Noble-metal/TiO_2-based ternary photocatalysts: from optimisation to environmental and energetic applications

Brief introduction – hypotheses, aim of the project

Removing organic pollutants from water using an energy-saving method with a possible "by-product" as hydrogen is a real challenge with promising results. Even if a relatively large number of publications are appearing regarding these aspects, a relatively small number of publications are trying to combine the "benefits" from more than one noble metal in a photocatalytically active composite. However, it was already shown that changing the noble metal component in the composite can "fine-tune" the applicability spectra of the catalyst toward different organic pollutants. Considering these aspects, it's more than likely that by "playing" with the Pt and Au ratio of the composite, new materials can be obtained with increased and/or optimised photocatalytic efficiencies.

General remarks regarding the composites

The selected synthesis strategy contained two approaches, the in situ reduction and impregnation methods, adapted from and described by Kmetykó et al. (Materials, 2014, 7, 7615-7633). In all cases, the total noble metal content was 1 wt. % In the case of in situ reduction TiO_2 (commercial Evonik Aeroxide P25-abbreviated as P25, Aldrich anatase-AA, and Aldrich rutile-AR) was added before the synthesis of the noble metals, while in the case of impregnation titania was added after the synthesis of the Au and Pt.

Regarding nomenclature of the composites (for better understandability), it has to be mentioned that they were defined as follows: the abbreviation of the titania photocatalyst + "_is" for the samples obtained by in situ reductions, or "_im" for the samples made with impregnation. This was completed with: "Au/Pt" when Au was reduced before Pt; "Pt/Au" when Pt was reduced before Au; or "Au&Pt" when both noble metals were obtained simultaneously. A relevant example is the case of AA_im_Au/Pt, which was obtained from Aldrich Anatase (AA), Au then Pt was reduced (Au/Pt) using the impregnation method (im).

Morpho-structural and optical properties

According to the XRD patterns, the composition of the semiconductors remained unchanged during/after the deposition of noble metal nanoparticles. It must be mentioned that the noble metal nanoparticles were not detectible, as their concentration was lower than the detection limit of the instrumentation, and some of the most intensive diffraction peaks (e.g. for at 38º (2θº) for Au) were covered by the triplet signal of anatase in the same region.

The light-absorption properties of the composites were characterised by DRS (Figure 1). In the first instance, in the DRS spectra of the composites, the reflectance values in the visible light region were higher for unmodified commercial catalysts than for the composites (while the commercial materials were white, the composites' colour varied from grey to purple, giving reflectance values between ≈40-60 % at visible light wavelengths). As it could be observed, the deposition of noble metal nanoparticles induced significant changes in the optical properties of some commercial titania-based photocatalysts, which were quantified by calculating the band-gap energies using the Kubelka-Munk equation. It was also observed, that all composites have smaller band-gap energies compared to their base-catalyst.

