Enhancement of photocatalytic activity of ZnO: a structural and morphological design

Doctoral (Ph.D.) theses

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1. A doktori munka összefoglalása

A félvezető alapú fotokatalizátorok népszerűsége egyre nő, mivel egyre széleskörű alkalmazási lehetőségeiknek köszönhetően, amelyek folyamatosan bővül. Doktori munkám során különböző morfológiájú ZnO fotokatalizátorokat állítottam elő, és megvizsgáltam, hogy a szerkezeti és morfológiai módosítások hogyan befolyásolják a fotokatalitikus aktivitást.

Elsőként a ZnO szolvotermális szintézise során alkalmazott redukált kísérleti terv (Box-Behnken) segítségével kimutattam, hogy egy szerkezeti jellemző, a krisztallitok (002) kristály síkok mentén történő preferenciális orientációja korrelál a fotokatalitikus aktivitással.

A félvezetők morfológiai módosítása szintén fontos szempont a heterogén fotokatalízis területén, mivel közvetlenül befolyásolhatja az aktivitást. A korábban említett szintézismódszert módosítottam ZnO gömbök előállítására, alakformáló szerként dietanolamint használva. Két különböző ZnO prekurzor, illetve azok keverékeinek alkalmazásával kimutattam, hogy a ZnO gömbök átlagos mérete 155 nm és 3 μm között hangolható. Ezen kívül kimutattam, hogy a korábban leírt szerkezeti jellemző továbbra is szabályozható, a gömb morfológia módosítása nélkül. Bebizonyítottam, hogy a gömbmorfológia és a fotokatalitikus teljesítmény külön-külön is hangolható.

Végül tovább módosítottam a szintézismódszert széngömb sablonok felhasználásával, hogy üreges gömbmorfológiájú ZnO-t állítsak elő. A sablonok alkalmazása ellenére a krisztallitok preferenciális orientációja továbbra is lehetséges, és az üreges gömb ZnO-k fotokatalitikus teljesítménye jobb volt, mint a referencia nem üreges, gömb ZnO-ké. A ZnO üreges gömbök katalitikus aktivitását tovább növeltem nemesfém (Au, Pt) nanorészecskékkel történő adalékolással.

Összességében az elért eredmények azt mutatják, hogy a krisztallitok (002) mentén történő preferenciális orientációja meghatározó szempont a fotokatalitikus aktivitás szempontjából, függetlenül az alkalmazott morfológiai módosításoktól.

2. Introduction and objectives

In the 21st century, environmental pollution has become our primary concern. Due to the growing population, in the agricultural and chemical industry drinking water is already in shortage in developing countries, which is expected to be an even more concerning problem in the future. Conventional water purification methods have always been costly to construct and implement. As such developing new alternative ways for waste-water treatment is an imperative task, that humanity needs to tackle considering for sustainable growth of Earth's population. Advanced oxidation processes (AOPs) are one of the most promising alternative techniques, which can offer not just more cost-effective, but also more efficient solutions. One prominent technique amongst AOPs is heterogeneous photocatalysis, which is based on the application of semiconductor photocatalysts, excitable by different light sources, such as sunlight. The excitation of the photocatalyst leads to the formation of free radicals, which can initiate the degradation of organic pollutants. It is easy to recognize the potential of heterogenous photocatalysis to become a viable green and non-selective solution for water remediation and wastewater treatment.

The development of semiconductors for photocatalytic applications dates back more than decades, but the light utilization of the most efficient photocatalysts is still insufficient for large-scale applications for water treatment, so research to enhance the photocatalytic activity of semiconductors is imperative.

The present Ph.D. dissertation aimed to synthesize zinc oxide (ZnO) based photocatalysts and enhance their photocatalytic activity by applying various methods and investigating their morpho-structural proprieties and applicability in photocatalytic degradation of various model pollutants. Another goal was also to investigate the applicability of a more advanced experimental design (Box-Behnken fractional factorial experimental design) to correlate synthesis parameters and photocatalytic activity. The research also focused on identifying key features, which can indicate good photocatalytic activity. Furthermore, various morphological modifications were applied, such as the preparation of ZnO solid and hollow spheres, also noble metal deposition was investigated whether concurrent structural and morphological modifications are possible or not. I identified and quantified casual relationships between structure characteristics, respective morphology and photocatalytic activity.

