Improvement of the photocatalytic activity of titanium dioxide by forming composites with different materials

Doctoral (Ph.D.) theses

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1. Introduction and objectives

It is now known for everyone that the amount of potable water on Earth is dropping drastically and is becoming more and more contaminated. Pesticides, detergents, phenols, oil and oil derivates, etc. can be found in our environment, causing great damage. Besides traditional physical, chemical, and biological wastewater treatment technologies, various alternative methods have been developed for water purification, and this circle is expanding. Heterogeneous photocatalysis, which is one of the advanced oxidation processes, could be an alternative method for wastewater treatment. This technique requires the presence of a photocatalyst, typically a semiconductor, which can be excited by the irradiation with a light of a proper wavelength. This could initiate the mineralization of the organic pollutant via multiple steps or possible intermediates.

During the Ph.D. dissertation my main goal was to investigate TiO_2 based composites. The bottom line was to broaden the applicability spectrum of titania by forming composites with different materials, such as with noble metal nanoparticles, copper nanoparticles or with lanthanide doped $NaYF_4$ in order to utilize upconverted light as well. In the first instance gold and platinum nanoparticles were deposited simultaneously on different commercial titanias, then copper nanoparticles were deposited on commercial titanias, then ternary composites were formed with Yb^{3+}, Er^{3+} and Tm^{3+} doped $NaYF_4$, gold nanoparticles and TiO_2. My aim was to investigate the photocatalytic activity, through the degradation of different model pollutants and hydrogen production, beside the morphological and structural properties of the prepared materials.

2. Experimental methods

As a preliminary study binary composites were obtained, where gold and platinum nanoparticles were deposited at the same time on three different commercially available titanias: Evonik Aeroxide P25, Aldrich anatase (AA) and Aldrich rutile (AR). With the aim of searching for a cheaper method copper nanoparticles were deposited on P25 and AA. In the interest of further improving the photocatalytic activity of TiO_2 ternary composites were formed with lanthanide doped $NaYF_4$ and gold nanoparticles. The morphological and structural properties of the as-prepared composites were investigated with the methods and instruments presented below.

The crystalline phase compositions and mean primary crystallite sizes of the photocatalysts were determined by **X-ray diffraction** (**XRD**) with a Rigaku diffractometer using Cu-Kα radiation (λ = 1.5406 Å) equipped with a graphite monochromator. The primary crystallite size of the prepared semiconductors was evaluated using the well-known Scherrer equation.

The morphological properties were investigated by **transmission electron microscopy (TEM)**. TEM micrographs were obtained using a FEI Tecnai G2 20 X-Twin HRTEM instrument to determine the composition of the samples. HRTEM micrographs were obtained JEOL 2100 FEG S/TEM microscope equipped with a spherical aberration probe corrector and a GATAN Tridiem energy filter operating at 200 kV.

During the **scanning electron microscopy (SEM)** measurements a Hitachi S-4700 Type II FE-SEM was used to determine the average particle size and morphology of the samples. The applied acceleration voltage was 10.0 kV.

The **BET isotherm** was used to calculate the specific surface areas of the composite samples, for which a BELCAT-A device was used to record the isotherms at 77 K via N_2 adsorption.

In the case of **diffuse reflectance spectroscopy (DRS)** the light absorption properties of the solid samples were measured. The spectra of the samples (λ =

300-800 nm) were registered by using a JASCO-V650 spectrophotometer with an integration sphere (ILV-724). The indirect band gap of the photocatalysts was determined via the Kubelka-Munk method.

UV-Vis measurements were executed by using a JASCO-V650 spectrophotometer, using distilled water as reference.

HPLC measurements were implemented on a Merck Hitachi device fitted with an L-4250 UV-VIS detector and a GROM Resin ZH 8 μm column.

GC measurements were carried out on a Hewlett Packard 5890 gas chromatograph fitted with a 5Å molecular sieve column and a thermal conductivity detector.