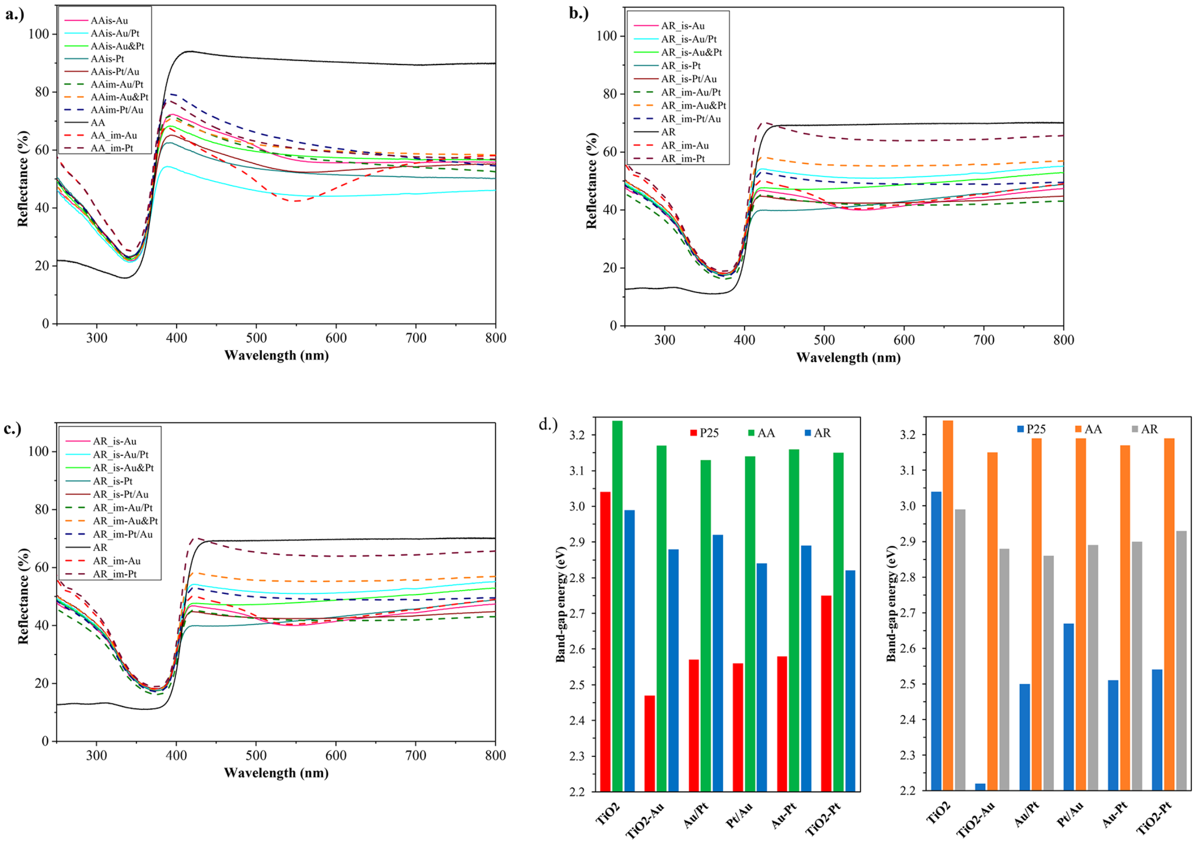

Figure 1: Influence of the noble metals on the optical properties of three commercial titania (a - AA; b - AR; c - P25; d, band gap energy comparison using the in situ sample series-left and impregnation series-right). The influence was significant when P25 was the base photocatalyst, while in the other cases, no changes were observed in their spectrum.

It was observed that the characteristic plasmonic bands of Au nanoparticles had disappeared when the reduction of Au and Pt was performed simultaneously using both synthesis pathways, i.e., impregnation and in situ. This spectral alteration could have two explanations:

- the Pt "covers" the Au nanoparticles, forming a so-called core-shell nanostructure
- the two noble metals are forming alloys in these ternary composites

When the reduction of the metals was carried out separately, using the in situ method, the plasmonic bands of the Au remained observable at ≈550 nm, driving us to the conclusion, that in this case, the nanoparticles were deposited separately onto the surface of the catalysts, while using the impregnation method we can observe that the plasmonic band of the Au disappears, offering a similar explanation for this phenomenon as that given for the same-time reduction method. In the third case, no plasmonic bands were observable when the Au was reduced after Pt (Pt/Au). This phenomenon's possible explanation lies in the formation of alloys, while in the case of a possible formation of Pt-Au core-shell particles, plasmonic bands should be visible (Pt being in the core and Au the shell of the nanostructure).

