Final Scientific Report for contract nr. 36 / 2018

Cod: PN-III-P1-1.1-PD-2016-1718

for the period May 2018 - April 2020

Hybrid composites based on doped ZnO micro-/nanoparticles for enhanced UV and visible light photocatalysis (PhotoCAT)

Project director: **Dr. Viorica-Elena Podasca**

Mentor: **Dr. habil Mariana-Dana Damaceanu**

- 2020 -

The project was structured in **3 stages** based on the following activities and sub-activities:

Stage 1

Activity 1.1. Synthesis of ZnO particles with different shapes and sizes

- synthesis of ZnO starting from zinc acetate, zinc nitrate or other zinc salts;
- variation of shapes and sizes by modifying the synthesis protocol: time, temperature, solvent etc.

Activity 1.2. Doping of ZnO particles with metals

- doping ZnO with Sn;
- doping with Ag;
- doping with Cu or other metals.

Activity 1.3. Characterization of the obtained particles

- particle characterization by ESEM/EDX, XRD techniques;
- characterization of particles by TEM or Raman microscopy to evaluate/confirm their size, shape and purity.

Activity 1.4. Synthesis of (meth)acrylic monomers

- synthesis of monomers starting from 2-isocyanatoethyl methacrylate;
- synthesis of (meth)acrylic monomers by conventional addition reaction or by acylation;
- other monomers will be obtained from commercial sources.

Stage 2

Activity 2.1. Synthesis of monomers and hybrid composite polymer films by photopolymerization technique

- synthesis of monomers and films by photopolymerization technique;
- characterization of the synthesized materials by FT-IR, ^{1}H NMR, ^{13}C NMR and other techniques.

Activity 2.2. Incorporation of ZnO micro-/nanoparticles into the polymeric matrix

- incorporation of simple ZnO or doped ZnO into organic matrices;
- *in situ* generation of micro-/nanoparticles during the photopolymerization reaction.

Activity 2.3. Characterization of the obtained polymer films

- characterization of the obtained materials by TEM, ESEM / EDX, as well as other characterization methods, to identify their specific characteristics.

Activity 2.4. Photocatalytic studies

- studies of photocatalytic degradation of an organic dye under visible irradiation in the presence of hybrid films;
- monitoring the changes in the UV-Vis absorption spectra of the dye solution as a function of irradiation time.

Stage 3

Activity 3.1. Photocatalysis studies

- performing degradation studies of some dyes under visible light irradiation in the presence of hybrid polymer films used as catalysts;
- monitoring the evolution over time of the specific dye absorption band using UV spectroscopy;
- evaluation of the catalyst efficiency in the photodegradation of dyes by complementary techniques such as ^{1}H NMR.

Activity 3.2. Evaluating the performance of the photocatalysts and optimizing their efficiency

- selecting the catalysts with the highest performances and perfecting their preparation;
- evaluation of the photocatalysis process compared to literature studies;
- critical analysis of the obtained results and performance evaluation in order to create new research directions.

Presentation of the project

The present project fully addresses the main objectives of Environment & Climate Action area of HORIZON 2020, which aims at achieving of resource, water efficient and climate change resilient economy and society, protecting and sustainable managing natural resources and ecosystems and ensuring a long-term supply and use of raw materials, in order to meet the needs of a growing global population within the sustainable limits of the planet's natural resources and eco-systems. It is expected that climate-related expenditure should exceed 35% of the overall Horizon 2020 budget, including mutually compatible measures improving resource efficiency. The world human population has substantially increased since the 15th century and, consequently, this yielded in the large-scale development of the agriculture and the associated chemical industry, increase in resource consumption. Along with the accelerated industrial revolution recorded in the last two centuries, the societal evolution lead to serious and diverse environmental problems, such as rising levels of atmospheric carbon dioxide, global warming, soil and water pollution.