3. Experimental and characterization methods

In the present work, zinc oxide-based photocatalysts were synthesized using the solvothermal method. Using a reduced experimental design (Box-Behnken), four synthesis parameters (concentration of the precursor in the reaction mixture, concentration of ethanol in the solvent, temperature and duration of the solvothermal treatment) were examined on three values. The synthesis method was modified using a morphological agent (diethanolamine) to prepare ZnO with solid spherical morphology or by applying carbon sphere (CS) templates to prepare ZnO hollow spheres (ZnO-HSs). The effect of the deposition of noble metals (Au/Pt) on ZnO-HSs was also investigated.

A Rigaku Miniflex II diffractometer was used for X-ray diffraction (XRD) measurements with the following operating parameters: Cu-K_α radiation (λ =1.5406 Å), 40 kV, and 30 mA, between 20 and 80 2θ°, applying 0.02° steps and $1°\cdot min^{-1}$ scan speed. Mean primary crystallite sizes were estimated by 3 different methods, that is, the Scherrer equation, the Williamson-Hall analysis (W-H) and the size strain plot (SSP).

A Jasco-V650 UV–Vis spectrometer with an integration sphere (ILV-724) was used for measuring the diffuse reflectance spectra (DRS) of the samples using $BaSO_4$ as the reference. Band-gap energies were calculated by the Kubelka Munk equation and Tauc plot representation. Possible electron transitions were estimated by the first derivative of the DRS. In some cases, the band gap tail energy, also called Urbach energy, was also determined using the Tauc plot.

The room-temperature photoluminescence (PL) emission spectra of the samples were recorded at 350 nm excitation wavelength using a Horiba Jobin Yvon Fluoromax-4 type spectrofluorometer and a 350 nm cut-off filter with a spectral window of 1 nm.

The surface of the ZnO samples was studied using Fourier transform infrared spectroscopy (IR) with a Jasco 6000 spectrometer in the 400–4000 cm^{-1} range applying 4 cm^{-1} spectral resolution.

Specific surface areas of the catalysts were determined by N_2 adsorption at 77 K, using a BELCAT-A device. The specific surface area was calculated via the BET method.

The morphology of the samples was analyzed by a Hitachi S-4700 Type II scanning electron microscope (SEM) and a FEI TECNAI G2 20 X-Twin type transmission electron microscope (TEM). During SEM measurements the electron beam was produced using a cold field emission gun applying 10 kV acceleration voltage, while in the case of TEM, 100 kV was set. The micrographs were further evaluated to determine the diameters and distribution of diameters in the ImageJ software.

The photocatalytic activity experiments were carried out in a Pyrex® glass tube reactor with a thermostatic jacket surrounded by six 6 W fluorescent lamps (Vilber-Lourmat T-6L UV-A, $\lambda_{max} \approx 365$ nm) with a distance between the reactor and lamps 5 cm. During the experiments, constant temperature (25 °C, by circulating water in the thermostatic jacket using an ultrathermostat), magnetic stirring (400 rpm) and the dissolved oxygen concentration (by bubbling with air at 30 $L \cdot h^{-1}$) were maintained.

The used model pollutants for degradation experiments were methyl orange, Na-ibuprofen, diuron and phenol. Quantitative analyses of the methyl orange present in the reaction solution during irradiation were carried out by UV-Vis spectrometry, and the concentrations of the other model pollutants were measured with high-performance liquid chromatography (HPLC). The device consisted of a Merck Hitachi L-7100 low-pressure gradient pump equipped with a Merck-Hitachi L-4250 UV–vis detector ($\lambda_{detection}$ = 210 nm for phenol, 214 nm for ibuprofen and 254 nm for diuron). A 50% v/v ethanol-water mixture was used as eluent for phenol and ibuprofen, respectively 70% v/v for diuron. The total organic carbon content was measured at the end of the photocatalytic tests after 4 hours of irradiation. The equipment used was an Analytik Jena N/C® 3100 apparatus with an NDIR detector. The furnace temperature was 800°C and 1.0 mL samples were injected. The measurements were made in triplicate.

