Doctoral (Ph. D.) Theses

Synthesis and characterization of visible light active copper-based semiconductors

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1. INTRODUCTION AND AIMS

The already available water purification methods do not provide a proper solution for the elimination of certain organic pollutants (including drug residues) from wastewaters. The advanced oxidation processes (AOPs) are worth considering as an applicable option for the removal of detectable pollutants, which exceed the legal limits in many cases.

One of the AOPs is heterogeneous photocatalysis, in which the excitation of a semiconductor with (visible) light allows the decomposition of these organic contaminants. The best situation would be if the excitation were to be carried out using sunlight, and thus water purification would be achieved with this hitherto untapped alternative energy source.

Although this solution may not seem very cost-effective at first glance, however if we consider that semiconductor production can be expensive , while is the operational costs are low, this technological option is viable.

Nevertheless, I think the real solution may be to combine the advantages of the already used classical water purification processes and photocatalysis, and thus could be the icing on the cake.

The aim of my doctoral work was to produce and develop copper-based semiconductors that exhibit efficient photocatalytic activity during excitation in visible light.

2. EXPERIMENTAL METHODS, PROCEDURES

The copper-based semiconductors to be tested were synthesized by two different methods (reduction, solvothermal production). The nomenclature of the samples was with labeling the precursor salt (Cl / Ac), stabilizer agent (EDTA / PVP) and the synthesis temperature (60 ° C / 70 ° C / 80 ° C / 180 ° C). The samples were characterized by different methods and their photocatalytic activity was also investigated.

The morphological characteristics of the samples were examined by scanning electron microscopy (SEM), and the homogeneity of the sample was studied in some samples by recording the element map. Transmission electron microscopy (TEM) measurements were performed to refine the morphological characterization of the samples.

X-ray diffractometry (XRD) measurements were performed to examine the crystal phase, degree of crystallinity, particle size and the effect of the heat treatment. From the X-ray diffractograms, the primary particle sizes of the samples were calculated using the Scherrer equation. Infrared spectroscopy (IR) was also used for further structural characterization of the particles.

Diffuse reflectance spectroscopy (DRS) was used to detect the reflectivity as well as the light absorption of the solid samples. From the diffuse reflection spectra, the band gap values of the photocatalysts were calculated with the Kubelka-Munk equation and the maximum light absorption of the samples by thus first-order derivation.

The particle size distribution of the samples in aqueous medium was monitored by dynamic light scattering measurements (DLS). Measurements were preceded by two hours of ultrasonic treatment to ensure a homogeneous suspension.

Nitrogen adsorption measurements were used to determine the specific surface area of the samples, and the Brunnauer-Emett-Teller (BET) relationship was used to evaluate the results.

Photocatalytic activity was measured by irradiation with visible light. To stabilize the experimental conditions and to reduce the heat generated by the light source, sodium nitrite (1 M aqueous solution) was circulated, this also ensured the exclusion of small amounts of UV photons from the light source.

The suspension concentration was 1 mg · mL^{-1} in each case, and an aqueous solution of methyl orange (30 mM) and rhodamine B (0.02 mM) was used as model contaminants. The first step of the test was preceded by a homogenization step for 10 minutes (ultrasonication, in dark) to establish adsorption equilibrium. Homogeneous distribution and oxygen saturation were also ensured by continuous air bubbling and agitation after the sample entered the reactor.

The duration of the test was 120 minutes in each case, during which samples were taken every 10 minutes in the first hour and every 20 minutes in the second hour. After centrifugation and filtration of the samples, the change in the concentration of the used model compound (methyl orange, rhodamine B) was monitored by spectrophotometric method.

From the results conversion values (%) were calculated, which show the percentage of the initial concentration of the model contaminant that was degraded during the 120-minute test during a given measurement.

3. NEW SCIENTIFIC RESULTS

T1. We proved that the Cu_2O particles showed different morphological characteristics under the influence of the stabilizing agent. In the presence of ethylenediaminetetraacetic acid (EDTA), isomorphic, homogeneously distributed microcubes were formed, while in the presence of polyvinylpyrrolidone (PVP), isomorphic microcrystals with a rhombocuboctahedral morphology were developed. In this case, by increasing the synthesis temperature, Cu nanoparticles appeared in addition to microcrystals as well.

PVP shows selective adsorption on the surface of copper oxide, stabilizing the newly formed crystals. During the preparation of the particles, it kinetically regulates the growth rate of Cu_2O on different crystal sides through adsorption to surfaces. In contrast, EDTA complexes the Cu^{2+} due to its chelating ligand properties, inhibiting its reduction to Cu^0.

Using PVP as a stabilizer agent, all the reflections characteristic of Cu_2O showed signs of the presence of copper nanoparticles in the sample. A certain amount of Cu nanoparticles may also increase the efficiency of photocatalytic activity. We have shown that by increasing the temperature of the synthesis, the amount of Cu appearing also increases. In contrast, EDTA, due to its chelating ligand properties, complexes the Cu2 + ion, inhibiting its reduction to Cu0.

T2. It has been proved that the size of the Cu2O particles can be controlled by increasing the synthesis temperature and the hydrodynamic diameter varies depending on the precursor salt used. We demonstrated that by

controlling the particle size and hydrodynamic diameter, the available specific surface area can be increased, thus supporting the increased outcome of photocatalytic processes.

As the synthesis temperature of the photocatalysts increased, the hydrodynamic particle size decreased when $Cu(Ac)_2 \cdot H_2O$ was used as a precursor. This means that the specific surface area available for the photocatalysis process increases, so that photocatalytic processes in aqueous suspensions, as well as photocatalytic activity, can be enhanced.