Chemical pollution of water is one of the major environmental problems in today's world, since polluted water poses a threat to wildlife, as well as to human health and welfare, given that it hinders the sustainable development of both society and economy. Different contaminants are released into water bodies along with the rapid industrialization. Dye effluent from textile industry is one of the most important sources of environmental pollution. Approximately 10,000 different dyes and pigments (annual production of almost 7×10^5 tons) are utilized by textile industry. These dyes absorb the sunlight and reduce the photosynthetic capability of aquatic plants and microorganism, but, on the other hand, many of these dyes are toxic, carcinogenic, and mutagenic. In recent years, treatment of waste water by physical and chemical methods has been the main focus in many studies. Advance Oxidation Processes (AOPs) have been effectively used to completely mineralize dyes present in textile waste water. Among these oxidation methods, photochemical catalysis appears as an emerging destructive technology leading to the total mineralization of many organic pollutants. A photocatalyst is a solid that can promote chemical reactions in the presence of light and is not consumed in the overall reaction. There is a list of demands that a photocatalyst should fulfil in order to be considered suitable for such application: it has to be able to utilize visible and/or UV light, photoactive, chemically and biologically inert, stable under irradiation, and non-toxic.

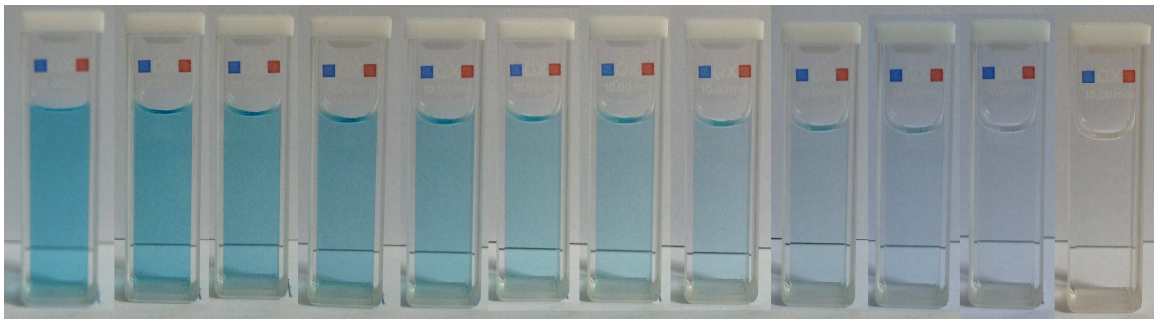
Several studies often highlighted the performance of ZnO in the degradation of some organic compounds, such as Remazol Brilliant Blue R, Remazol Black B, Reactive Blue 19 etc. In addition, ZnO has more functions than TiO_2 and the through research showed that ZnO can also be used in acidic or alkaline conditions.

The main objectives of the **PhotoCAT project** were the synthesis and characterization of ZnO micro-/nanoparticles, photopolymerizable monomers, new photopolymers incorporating ZnO micro-/nanoparticles, as well as the investigation of the obtained materials by different methods, with emphasis on evaluating their performance in photocatalytic experiments. To achieve these objectives, ZnO particle were synthesized using zinc acetate, zinc nitrate or other zinc salts as raw materials. The shape and size of the synthesized particles were varied, by modifying the synthesis protocol and by doping ZnO with metals, such as Sn, Cu, Ag or others. The evaluation/confirmation of the size, shape and purity of the obtained particles was carried out by means of ESEM / EDX, SAXS, XRD, TEM or Raman microscopy techniques. Also, new monomers and photopolymers were prepared incorporating these ZnO micro-/nanoparticles, also conducting an extensive study on their physico-chemical properties. The obtained hybrid materials were subjected to photocatalysis studies in the presence of organic dyes, evaluating their photocatalytic performance, with emphasis on optimizing their efficiency.