4. Summary of new scientific results

T1. A higher intensity ratio of X-ray diffraction peaks corresponding to crystallographic planes (002) and (100) leads to higher photocatalytic activity.

T1.1. Box-Behnken fractional factorial design was successfully applied to correlate the parameters of the solvothermal synthesis ZnO and maximize the photocatalytic degradation of methyl orange and the ratio of intensities of XRD reflections corresponding to crystallographic planes (002) and (100) ($r_{(002)/(100)}$). A full quadratic equation was fitted for both outputs using an analysis of variance. It was determined that amongst the solvothermal synthesis parameters, the composition of the solvent (ethanol-water) and the solvothermal treatment temperature have the highest impact on $r_{(002)/(100)}$ and the photocatalytic activity.

T1.2. It was proven via photocatalytic activity and X-ray diffraction measurements that with higher $r_{(002)/(100)}$, higher photocatalytic performance was observable for the degradation of methyl orange under UV-A irradiation. Response surface methodology was used to further examine the correlations between the $r_{(002)/(100)}$ and photocatalytic performance, which confirmed that the two outputs behave similarly in functions of synthesis parameters and are also related. The reason for the enhanced photocatalytic activity was deduced to be the different light-harvesting capabilities of the various facets corresponding to the crystallographic planes (002) and (100). No notable differences were observed between the various ZnO samples by DRS and SEM measurements.

T1.3. It was established that maximizing the photocatalytic performance of the catalyst leads to a higher $r_{(002)/(100)}$. The two correlations were optimized to determine new experimental conditions to achieve higher photocatalytic activity and $r_{(002)/(100)}$ in the given intervals of the parameters' values. The optimization resulted in the same parameter sets for both outputs and were used to carry out new experiments. The samples prepared during the optimization experiments were examined using XRD, DRS, SEM and their photocatalytic performance was measured, which confirmed the improved photocatalytic performance and higher $r_{(002)/(100)}$.

T2. ZnO solid spheres with a tunable average diameter and a tunable ratio of intensities of (002) and (100) can be synthesized with a mixed precursor approach.

T2.1. Spherical ZnO photocatalysts were successfully synthesized using diethanolamine as the morphological agent and two different precursors. It was determined that at least 99% ethanol concentration is necessary for the spherical morphology and at this concentration can be achieved high photocatalytic activity while maintaining the spherical morphology. Using XRD, it was proven that water is necessary for the efficient crystallization of ZnO, but in excess could lead to the formation of $Zn(OH)_2$ crystal phase. It was proven via photocatalytic activity measurements that the higher activity is caused by the lack of $Zn(OH)_2$ phase, during the degradation of phenol under UV-A irradiation.

T2.2. The average diameter of the ZnO spheres can be tuned in the range of 0.105-3.300 μm by adjusting the composition of the precursor mixture prepared from zinc-acetate and –acetylacetonate, also to a lower extent by the temperature of the solvothermal treatment. Using SEM measurements, the average diameter of spheres was determined for ZnO prepared from pure and a mixture of precursors (zinc acetylacetonate and acetate). It was shown that the diameter of spheres obtained from precursor mixtures is proportional to the composition of the mixture.

T2.3. The anisotropic growth of the ZnO crystallites can be induced towards (002) orientation by the synthesis temperature. The XRD and SEM measurements showed that the preferential orientation of crystallites is still possible despite the applied morphological modification. The ratio of intensities of XRD peaks corresponding to (002) and (100) ($r_{(002)/(100)}$) was increased with the increased temperature. The cause of the change in $r_{(002)/(100)}$ was the size anisotropy of the crystallites in the two directions of the crystals, which was deduced using three different calculation methods of crystallite size, Scherrer equation, W-H and SSP.

T2.4. The mechanism of formation of the ZnO spheres from anisotropic crystallites was pointed out. The formation of spheres takes place in three phases: crystallite formation, preferential growth and agglomeration into spherical particles. TEM measurements revealed that the spheres are composed of smaller crystallites, which was also supported by estimations made from specific surface area measurements. In addition, TEM measurements revealed that the size of those crystallites can be more accurately estimated using the W-H method.