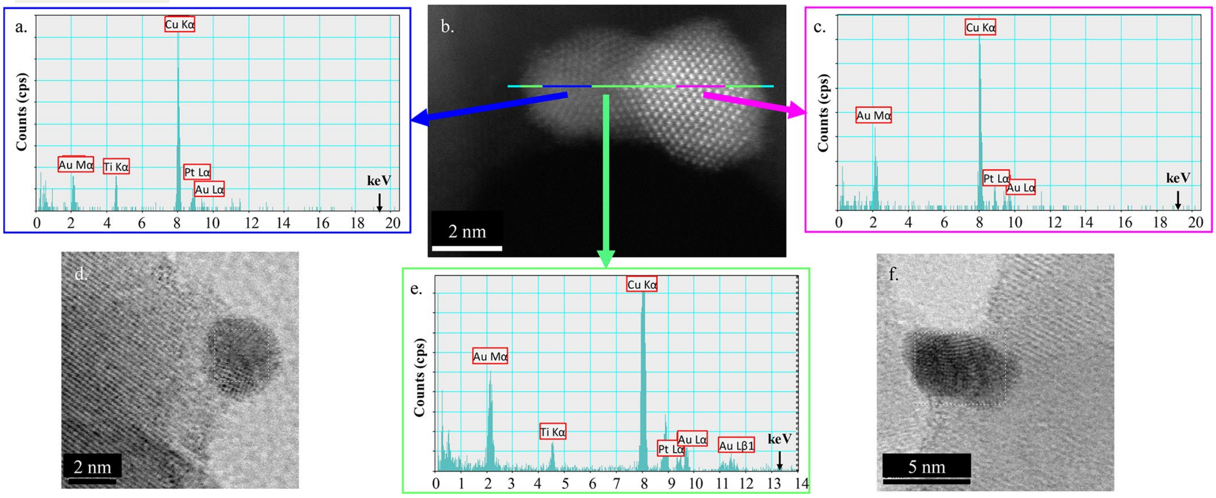

Figure 2: STEM-HAADF (b) micrograph, HR-TEM (d, f) images, and EDS spectra (a, c, and e) of P25imp-Au/Pt sample, showing the presence of both Au and Pt. No core−shell particles and no alloys were detected, just nanoparticles, which show Pt and/or Au presence.

As detailed above, different composite build-up scenarios were possible in the case of all ternary composites. That is why the visualisation of the particles was mandatory using electron microscopy techniques. To elucidate the (partial) discrepancies from DRS measurements, HRTEM and EDS measurements were involved in morphological and structural investigations (Figure 2). The smallest (2-4 nm) nanoparticles were found when both precursors were reduced simultaneously (samples TiO2-Au&Pt). In this case, a high number of noble metal clusters were also detected. However, the relationship between gold and platinum was still open. That is why STEM-HAADF, HR-TEM, and EDS spectra were simultaneously investigated to reveal the nature of the nanoparticles. It was found that the individual nanoparticles were of Au (studying the lattice fringes), while in the case of twin and larger noble metal nanoparticles, the signature of Pt (using EDS) was also detected. This points out that Pt is present in any case in the form of very small nanoclusters, excluding the presence of core-shell nanoparticles.

Photocatalytic investigations

In general, it can be observed that the P25-based composites showed the highest photocatalytic efficiencies, degrading more than 75% of the **oxalic acid**. The highest degradation values (≈95%) were obtained for both ternary composite synthesis pathways, where Pt was deposited after Au (P25_is_Au/Pt and P25_im_Au/Pt). Regarding the AA-based composite series, the highest decomposition (69 %) was obtained with the monometallic Pt-containing composite (AA_is_Pt), which was followed closely by the bimetallic composite (Au and Pt - AA_is_Au/Pt), having a degradation efficiency of ≈ 65 %. On the other hand, the composites made by impregnation showed a lower yield, between 32-35%. The AR-based catalysts showed exciting results as the highest performing one was AR_is_Au&Pt (58%), followed by AR_is_Au/Pt (54%). It should be mentioned that the reference photocatalyst AR_is_Pt showed 56% of oxalic acid degradation. All samples from the AR series obtained by impregnation showed lower photocatalytic activity than their in situ counterparts (30-40% oxalic acid removal).