Photocatalytic activities of the composites were determined by the decomposition of rhodamine B solution under UV- (λ_{max}=365 nm), visible- (λ>400 nm) and near-infrared light (λ>850 nm) irradiation; or oxalic acid solution under UV light; or salicylic acid solution; or methyl orange solution; or ketoprofen solution under UV light. The reactor was surrounded either by 6 × 6 W black light lamps (9.53 W/m^2 energy flux at the reactor position) or 4 × 24 W conventional compact fluorescent lamps (Düwi 25920/R7S-24W; 81.37 W/m^2 energy flux at the reactor position) or 4 × 150 W NIR lamps (Philips IR RED R250 250 W; 52.25 W/m^2 energy flux at the reactor position). The concentration of the samples was measured by HPLC or UV-Vis spectroscopy. For the **H_2 production measurements** the catalyst was dispersed in oxalic acid solution and poured into a glass reactor (total volume: 150 mL), and it was irradiated with 10 × 15 W UV fluorescent lamps (λmax =365 nm, LightTech Kft., Budapest, Hungary). The reactor was connected through a PTFE tube to a gas chromatograph.

3. Summary of the new scientific results

T1. The presence of the noble metals does not influence the structural properties of the commercial titanias, but it does so their optical properties.

T1.1. I have proved that during the deposition of the two noble metal nanoparticles, they appear separately on the titania crystals, they don't form alloys and have and average size of 1-5 nm.

T1.2. Analyzing the DRS spectra, I observed that all composites have smaller band gap energies compared to their base catalyst. In case of AA and AR based composites the decrease of the band gap was less than for the P25 based catalysts, due to the fact that that the particles that build up the base-catalysts are significantly smaller in the case of P25 than for AA and AR, and the differences were more accentuated for these particles than for larger particles of the catalysts.

T2. The synthesis strategies (in situ or impregnation), reduction approaches (sequential or simultaneous) and ratio between the noble metals play an important role in the outcome of the photocatalytic activity. I ascertained that generally, the P25 based composites showed the highest photocatalytic activity, degrading more than 75% of the model pollutant.

T2.1. I have demonstrated that for the P25 based composites from the two applied synthesis strategies the impregnation method proved to be more efficient than the in situ method. For the AA and AR based composites this tendency is inverted, because they have higher particle sizes than P25 and in situ reduction ensures a more homogeneous dispersion.

T2.2. I found that for the P25 and AA based composites the best photocatalytic activity was performed when Pt was deposited after Au, while for the AR based composites the highest activity was achieved when the noble metals were reduced at the same time.

T2.3. I confirmed that by changing the ratio of the noble metals from 0.5%-0.5% to 0.25%-0.75% and 0.75%0-25% respectively had a different effect on each base catalyst. I proved that the photocatalytic activity was improved only in the case of the AR based composites for both synthesis strategies. For the P25 based composites the change in the composition improved the photocatalytic activity for the catalyst made with impregnation. The photocatalytic activity of the AA based composites was not enhanced by the composition change.

T3. I proved that there is a cheaper way of achieving composites with TiO_2, by depositing copper nanoparticles on P25 and AA. Although photocatalytic activity was observed, based on the results I concluded that sometimes it is worth utilizing the noble metal nanoparticles with higher cost, but better photocatalytic properties.

T4. The ternary composites, consisting of home-made anatase TiO_2, lanthanide doped $NaYF_4$ and Au nanoparticles show better photocatalytic activity under visible light than under UV light.

T4.1. I pointed out that the calcination (it promotes the crystallization) improved the photocatalytic activity of the composites under UV light. In contrast, I did not observe such a significant impact of the calcination during the degradation under visible light, which means that crystallinity/particle size has no significant role in determining visible light activity.

T4.2. Contrary to the literature data, the increase in photocatalytic activity with the deposition of Au nanoparticles was only observed for the TiO_2_calc sample. On the other hand, I have to highlight that there is not such a great difference between the activity of the samples with or without Au.

T5. The outcome of the photocatalytic activity of the calcinated sample of lanthanide doped $NaYF_4$ TiO_2 and Au nanoparticles supports the results of the photoluminescence measurements.

T5.1. During the photoluminescence measurements when the excitation wavelength was applied at 900 nm a band at 400 and 460 nm was detected, pointing out the possible activation of this catalyst under infrared irradiation.

T5.2. I observed that in the case of the sample *NYF-TiO_2_calc_Au* photocatalytic activity was achieved, when 12.5% of the model pollutant was degraded under near-infrared light.