T2.5. Size anisotropy is the most determining factor of the photocatalytic activity of ZnO for phenol degradation under UV-A irradiation. The photocatalytic performance of ZnO spheres was correlated with the structural feature ($r_{(002)/(100)}$), specific surface area, the average diameter of ZnO spheres, and $r_{(002)/(100)}$ influenced the catalytic activity. Using photoluminescence measurements and XRD data, it was deduced that the increased orientation of crystallites along (002) is due to the increased trapping of photogenerated electrons at oxygen vacancy sites, which have a higher probability of formation on facets corresponding to (002) planes.

T3. The formation of hollow spherical morphology and noble metal deposition increases the photocatalytic activity of ZnO.

T3.1. The hollow spherical morphology of ZnO was successfully achieved by applying carbon sphere templates and in the solvothermal synthesis of ZnO, respectively their removal by heat treatment. Also, the synthesis parameters, such as synthesis method, precursor, and precursor/CS mass ratio were tuned to optimize hollow spherical morphology. The coating of the CSs was the most successful in the case of zinc acetylacetonate used as precursor.

T3.2. The structural orientation, specific to the original synthesis method (T1.1), was preserved and further intensified by applying the CS templates proved by XRD measurements. The increased presence of oxygen vacancies in the ZnO HSs was proved by PL measurements and the cause was established to be the removal of surface oxygens, due to the increased orientation in the direction of (002). In addition, despite the high carbon content of the ZnO-CS composites, the preferential orientation was less changed due to calcination compared to the calcined reference materials (ZnO nanorods and solid spheres).

T3.3. It was proved that Au and Pt nanoparticles can be deposited on the surface of ZnO HSs while retaining the unique morphology and greatly improving the photocatalytic activity. The photocatalytic activity of HSs was superior to the reference materials (template ZnO nanorods and solid spheres) and the noble metal-HSs composite to the plain ZnO HSs. ZnO HSs, respective their noble metal composites showed superior photocatalytic activity in the case of degradation of three different model pollutants phenol, diuron and ibuprofen. The best-performing catalyst (ZnO-HS-Pt) was measured in simulated wastewater treatment, which reduced only slightly its catalytic activity, despite the relatively high concentration of inorganic impurities in the suspension.

5. Applicability of the scientific results

During the present research, zinc oxide-based photocatalysts were synthesized and increased their photocatalytic performance by applying various methods. The results presented may provide a good guideline that by applying more advanced experimental designs the effect of synthesis parameters and photocatalytic activity can be easily correlated, and can also be used to relate certain material proprieties to the photocatalytic activity. The results demonstrate methods to enhance the photocatalytic performance of ZnO photocatalysts by modifying their structural, morphological and optical properties. Moreover, these modifications are not exclusive and can be applied concurrently.

Considering the increasing expansion of the research field, it could seem disappointing that heterogenous photocatalysis still falls behind the requirements of a large-scale application. As such, the main aim of the present work is to highlight a structural feature as a key indicator of possible high photocatalytic activity, which is the preferential orientation of the crystallites along the (002) crystallographic plane. I hope that these results may represent valuable insight into the development of new types of photocatalysts and other materials too.

6. Publications and conference participations

Hungarian Scientific Bibliography (MTMT) identifier: 10078813

Publications related to the scientific topic of the dissertation:

[1] **Z. Kovács,** C. Molnár**,** U. L. Štangar, V.-M. Cristea, L. Baia, Zs. Pap, K. Hernadi: *Optimization Method of the Solvothermal Parameters Using Box–Behnken Experimental Design—The Case Study of ZnO Structural and Catalytic Tailoring*
Nanomaterials, 11(5) (2021) 1334.
IF = 5.719

[2] **Z. Kovács,** C. Molnár**,** T. Gyulavári, K. Magyari, Zs.-R. Tóth, L. Baia, Zs. Pap, K. Hernadi: *Solvothermal synthesis of ZnO spheres: Tuning the structure and morphology from nano- to micro-meter range and its impact on their photocatalytic activity*
Catalysis Today, 397-399 (2022) 16-27.
IF = 6.562

[3] **Z. Kovács,** V. Márta, T. Gyulavári, Á. Ágoston, L. Baia, Zs. Pap, K. Hernadi: *Noble metal modified (002)-oriented ZnO hollow spheres for the degradation of a broad range of pollutants*
Journal of Environmental Chemical Engineering, 10(3) (2022) 107655.
IF = 7.968

