regarding water splitting obtained in a joint collaboration with the group of Dr. Jaime Valente from Instituto Mexicano del Petroleo. The manuscript that include these resukts are now in work to be prepared.



P4 - UV LAMP - 45 mg catalizator; 20%MeOH; 80% apa

time (h)	arie H2	calibrare*A(%)	H2%*V(gaz)	moli H2	H2 mmoli	H2 micromoli
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	3495	1.67402E-05	2.511E-09	1.2855E-10	1.29E-07	0.000128545
6	5958	2.85373E-05	4.2806E-09	2.1928E-10	2.19E-07	0.000219283
7	4738	2.26938E-05	3.4041E-09	1.6976E-10	1.7E-07	0.000169762
8	7690	3.68332E-05	5.525E-09	2.7553E-10	2.76E-07	0.000275532
20	20583	9.85875E-05	1.4788E-08	7.4051E-10	7.41E-07	0.000740507

P11 - UV LAMP - 45 mg catalizator; 20%MeOH; 80% apa

time (h)	arie H2	calibrare*A(%)	H2%*V(gaz)	moli H2	H2 mmoli	H2 micromoli	presiune (psi)	Temperatura (C)	Vgaz= 15.5mL
0	0	0	0	0	0	0	3.5	10.8	
1	0	0	0	0	0	0	4.5	21	
2	2837	0	0	0	0	0			
3	4923	0.002357995	3.6549E-07		0	0			
4	6293	0.003014191	4.672E-07	2.524E-08	2.52E-05	0.025240015			
5	4381	0.002098391	3.2525E-07	1.709E-08	1.71E-05	0.017090466			
6	6284	0.003009881	4.6653E-07	2.4481E-08	2.45E-05	0.024480961			
7	6189	0.002964378	4.5948E-07	2.4103E-08	2.41E-05	0.024102705			
8	9074	0.004346222	6.7366E-07	3.535E-08	3.54E-05	0.035350133			

P4 redus H2 simulator solar - obtinere hidrogen vechea metoda

time (h)	arie H2	calibrare*A(%)	H2%*V(gaz)	moli H2	H2 mmoli	H2 micromoli	presiune (
0	0	0	0	0	0	0	
1	5028	2.40829E-05	3.7328E-07	1.8311E-08	1.83E-05	0.018310869	
2	15770	7.55344E-05	1.1708E-06	5.724E-08	5.72E-05	0.057239526	
3	53609	0.000256774	3.98E-06	1.9458E-07	0.000195	0.194581721	
4	99352	0.000475872	7.376E-06	3.5942E-07	0.000359	0.359415191	
5	161524	0.00077366	1.1992E-05	5.6782E-07	0.000568	0.567818062	
6	265346	0.001270942	1.97E-05	9.3279E-07	0.000933	0.93279173	
7	329746	0.001579402	2.4481E-05	1.1592E-06	0.001159	1.159182131	

OBJECTIVE 4.2: Analysis of the obtained results; Strategies for developing at international level the research subject of the project.

Activity 4.2.1. Results analysis, patent proposal. Research proposal for continuing the research activities.

Inside this project, we developed co-joined research activities at international level with:

1. Japanese researchers from Chiba University (Professor Yasuo Izumi, Chiba University):

The conjoint results were disseminated as:

Applied Catalysis B: Environmental (Elsevier Press) 199 (2016) 260–271. (I.F. 8.328)

Harnessing self-supported Au nanoparticles on layered double hydroxides comprising Zn and Al for enhanced phenol decomposition under solar light; G. Mikami, E. F. Grosu, S. Kawamura, Y. Yoshida, G. Carja, Y. Izumi; Florentina Grosu is, as a Ph.D. student, a young researcher member of the project team.

Applied Catalysis A (Elsevier Press) 504, pp. 238-247, 2015 (I.F. 4.012) Tailoring assemblies of plasmonic silver/gold and zinc-gallium layered double hydroxides for photocatalytic conversion of carbon dioxide using UV-visible light; Kawamura, S., Puscasu, M.C. (young researcher, postdoc, member of the project team), Yoshida, Y., Izumi, Y., Carja, G. (project leader).

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 70 (2015), No. 5, pp. 841-852 L (I.F. 1.89) Photocatalytic conversion of carbon dioxide using zn–cu–ga layered double hydroxides assembled with cu phthalocyanine: Cu in contact with gaseous reactant is needed for methanol generation; Kawamura, S., Ahmed, N., Carja, G (project leader), Izumi, Y.

2. Belgian researchers from Antwerp University, Belgium (Professor Pegie Cool)

Catalysis Today (Elsevier Press) vol. 252, pp. 7-13, 2015 (I.F. 4.312), Photo-responsive behavior of γ-Fe2O3 NPs embedded into ZnAlFe-LDH matrices and their catalytic efficiency in wastewater remediation; EM Seftel, M Puscasu (young researcher, postdoc, member of the project team), M. Mertens, P Cool, G. Carja (project leader).