4. Applicability of the new scientific results

During my research I successfully synthetized different TiO_2 based binary composites with Au and Pt, or Cu nanoparticles and ternary composites with lanthanide doped $NaYF_4$ and Au nanoparticles.

In my preliminary study, the composites of commercial titanias and gold and platinum nanoparticles I got excellent results. To reduce the cost of the composites, I deposited copper nanoparticles to two commercial titanium dioxide, of which only a few of which had better activity than the base catalyst. So, finally I started to further develop the first composite systems (by making the ternary composites), so that they could be useful under near-infrared light as well, which makes up a larger proportion of sunlight than UV light. The photoluminescence measurements proved that these composites could be active under infrared light. In the case of the sample named NYF-TiO_2_calc_Au was observed a 12.5% degradation efficiency. Although, in such a less researched field, 4 years is a very short time to achieve excellent results, which is why a lot of research is needed in the future to obtain higher efficiency. Overall, I think that my research could be a starting point to those who dedicate themselves to study these kinds of materials. Photocatalysis under near-infrared light is still not very popular in this area of research, but I hope that my results can contribute to this, and one day this method will be used at a larger scale.

5. Publications and conference participations

Hungarian Scientific Bibliography (MTMT) identifier: 10062606

Publications related to the scientific topic of the dissertation:

[1] **B. Hampel**, G. Kovács, Z. Czekes, K. Hernadi, V. Danciu, O. Ersen, M. Girleanu, M. Focsan, L. Baia, Z. Pap: *Mapping the Photocatalytic Activity and Ecotoxicology of Au, Pt/TiO_2 Composite Photocatalysts*

ACS Sustainable Chemistry and Engineering, 2018, 6(10), 12993–13006

IF = 7.06

Citations = 12

[2] **B. Hampel**, K. Hernadi, L. Baia, Z. Pap: *The impact of Au nanoparticles and lanthanide-doped $NaYF_4$ on the photocatalytic activity of titania photocatalyst*

Applied Surface Science, 2021, 547, 149123

IF = 6.707

Citations = 1

[3] B. Hampel, L. Baia, K. Hernadi, Z. Pap: The influence of the ratio of Au and Pt nanoparticles in ternary composites with TiO_2

Metals, 2021, 11(4), 628

IF = 2.351

Citations = 0

[4] B. Hampel, Z. Pap, A. Sapi, A. Szamosvolgyi, L. Baia, K. Hernadi: Application of TiO_2-Cu Composites in Photocatalytic Degradation Different Pollutants and Hydrogen Production

Catalysts, 2020, 10(1), 85

IF = 4.146

Citations = 8

[5] B. Hampel, K. Hernadi, Z. Pap: Rare earth doped luminescent materials as photocatalysts for enhanced photocatalytic reactions
Green Photocatalytic Semiconductors – Recent Advances and Applications, Springer Nature Switzerland AG, pp 258-280 (2022)

ΣIF = 20.264

ΣCitations = 21

National and international conference participations:

1. **Hampel Boglárka**
Arany-platina-TiO_2 kompozit fotokatalizátorok aktivitásának és hidrogénfejlesztő képességének vizsgálata
XVII. reál- és humántudományi Erdélyi Tudományos Diákköri Konferencia (ETDK)
Kolozsvár, Romania (2014)

2. **Hampel Boglárka**, Dr. Kovács Gábor, Dr. Pap Zsolt, Dr. Virginia Danciu, Dr. Dombi András, Dr. Hernádi Klára, Dr. Lucian Baia
Kereskedelmi titán-dioxidok fotokatalitikus aktivitásának és hidrogénfejlesztő képességének finomhangolása arany és platina nanorészecskék együttes alkalmazásával
XX. Nemzetközi Vegyészkonferencia
Kolozsvár, Romania (2014)

3. **Hampel Boglárka**
Arany-platina-TiO_2 kompozit fotokatalizátorok aktivitásának és hidrogénfejlesztő képességének vizsgálata
XXXII. Országos Tudományos Diákköri Konferencia (OTDK), Kémiai és Vegyipari Szekció
Veszprém, Hungary (2015)