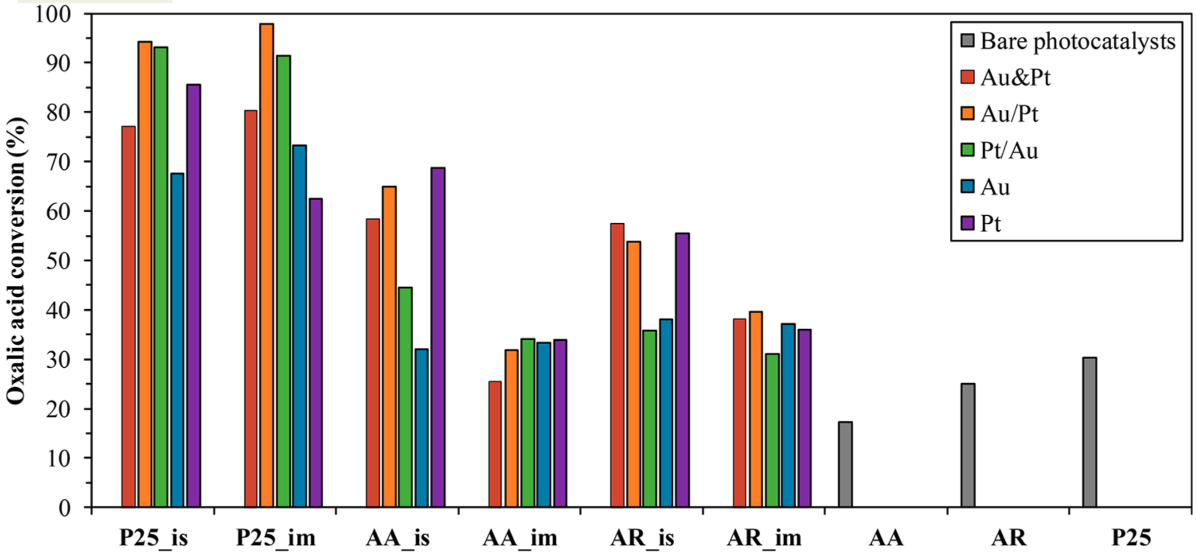

Figure 3 Oxalic acid degradation performances after 1 h of the obtained nanocomposites under UV light. All of the composites showed higher photocatalytic activity than their corresponding base photocatalyst. Results after 2 h were omitted as each composite degraded the oxalic acid totally.

Comparing the yields, we can conclude that the presence of noble metal nanoparticles increased the catalyst's efficiency. By comparing the performances of the nanocomposites obtained by different synthesis pathways, some tendencies can be noticed. Thus, the Aldrich-titania-based composites have lower efficiencies when the impregnation method was used (yields in the 25-34% range for AA impregnation and in the 32-69% range for in situ, and, the 31-41% range for AR impregnation and in the 35-58% range for in situ) For P25-based catalysts this tendency is inverted, as the materials prepared with impregnation have slightly higher conversion in two cases compared to those with in situ method.

On the other hand, the efficiency values obtained for P25-based composites were higher, while the efficiencies obtained in the case of AA-based composites were not so low, considering the relatively small surface area of the base catalyst. This behaviour can be explained by the relatively large number of available charges on the catalyst's surface normalising to their specific surface area.

In the case of **methyl-orange**, it can be generally concluded that the obtained yields for the composites based on P25 were lower than for the main catalyst (≈66%). When the in situ approach was used for the synthesis of the photocatalysts, the yields were slightly higher than those for the main catalyst, but during the second hour, the sequence of the activity has changed (the three best-performing catalysts being the P25 > P25_is-Au/Pt > P25_im_Pt/Au). In the case of AA-based materials, it was observed that the composites had generally higher yields than those of the main catalyst, reaching a degradation yield of >90% (≈40 % for the AA) for most of the composites until the end of the photocatalytic test (2 hours), obtaining higher efficiencies for the samples prepared with in situ method, but also for the samples prepared by impregnation some yields were higher than 80% (e.g. AA_im_Au-Pt). For the AR-based composites, the composites' yield was lower than those obtained for the primary catalyst, obtaining 65% of degradation for the AR, while the best-performing composites were AR_is-Au-Pt and AR_im-Pt-Au, both having yields between 40-45%.

In the case of degradation of **phenols**, it can be concluded that the P25 is a versatile and quite efficient photocatalytic material, reaching 87% of degradation yield toward the selected model pollutant. Generally, it was observed that the noble-metal based composites had lower efficiencies toward phenol, between 72-52% (with the best performing composite of P25_is_Pt/Au, while the P25_im_Au/Pt gave the lowest efficiency). This activity drop could have several causes, like the efficiency of the electron transfer processes, hint already given in the optical properties of the P25-based composites, as the electron transition band corresponding to the rutile phase diminished significantly, suggesting that a fraction of the electron transitions are "lost". The pure AA also proved to be active in the degradation of phenol, although the manifested degradation yield is inferior to that of P25 (63% vs. 87%). Based on the behaviour of P25, it was expected that the deposition of the nanoparticles would decrease the efficiency of the composites, but surprisingly this was not the case, as most of the composites had an enhanced efficiency with a factor of ≈1.5, reaching degradation yields higher than 90% in most of the cases (e.g. 99% for AA_is_Pt/Au). The AR was a relatively poor photocatalyst, showing only 41% yield toward phenol degradation.