Conclusions

- The synthesis of ZnO micro-/nanoparticles of various shapes and sizes have been successfully performed.
- A method has been developed for doping ZnO particles with different metals, in this case with Sn, Ag and Cu.
- Simple and doped ZnO particles were characterized by ESEM/EDX, XRD, UV-vis spectroscopy, TEM and Raman microscopy to assess/confirm their size, shape and purity.
- Numerous (meth)acrylic monomers were synthesized and their structure was confirmed by ^{1}H NMR and FTIR spectral techniques.
- A series of hybrid composites using a combination of monomers together with metal particles were also synthesized by photopolymerization technique.

- The FTIR measurements indicated a good photoreactivity of the monomers in the photopolymerization process, even if it occurred in the absence or in the presence of metal particles.
- The incorporation and homogeneous distribution of the particles in the organic phase was fully confirmed by ESEM/EDX and TEM measurements.
- The photocatalytic activity tests highlighted that the prepared cube-shaped ZnO-SnO_2-based composites are very effective in treating wastewater containing dyes, having a real potential for practical applications.



- In photodegradation tests in ambient conditions and by irradiation with visible light, the 5% ZnO-Ag1 composite film had a better efficiency than the films containing only ZnO used as photocatalysts.
- The features highlighted in this report recommend the use of such hybrid composite films in the photodegradation of organic dyes and also offer a new perspective in the development of high efficiency photocatalysts.

Results

The scientific results resulting from the studies carried out within the PhotoCat project were disseminated in the form of 2 ISI articles, 2 oral presentations and 4 posters presented at national / international scientific events, as follows:

Articles

1. Photopolymerized Films with ZnO and Doped ZnO Particles Used as Efficient Photocatalysts in Malachite Green Dye Decomposition, Viorica-Elena Podasca, Mariana-Dana Damaceanu, Appl. Sci. 2020, 10(6), 1954; https://doi.org/10.3390/app10061954.

2. Fabrication of ZnO doped Ag composites for highly efficient visible-light photocatalysis in the degradation of an organic dye, Viorica-Elena Podasca, Mariana-Dana Damaceanu, Particles (2020).

Oral presentation

1. Synthesis of hybrid composites containing ZnO doped particules for photocatalysis applications, Viorica-Elena Podasca, Mariana-Dana Damaceanu, a XXXV-a Conferinta Nationala de Chimie, 02-05 octombrie 2018, Caciulata, Valcea, Romania.

2. Photocatalytic degradation of Malachite green dye under visible light using polymeric films containing synthesized ZnO and ZnO-SnO_2 particles, Viorica-Elena Podasca, "Alexandru Ioan Cuza" University Days, Faculty of Chemistry Conference IasiCHEM, 25-26 October 2018, Iasi, Romania.

Poster

1. Synthesis of new materials containing ZnO doped particles for purification of waste waters, Viorica-Elena Podasca, Mariana-Dana Damaceanu, 1st International conference on Nanotechnologies and Bionanoscience (NanoBio 2018), 24-28 September 2018. Heraklion City, Crete, Greece.

2. Preparation and photocatalytic properties of polymer hybrid composites containing ZnO doped Ag particles, Viorica-Elena Podasca, Mariana-Dana Damaceanu, Tinca Buruiana, 21st Romanian International Conference on Chemistry and Chemical Engineering (RICCCE21), September 4-7, 2019, Constanta-Mamaia, Romania.

3. Sinteza si activitatea fotocatalitica a unor compozite hibride continand ZnO dopat, Viorica-Elena Podasca, Mariana-Dana Damaceanu, Tinca Buruiana, Zilele Academice Iesene a XXVII-a Sesiune de Comunicari Stiintifice a Institutului de Chimie Macromoleculara „Petru Poni" Iasi, Progrese in stiinta compusilor organici si macromoleculari (ZAI 2019), 2-4 octombrie 2019, Iasi, Romania.

4. Synthesis of polymer composites containing ZnO doped Ag particles for photocatalytic degradation of organic dyes, Viorica-Elena Podasca, Mariana-Dana Damaceanu, Tinca Buruiana, International Conference "Achievements and Perspectives of Modern Chemistry", October 9-11, 2019, Chisinau, Republic of Moldova.