4. **Hampel Boglárka**
Kereskedelmi titán-dioxidok fotokatalitikus aktivitásának és hidrogénfejlesztő képességének finomhangolása arany és platina nanorészecskék együttes alkalmazásával
XVIII. reál- és humántudományi Erdélyi Tudományos Diákköri Konferencia (ETDK)
Kolozsvár, Romania (2015)

5. **Boglárka Hampel**, Gábor Kovács, Zsolt Pap, Virginia Danciu, András Dombi, Klára Hernádi, Lucian Baia
Fine tuning of the photocatalytic activity and hydrogen production capacity of Au, Pt/different commercial titania composites
E-MRS Spring Meeting,

Lille, France (2015)

6. **Hampel Boglárka**, Dr. Kovács Gábor, Dr. Pap Zsolt, Dr. Virginia Danciu, Dr. Dombi András, Dr. Hernádi Klára, Dr. Lucian Baia, Ovidiu Ersen, Emilia Girleanu

Arany, platina, TiO_2 vegyes kompozit fotokatalizátorok szerkezeti és optikai tulajdonságainak vizsgálata
XXI. Nemzetközi Vegyészkonferencia
Csíksomlyó, Romania (2015)

7. **Hampel Boglárka**, Pap Zsolt, Kovács Gábor, Virginia Danciu, Hernádi Klára, Lucian Baia

Kereskedelmi titán-dioxid Cu-nanorészecske kompozitok előállítása és réz tartalmának optimalizálása
XXII. Nemzetközi Vegyészkonferencia
Temesvár, Romania (2016)

8. **Hampel Boglárka**, Pap Zsolt, Kovács Gábor, Hernádi Klára, Lucian Baia

Kereskedelmi titán-dioxidok kompozitba vitele különböző tömegszázalékban jelen levő Cu nanorészecskékkel
Erdélyi Természettudományi Konferencia
Kolozsvár, Romania (2016)

9. **Hampel Boglárka**

The characterization and photocatalytic properties of TiO_2/Cu nanocomposites
XIV. International Conference Students for Students
Kolozsvár, Romania (2017)

10. **Hampel Boglárka**

Kereskedelmi titán-dioxidok fotokatalitikus aktivitásának és hidrogénfejlesztő képességének finomhangolása arany és platina nanorészecskék együttes alkalmazásával
XXXIII. Országos Tudományos Diákköri Konferencia (OTDK), Kémiai és Vegyipari Szekció
Miskolc, Hungary (2017)

11. **Boglárka Hampel**, Zsolt Pap, Szilvia Fodor, Gábor Kovács, Virginia Danciu, Klára Hernádi, Lucian Baia

Preparation of TiO_2-Cu and TiO_2-Cu-Pt nanocomposites and investigating their photocatalytic properties
5th European Conference on Environmental Applications of Advanced Oxidation Processes, Prague, Czech Republic (2017)

12. **Hampel Boglárka**, Pap Zsolt, Hernádi Klára, Kovács Gábor, Lucian Baia

TiO_2-cu nanokompozitok előállítása és vizsgálata valós- és modellszennyezők lebontására
23rd International Symposium on Analytical and Environmental Problems
Szeged, Hungary (2017)

13. **Hampel Boglárka**, Pap Zsolt, Hernádi Klára, Kovács Gábor, Lucian Baia

TiO_2-Cu nanokompozitok alkalmazása ketoprofen bontására
XXIII. Nemzetközi Vegyészkonferencia
Déva, Romania (2017)

14. Boglárka Hampel, Zsolt Pap, Lucian Baia, Klára Hernádi
Preparation of lanthanide doped $NaYF_4$-TiO_2-Au composites and their photocatalytic activity
12th InternationalConference on Physics of Advanced Materials
Heraklion, Greece (2018)

15. Hampel Boglárka, Hernádi Klára, Pap Zsolt, Lucian Baia
Lantanoidákkal dópolt $NaYF_4$-TiO_2-Au kompozitok előállítása és fotokatalitikus vizsgálata
XXIV. Nemzetközi Vegyészkonferencia
Szovátafürdő, Romania (2018)

16. Boglárka Hampel
Preparation and characterization of lanthanide doped $NaYF_4$-TiO_2-Au composites
II. SUSTAINABLE RAW MATERIALS International Project Week and Scientific Conference
Szeged, Hungary (2018)