Testing on real wastewater samples

The best photocatalysts were tested under real conditions in Pata Rât, Cluj county, Romania (15 km east from Cluj-Napoca/Kolozsvár). This neighbourhood was chosen as a toxic waste landfill, while circa 1500 Roma people spend their lives here. Moreover, appx 1/3 of these people are children not turning 18 years of age. Their living conditions are inhuman, acquiring heat through waste-burning, without clean water, and few homes lack electricity. Due to the toxic environment, the pollution of their surface waters is high, while the access to potable water is limited.

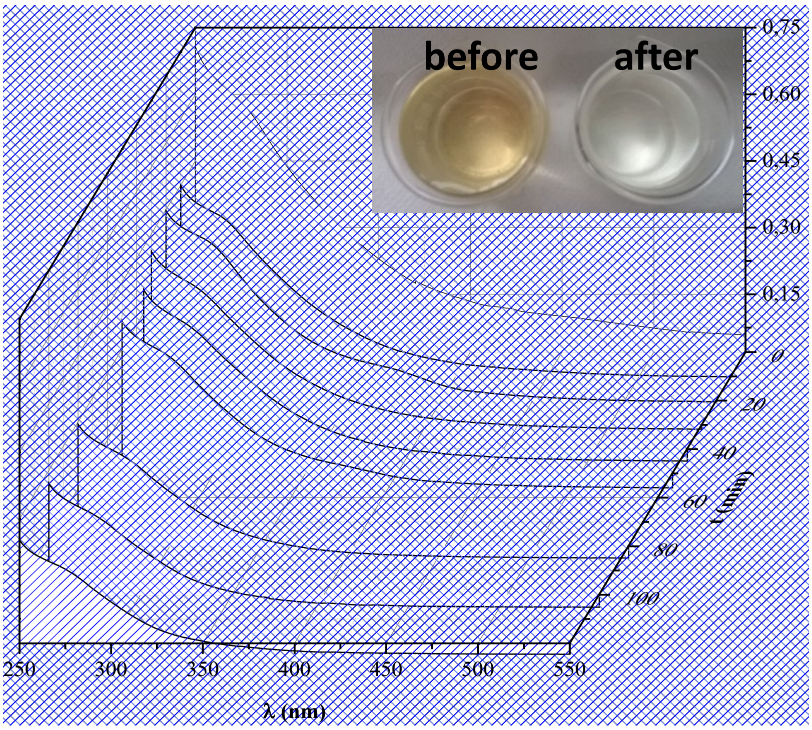

Figure 4. Photocalytic treatment of real wastewater samples, using Pt/P25_is_Au/Pt composite

The materials considered for this investigation were based on the most efficient reduction method applied to synthesise the composites, which was in most cases Au/Pt composites and their bare counterparts. It is worth mentioning that these wastewaters generally contained heavy metals and xenobiotic organic pollutants. These wastewaters usually had a yellow-brownish colour, so their photocatalytic treatment was investigated using an Able-Jasco V650 spectrophotometer. The results have shown that all the investigated composites and their reference counterparts could remove the pollutants from these wastewaters, decreasing the amount of pollutants to 22-38% of their original concentrations (Au-AA and Pt/P25_is_Au/Pt (Figure 4), respectively).