ΣIF = 20.249

ΣCitations = 16 (Independent: 14)

Other publications:

[4] T. Gyulavári, K. Kovács, **Z. Kovács**, E. Bárdos, G. Kovács, K. Baan, K. Magyari, G. Veréb, Zs. Pap, K. Hernadi: *Preparation and characterization of noble metal modified titanium dioxide hollow spheres – new insights concerning the light trapping efficiency*
Applied Surface Science, 534 (2020) 147327.
IF = 6.182

[5] T. Gyulavári, V. Márta, **Z. Kovács**, K. Magyari, Zs. Kása, G. Veréb, Zs. Pap, K. Hernadi: *Immobilization of highly active titanium dioxide and zinc oxide hollow spheres on ceramic paper and their applicability for photocatalytic water treatment*
Journal of Photochemistry and Photobiology A: Chemistry, 427 (2022) 113791.
IF = 5.141

ΣIF = 11 .323

ΣCitations = 14 (Independent: 12)

International conference participations:

(1) **Zoltán Kovács**, Tamás Gyulavári, Zsejke-Réka Tóth, Áron Ágoston, Klára Magyari, Zsolt Pap, Klára Hernádi, Lucian Baia: *Preparation of ZnO photocatalysts with tunable spherical morphology, structure and evaluation of their photocatalytic activity*
11th European Conference on Solar Chemistry and Photocatalysis: Environmental Applications Turin, Italy (2022) – poster presentation

(2) Zsolt Kása, Eszter Orbán, **Zoltán Kovács**, Klára Hernádi, Imre Ábrahám, Zsolt Pap: *BiOI immobilization technique on ceramic paper and photocatalytic application*
6th European Conference on Environmental Applications of Advanced Oxidation Processes
Portoroz, Slovenia (2019) – poster presentation

(3) **Zoltán Kovács**, Zsolt Pap, Klára Hernádi, Lucian Baia: *Comparison of photocatalytic properties of ZnO/strontium aluminate phosphor composites prepared by in-situ solvothermal and impregnation methods*
6th European Conference on Environmental Applications of Advanced Oxidation Processes
Portoroz, Slovenia (2019) – poster presentation

(4) Alpár Ravasz, Endre-Zsolt Kedves, Zsejke-Réka Tóth, Enikő Bárdos, Szilvia Fodor, **Zoltán Kovács**, Zsolt Pap, Klára Hernádi, Lucian Baia: *Photocatalytic investigation of AgBr, BiOI, Cu_2O and ZnO semiconductors' binary compositeswith orthorhombic MoO_3*
6th European Conference on Environmental Applications of Advanced Oxidation Processes
Portoroz, Slovenia (2019) – poster presentation

(5) **Zoltán Kovács**, Zsolt Pap, Klára Hernádi, Lucian Baia: *Optimization of solvothermal synthesis of ZnO for the enhancement of the photocatalytic efficiency using Box-Behnken design*
II. Sustainable Raw Materials International Project Week And Scientific Conference
Szeged, Hungary (2019) – oral presentation

(6) **Zoltán Kovács**, Zsolt Pap, Klára Hernádi, Vasile-Mircea Cristea, Lucian Baia: *Optimization of solvothermal synthesis of ZnO for the enhancement of the photocatalytic efficiency using Box-Behnken design*
12th International Conference on Physics of Advanced Materials
Crete, Greece (2018) – oral presentation

(7) **Zoltán Kovács**, Zsolt Pap, Lucian Baia, Klára Hernádi: *The synthesis of shape-tailored zinc oxide nanostructures and blackbox modelling approach of its synthesis procedure*
5th European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP5)
Prague, Czechia (2017) – poster presentation

National conference participations:

(1) **Zoltán Kovács**, Klára Hernádi, Lucian Baia, Zsolt Pap: *Kémiai kicsapás és szolvotermális módszerrel előállított Dy(III)-val szennyezett ZnO alapú fotokatalizátorok előállítása és fotokatalitikus vizsgálata*
A Magyar Tudományos Akadémia Analitikai és Környezeti Kémiai Bizottságának 8. Környezetkémiai Szimpóziuma
Siófok, Hungary (2018) – oral presentation