Applied Catalysis B: Environmental, 164 (2015) 251 –260, (I.F. 8.328), (ELSEVIER PRESS); Fabrication of CeO2/LDHs self-assemblies with enhanced photocatalytic performance: a case study on ZnSn-LDH matrix; E. M. Seftel (researcher Antwerp University, M. C. Puscasu (postdoc, member of the project team), M. Mertens (researcher VITO Institute, Belgium), P. Cool (professor Antwerp University, Belgium) G. Carja (professor, project leader).

Applied Catalysis B: Environmental, 150– 151 (2014) 157– 166 (I.F. 8.328), (ELSEVIER PRESS); Assemblies of nanoparticles of CeO_2–ZnTi-LDHs and their derived mixed oxides as novel photocatalytic systems for phenol degradation;

E. M. Seftel (Postdoc Antwerp University, Belgium), M. C. Puscasu (young researcher, Ph.D. Student), M. Mertens (researcher VITO Institute Belgium), P. Cool (professor Antwerp University, Belgium), G. Carja (professor, project leader).

3. Mexican Researchers from Instituto Mexican of Petroleo (group of Professor Jaime Sanchez Valente); this cooperation has just begun in May this year. 28 catalytic samples were characterized and tested in water splitting process and just now the results have analyzed and have prepared for dissemination.

- PATENT PROPOSAL: OSIM registration number A/00637 din 14.09.2016

Title: Assemblies of nanoparticles of cobalt oxides and layered double hydroxides for applications in captions and photocatalytic reductions of CO_2 from humid gases.

Authors: Carja Gabriela (project leader) Darie Mihaela (Ph. D. student, young researcher, member of the research team), Mureseanu Mihaela (experienced researcher of the research team). The research described in this patent was presented at 2 international conferences. Hence, this patent proposal has been already awarded the gold medal at the International Fairs of Innovation, INVENT-INVEST, September 2016, Iasi, Romania.

- Research proposal; a new research proposal was proposed and this is now in the second phase of the competition.
- Other results of the project disseminated in 2016:

-1 manuscript, under review, submitted to Applied Clay Science (Elsevier Press Impact Factor 2015 2.586)

Authors: Mihaela Mureseanu (member of the project team), Alina Vieru, Radu-Dorin Andrei, Mihaela Darie (member ogf the project team), Gabriela Carja (member of the project team).

-2 manuscripts under preparation.

Dissemination through participation at international scientific meetings_

Oral presentations:

-G. Carja, M. Mureseanu, E. F. Grosu, L. Dartu, V. Parvulescu Self-supported nanoparticles of gallium and indium on ZnMeLDHs (Me:Al, Ga) for efficient photocatalysis under solar irradiation ROMCAT 2016, Timisoara 6-8 iunie 2016. This thematic was developed in collaboration with The Institute of Physical Chemistry of the Romanian Academy, I. G. Murgulescu, Bucuresti.

-G Carja, E. F. Grosu, C. Petrareanu, N. Nichita, Antiviral effect against hepatitis B virus of nanocomposites self-assemblies of plasmonic gold/layered double hydroxides 12th International Conference on Colloid and Surface Chemistry ICCSC 2016, Petru Poni Institute of Macromolecular Chemistry, Iasi, May 2016.

-G. Carja, Identification of key research and innovation topics in materials science, microsensors for engineering and medical applications and biosensors; Strategic Workshop inside FP7 Project NANOSENS Iasi, 19-21 September 2016: Presentation of the research patented as OSIM A/00637, title: Assemblies of nanoparticles of cobalt oxides and layered double hydroxides for applications in photocatalytic reductions of CO2.

-M. Darie, M. Vizitiu, S. Dranca, G. Carja Plasmonic nanoparticles - layered double hydroxides nanocomposites for efficient UV and solar-driven photocatalysis 3rd International Conference on Chemical Engineering Romania, Iași, 9 – 11 November 2016.

-Carja G., Darie M., Mureseanu M., Presentation of the patent: Assemblies of nanoparticles of cobalt oxides and layered double hydroxides for applications in captions and photocatalytic reductions of CO2 from humid gases. International Fair of Inventions INVENT-INVEST September, Iasi Romania, 2016

Posters:

E.F. Grosu, E.M Seftel, P. Cool, G. Carja Diclofenac removal from aqueous solution using ZnAlLDH and ZnCoAlLDH and their derived mixed oxides as highly efficient photocatalysts under solar irradiation, International Conference on Chemical Engineering Romania, Iași, 9-11 November 2016.

- E-MRS Spring Meeting, Symposium A Hybrid Materials: from laboratory to market: Lille France, 1-5 May 2016

G. Carja M. Mureseanu, E. F. Grosu, L. Dartu, V. Parvulescu, Self-supported nanoparticles of gallium and indium on ZnMeLDHs (Me:Al, Ga) for efficient photocatalysis under solar irradiation