Photocatalytic H_2 production

In general, as it was slightly predictable, P25-based composites gave the highest H2 production rates (the sacrificial agent is the same as the model pollutant described in the previous report). The best performing (Figure 8) composite also came from this series, as the P25_im_Pt/Au had the highest H2 production rate, namely 1567 µmol of H2 during the whole experiment (2 h). It is interesting to observe that the P25_is_Au&Pt/P25_is_Au/Pt and P25_im_Au&Pt/P25_im_Au/Pt composite pairs have a relatively small difference in their H2 production efficiencies (1429 µmol vs 1417 µmol/1289 µmol vs 1221 µmol), although their build-up was quite different, as it was shown in the first report. In the case of the reference samples, the Pt-based ones had the highest efficiency (1126 µmol of H2 – P25_im_Pt). While in the case of both noble metals, the reference samples which were obtained by impregnation were slightly more efficient (P25_im_Pt - 1126 µmol vs 986 µmol - P25_is_Pt; P25_im_Au - 750 µmol vs 657 µmol - P25_is_Au).

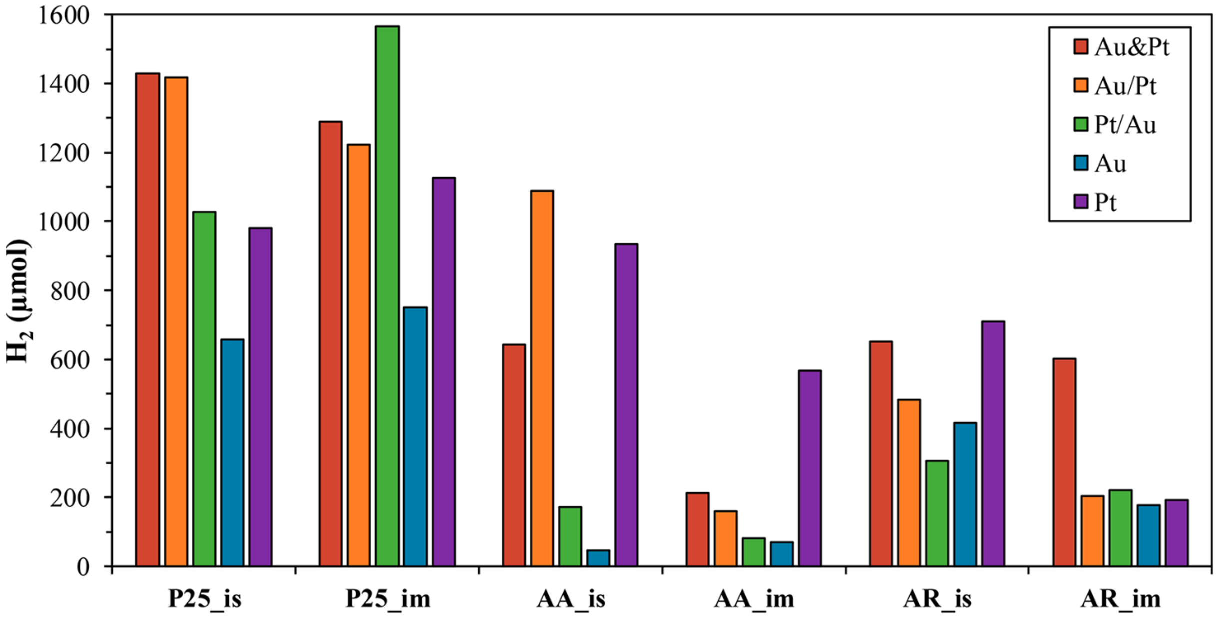

Figure 5 Photocatalytic H2 production capacities of the used nanocomposites. The bare photocatalysts were not shown, as they do not produce hydrogen under these experimental conditions

It can be summarised that the Aldrich-based composites' photocatalytic efficiency was generally lower than that of P25-based composites. The hydrogen production rates showed significantly different values for the materials obtained using different composite synthesis pathways: the in situ preparation method generally resulted in higher efficiencies than those obtained by the impregnation method, including for all of the reference samples, while this difference was not so accentuated for the P25-based composites. On the other hand, it can be also observed that the noble-metal deposition sequence has a much stronger influence on the activity of the anatase-based composites in comparison with those achieved for the samples synthesised by using Aldrich rutile, where the performances were decreased with 44−85% comparing the results obtained by impregnation to their in situ analogues. The differences between rutile-based composites were smaller, but generally, the in situ preparation pathway yielded higher yields (with 5−53%) than their analogs prepared with impregnation.