17. Boglárka Hampel, Zita Berlinger, Klára Hernádi, Lucian Baia, Zsolt Pap
Preparation and characterization of lanthanide doped $NaYF_4$-TiO_2-Au composites
6th European Conference on Environmental Applications of Advanced Oxidation Processes
Portorose, Slovenia (2018)

18. Boglárka Hampel, Gábor Kovács, Zsolt Czekes, Klára Hernádi, Lucian Baia, Ovidiu Ersen, Zsolt Pap
Correlation between photocatalytic activity and ecotoxicology of noble metal/TiO_2 nanocomposites
6th European Conference on Environmental Applications of Advanced Oxidation Processes
Portorose, Slovenia (2018)

19. Hampel Boglárka, Pap Zsolt, Hernádi Klára, Lucian Baia
Szén-nanogömb templátra épített lantanoida ionokkal dópolt $NaYF_4$-Au kompozitok előállítása és fotokatalitikus vizsgálata
XXV. Nemzetközi Vegyészkonferencia
Kolozsvár, Romania (2019)

National and international conference participations as co-author:

20. Pap Zsolt, Kovács Gábor, Székely István, Kedves Zsolt, Saszet Kata, **Hampel Boglárka**, Fodor Szilvia, Tóth Zsejke-Réka, Orbán Eszter, Kovács Zoltán, Hernádi Klára, Dombi András, Kása Zsolt, Vajda Kriszta, Karácsonyi Éva, Virginia Danciu, Adriana Vulpoi, Veronica Cosoveanu, Lucian Baia
Nanoszerkezetű fotokatalizátorok és kompozitjaik-alakszobrászat és aktivitás
XX. Nemzetközi Vegyészkonferencia
Kolozsvár, Romania (2014)

21. Szilvia Fodor, Kata Saszet, **Boglárka Hampel**, Tünde Makó, Melinda Abrudbányai, Henrietta Vadas, Virginia Danciu, Lucian Baia, Emese Gál, Gábor Kovács, Zsolt Pap
Solar light activated photocatalysts in the service of the society: the sinergy of photocatalysis and sociology
E-MRS Spring Meeting,
Lille, France (2015)

22. Czekes Zsolt, **Hampel Boglárka**, Kovács Gábor, Pap Zsolt, Baia Lucian
TiO_2 fotokatalizátorok aktivitása és ökotoxikológiai vizsgálata
XXI. Nemzetközi Vegyészkonferencia
Csíksomlyó, Romania (2015)

23. Zsolt Czekes, **Boglárka Hampel**, Gábor Kovács, Zsolt Pap, Lucian Baia
Enhanced photocatalytic activity without increased ecotoxicological risk in noble metal modified TiO_2 nanocrystals
Göttingen, Germany (2016)

24. Zsolt Pap, Szilvia Fodor, Tamás Gyulavári, Gábor Kovács, Zsejke-Réka Tóth, Zsolt Kása, Enikő Bárdos, Georgina Rózsa, Gergő Simon, Zsuzsanna Kozmér, Mihai Rusu, Klára Hernádi, Lucian Baia, Monica Baia, István Székely, Zsolt Kedves, Bíborka Boga, Alpár Ravasz, **Boglárka Hampel**, Zoltán Kovács, Kata Saszet, Virginia Danciu, Veronica Co oveanu, Vajda Krisztina, Éva ș Karácsonyi, Lucian Cristian Pop, Zsolt Czekes, Zsuzsanna Nagy, Klára Magyari, Milica Todea, Adriana Vulpoi, Gábor Veréb, Eszter Orbán, András Dombi
Új nanokompozitok és nanoszerkezetek a víztisztításban
XXII. Nemzetközi Vegyészkonferencia
Temesvár, Romania (2016)

25. **Hampel Boglárka**, Kovács Gábor, Czekes Zsolt, Hernádi Klára, Pap Zsolt
Au, Pt/TiO_2 alapú kompozitok fotokatalitikus aktivitásának és ökotoxikológiai hatásának vizsgálata
XXIV. Nemzetközi Vegyészkonferencia
Szovátafürdő, Romania (2018)