(2) **Zoltán Kovács**, Szilvia Fodor, Lucian-Cristian Pop, Zsolt Pap: *A ZnO/Pt/redukált grafit-oxid hármas kompozit fotokatalizátorok előállítása és összehasonlítása kémiai redukciós és impregnálás módszerrel*
XXIV. Nemzetközi Vegyészkonferencia, 24th International Conference on Chemistry

Sovata, Romania (2018) – poster presentation

(3) Alpár Ravasz, Endre-Zsolt Kedves, Zsejke-Réka Tóth, Enikő Bárdos, Szilvia Fodor, **Zoltán Kovács**, Zsolt Pap, Klára Hernádi, Lucian Baia: *MoO_3 hatása az AgBr, BiOI, Cu_2O és ZnO fotokatalizátorok aktivitására*
XXIV. Nemzetközi Vegyészkonferencia : 23rd International Conference on Chemistry
Sovata, Romania (2018) – poster presentation

(4) **Zoltán Kovács**, Zsejke-Réka Tóth, Zsolt Pap, Klára Hernádi, Lucian Baia, Gábor Kovács: *AgBr/ZnO fotokatalizátorok jellemzése és fotokatalitikus aktivitásának vizsgálata*
XXIII. Nemzetközi Vegyészkonferencia : 23rd International Conference on Chemistry
Deva, Romania (2017) – poster presentation

(5) **Zoltán Kovács**, Zsolt Pap, Vasile-Mircea Cristea, Klára Hernádi: *A ZnO szolvotermális előállítása és fotokatalitikus aktivitásának optimalizálása Box-Behnken kísérlettervezet segítségével*
XXIII. Nemzetközi Vegyészkonferencia : 23rd International Conference on Chemistry
Deva, Romania (2017) – oral presentation

(6) **Zoltán Kovács**, Zsolt Pap, Lucian Baia, Klára Hernádi: *ZnO alapú fotokatalizátorok hidrotermális előállítása, strukturális és fotokatalitikus vizsgálata*
XXII. Nemzetközi Vegyészkonferencia : 22rd International Conference on Chemistry
Timișoara, Romania (2016) – poster presentation

(7) Zsolt Pap**,** Szilvia Fodor, **Zoltán Kovács**, Tamás Gyulavári, Gábor Kovács, Zsejke-Réka Tóth, Zsolt Kása, Enikő Bárdos, Georgina Rózsa, Gergő Simon, Zsuzsanna Kozmér et al.: *New nanocomposites and nanostructures in water cleaning*
XXII. Nemzetközi Vegyészkonferencia : 22rd International Conference on Chemistry
Timișoara, Romania (2016) – oral presentation

(8) **Zoltán Kovács**, Bíborka Boga, István Székely, Gábor Kovács, Lucian Baia, Klára Hernádi, Zsolt Pap: *Sensors of the future and the shape controlled photocatalysts. Simultaneous pollutant removaland detection*
5th Symposium on Environmental Chemistry
Tihany, Hungary (2016) – oral presentation

(9) Zsolt Pap**,** Gábor Kovács, Zsejke-Réka Tóth, Krisztina Vajda, Éva Karácsonyi, Zsolt Kása, Szilvia Fodor, Endre-Zsolt Kedves, István Székely, Kata Saszet, **Zoltán Kovács** et al.: *The Functioning Mechanism of Photocatalytic Systems from the Charge Transfer Point ofView. The Adventure of the Electron.*
XXI. Nemzetközi Vegyészkonferencia : 21th International Conference on Chemistry
Șumuleu Ciuc, Romania (2015) – oral presentation

(10) Zsolt Pap**,** Gábor Kovács, István Székely, Endre-Zsolt Kedves, Boglárka Hampel, Szilvia Fodor, Zsejke-Réka Tóth, Eszter Orbán, **Zoltán Kovács** et al.: *Nanoszerkezetű fotokatalizátorok és kompozitjaik – alakszobrászat és aktivitás*
XX. Nemzetközi Vegyészkonferencia : 20th International Conference on Chemistry
Cluj-Napoca, Romania (2014) – oral presentation