Ecotoxicological investigations

However, these relatively high activities can turn into a severe drawback if these materials spread out in our surroundings. To complete the main workplan, ecotoxicological investigations were carried out using a simple aquatic plant. One can imagine if such powders could escape into natural waters and accumulate in static waters, such as lakes. Therefore, the assumption of an environmental impact could be a reality. Thus, Lemna minor was considered a model organism, using a shallow-water approach (10 cm), without stirring, using SIS Lemna solution. Au/Pt composites were the most efficient ones in degrading oxalic acid and were used in the ecotoxicological tests. It was found that considering a simplified "lake" approach, the presence of different materials changed the pH and the conductivity of the media but did not influence the growth of Lemna minor, pointing out that the ecotoxicology of photocatalysts might be more complicated as it seems because it did influence the properties of the medium which may be not appropriate for other species (e.g., single-cell species, other plants, etc.).

Supplementary investigations - Future prospects - Outlook

Considering the valuable results of the above-presented noble-metal-based titania composites, the attention of the Project Leader was adjusted toward some more cost-efficient materials. Namely, some investigations related to Ag-based photoactive materials (e.g. TiO2-based composites, silver halides) were also performed with the financial support of the current project.

Dissemination of the results

Besides the "regular scientometry" of a project like this (peer-reviewed articles, impact factors, conferences etc.), I would like to mention separately as the Project Leader obtained a special prize/distinction (together with Boglárka Hampel) from Dr Paál Zoltán foundation, for the ***Best article in heterogeneous catalysis*** in 2018 in Hungary (prize awarded biannually). On the same occasion, a presentation was held by the PL and B.H. in the framework of the workshop of the Catalysis Working Committee of the Hungarian Academy of Sciences.

Moreover, during this time, when this project founded the main income source of the PL, numerous students were guided by the PL, to successfully present at different stages of TDK (local TDKs, MTDK – TDK for engineers, in Timisoara, Romania, presentations at the Students for Students conference, Cluj-Napoca, Romania) or to prepare their B.Sc. and M.Sc. theses. Enlightening the international collaborations during this period, I would like to highlight the M.Sc. thesis supervised partially by the PL, defended with 48/50 points at the Amity University, New Delhi, India, by Mr. Saurav Maity.

Articles in peer-reviewed journals:

- Hampel, B., **Kovács, G.,** Czekes, Zs., Hernádi, K., Danciu, V., Ersen, O., Girleanu, M., Focsan, M., Baia, L., and Pap, Z. Mapping the photocatalytic activity and ecotoxicology

of Au, Pt/TiO_2 composite photocatalysts, ACS Sustainable Chemistry and Engineering (2018) 6(10), 12993-13006. (I.F.: 6,140) – (shared) first author

- Gyulavári, T., Kovács, K., Kovács, Z., Bárdos, E., **Kovács, G**., Baán, K., Magyari, K., Veréb, G., Pap, Zs. and Hernádi, K., Preparation and characterization of noble metal modified titanium dioxide hollow spheres – new insights concerning the light trapping efficiency, Applied Surface Science (2020), 534, 147327 (I.F.: 5.270)
- Rápó, E., Posta, K., Csavdári, A., Vincze, B.É., Mara, Gy., **Kovács, G**., Haddidi, I. and Tonk, Sz. Performance comparison of Eichornia crassipes and Salvinia natans on azodye (Eriochrome Black T) phytoremediation, Crystals (2020) 10, 565 (I.F.: 2.404)
- Tóth, Z. R., Hernádi, K., Baia, L., **Kovács, G**. and Pap, Zs. Controlled formation of Ag-AgxO nanoparticles on the surface of commercial TiO_2 based composites for enhanced photocatalytic degradation of oxalic acid and phenol, Catalysis Today (2021) in press (I.F.:5.825) – corresponding author
- Vajda, K., Hernádi, K., Cotet, C., **Kovács, G**., Pap, Z., Shape-tailored TiO2 photocatalysts obtained in the presence of different types of carbon materials, Journal of Nanoscience and Nanotechnologies (2021) 21(4), 2360-2367 (I.F.: 1.483)
- Tonk, Sz., Aradi, L.-E., Kovács, G., Turza, A., Rápó, E., Effectiveness and Characterization of Novel Mineral Clay in Cd2+ Adsorption Process: Linear and Non-Linear Isotherm Regression Analysis, Water (MDPI) (2021), 14, 279 (I.F.: 3.103)
- Ljupkovic, R., Baia, M., **Kovács, G**., Synthesis, morpho-structural properties and photocatalytic applicability spectra of ternary noble metal-TiO_2 composites: a review, manuscript before submission to Materials (MDPI) – corresponding author

Conference presentations:

- Saszet Kata, Pap Zsolt, **Kovács Gábor**, Danciu Virginia, Hernádi Klára, Baia Lucian, *Variations in the Composition of a TiO_2, WO_3 and Gold Nanoparticle Composite and its Effect on the Photocatalytic Activity*, XXIII. International Conference on Chemistry, Déva, Romania, 25-28th of October, 2017
- Tóth Zsejke-Réka, **Kovács Gábor**, Lucian Baia, Pap Zsolt, Hernádi Klára, *Synthesis, characterization and photocatalytic activity of spherical gold nanocages/TiO2 and silver nanospheres/TiO2 composites*, III. International Symposium on Nanoparticles/Nanomaterials and Applications, Costa de Caparica, Portugal, 22-25th of January, 2018
- Hampel Boglárka, **Kovács Gábor**, Czekes Zsolt, Hernádi Klára, Pap Zsolt, *Investigating the Photocatalytic Activity and Ecotoxicology of Au, Pt/TiO2 Composite Photocatalysts*, XXIV. International Conference on Chemistry, Szovátafürdő, Romania, 24-27th of October, 2018
- Tóth Zsejke-Réka, **Kovács Gábor**, Lucian Baia, Pap Zsolt, Hernádi Klára, *Stability Investigations of Visible Light Silver-halide (AgX, X=Cl-, Br-, I-) Photocatalysts*, XXIV. International Conference on Chemistry, Szovátafürdő, Romania, 24-27th of October, 2018
- Boglárka Hampel, Enikő Eszter Almási, Klára Hernádi , Zsolt Pap, Zsolt Czekes, **Gábor Kovács**, *Investigations of photocatalytic actrivity and ecotoxicology of Au, Pt/TiO_2 composite catalysts,* II. Sustainable Raw Materials International Project Week And Scientific Conference, Szeged, Hungary, May 6-10, 2019
- Boglárka Hampel, **Gábor Kovács**, Czekes Zsolt, Hernádi Klára, Baia Lucian, Ersen Ovidiu, Pap Zsolt, *Correlation between photocatalytic activity and ecotoxicology of noble metal/TiO_2 nanocomposites,* 6th European Conference on Environmental Applications of Advanced Oxidation Processes, Portoroz, Slovenia, 26-28th of June, 2019

- Tóth Zsejke-Réka, **Kovács Gábor**, Pap Zsolt, Hernádi Klára, *Effect of the Commercial TiO_2 Anatase and Rutile Crystal Phases on the Formation of Ag and AgO Nanoparticles*, XXV. International Conference on Chemistry, Kolozsvár, Romania, 24-26th of October, 2019
- **Kovács Gábor,** Hampel Boglárka, Czekes Zsolt, Pap Zsolt, Hernádi Klára, *Investigating the Photocatalytic Activity and Ecotoxicology of Noble Metal/TiO_2 Composite Photocatalysts*, XXV. International Conference on Chemistry, Kolozsvár, Romania, 24-26th of October, 2019
- Kiss János, Tóth Zsejke-Réka, Pap Zsolt, Hernádi Klára, **Kovács Gábor**, *Applicability and Structure Modification of AgBr Photocatalysts with Differently Structured and Concentrations of Shape-tailoring Agents,* XXV. International Conference on Chemistry, Kolozsvár, Romania, 24-26th of October, 2019
- Tóth Zsejke-Réka, Debreczeni Diána, Kiss János, Pap Zsolt, Hernádi Klára, **Kovács Gábor**, *Synthesis, characterization and applicability of Ag-based photoactive materials*, XXVI. International Conference on Chemistry, online event, 30th of October, 2020