T3. We have demonstrated that the concentration of photogenerated holes (h^+) in the Cu_2O samples can be controlled by the applied reducing sugars, which is also related to the degree of crystallinity of the samples.

The resulting localized surface plasmon resonance, which confirms the appearance of copper vacancies, is related to the degree of crystallinity of the samples. The peak suggesting this is found in the Cu_2O_XY and Cu_2O_AR samples for the primary derivatives of the diffuse reflection spectra, which showed the highest degree of crystallinity during the evaluation of the XRD patterns.

The activity of Cu_2O photocatalysts by using different reducing sugars depends on the specific surface area of the sample and the optical properties of the different copper species. The change in the ratio of the conduction band (639 nm) to the exciton band (595 nm) as well as the change in the specific surface area of the particles explain the magnitude of the photocatalytic excitability.

T4. The appearance of the defect sites during the preparation of copper sulfide samples is confirmed by the vibration peak of the Cu-S bond (270 cm^{-1})

and the vibration peak of the $Cu_{2-x}S$ ($0,6 \leq \times \leq 1$) vacancies - $Cu_{vac}S$ (322 cm^{-1}). We found that the value of this ratio varies as a function of precursor salt used, so that the appearance of defect sites influencing the photocatalytic activity becomes controllable.

To study the transformations of the crystalline structure (150–1500 cm^{-1}), in evaluating the results of Raman studies we observed a signal at 476 cm^{-1} to vibrate (stretch) the covalent S-S bonds with a higher intensity in the Cu_xS^{Ac} sample series. In addition, the peak responsible for the vibration of the Cu-S bond (270 cm-1) and, at 322 cm^{-1}, the peak explaining the appearance of the vacancies ($Cu_{vac}S$) also appear.

For samples obtained from $CuCl_2$, the peak intensity associated with the defect sites shows a higher value. Because the presence of defect sites can improve photocatalytic performance, these observations can be positive predictions when evaluating activity tests.

T5. Depending on the stabilizer used, the formation of Cu_xS particles with different morphological characteristics can be observed: the morphology of the microparticles produced in the presence of EDTA is lamellar, with the use of PVP the particles with lamellar morphology build hierarchical structures - which show spherical morphology.

The advantage of producing PVP-stabilized particles is that they can control particle size and maintain a constant particle morphology. As demonstrated for Cu_xO samples, EDTA can form the Cu^{2+} complex compound (chelate), which can prevent the complete reduction of Cu^{2+} to Cu.

The effect of the stabilizer is also closely related to the change in the degree of crystallinity of the samples. The degree of crystallinity of the Cu_xS^{Cl} sample series differs from the values observed for the Cu_xS^{Ac} sample series, this value is higher for samples obtained from $CuCl_2$. It can also be observed in these samples that the intensity of the reflection responsible for the crystal plate (008) is significantly higher compared to the Cu_xS^{Ac} series.

T6. Subsequent heat treatment increases the specific surface area of the catalysts, which can be explained by the rearrangement of hierarchical structures. This phenomenon affects the photocatalytic activity and adsorption capacity of the samples. We have demonstrated that morphological degradation (PVP) or the formation of spherical-oriented hierarchical particles (EDTA) occurs as a function of the stabilizer.

Several changes can be observed under the heat treatment: in the case of the Cu_xS^{Cl} sample series, the PVP-stabilized sample undergoes morphological degradation under the heat treatment, in the case of the Cu_xS^{Cl} sample series with the EDTA-stabilized sample, on the other hand.

For Cu_xS^{Ac} samples, no significant change was observed as a result of heat treatment; the values observed during the examination of the basic catalysts do not change significantly.

4. APPLICABILITY OF THE SCIENTIFIC RESULTS

The aim of my doctoral research was the synthesis of copper-based semiconductors that show photocatalytic activity under visible light, thus providing an opportunity to modernize water purification processes.

For me the doctoral research work carried out was beneficial from a scientifical point of view but also for my professional development, since I was able to discuss my experiences at conferences with researchers who had encountered such problems on similar topics from other corners of the world, and due to the different shared perspectives, these scientific exchanges could help to drive towards a common goal.

The present work proved that copper-based compounds have many possibilities and I think that with my work I was able to underline that subtle changes in production parameters (temperature, reducing agent, stabilizer agent, precursor salt) can result in significant differences in structural, morphological, optical, and photocatalytic activity of the samples.

5. SCIENTIFIC ACTIVITY

5.1. PUBLISHED PAPERS, RELATED TO THE THESIS

1. **Sz Fodor**, K Mucsi, Zs Pap, K Hernádi, L Baia, Hőmérséklet hatása a réz-alapú fotokatalizástorok előállításában és hőkezelésében, *Proceedings of the 23rd International Symposium on Analytical and Environmental Problems* 23 (**2017**) 401-405. (ISBN:978-963-306-563-1)

2. **Sz Fodor**, L Baia, M Focșan, K Hernádi, Zs Pap, Designed and controlled synthesis of visible light active copper(I)oxide photocatalyst: From cubes towards the polyhedrons - with Cu nanoparticles, *Applied Surface Science* 484 (**2019**) 175–183.

(I.F. 4,439)

3. **Sz Fodor**, L Baia, K Hernádi Zs Pap, Controlled Synthesis of Visible Light Active CuxS Photocatalyst: The Effect of Heat Treatment on Their Adsorption Capacity and Photoactivity, *Materials* 13 (**2020**) 3665.

(I.F. 3,057)

4. **Sz Fodor**, L Baia, K Baán, G Kovács, Zs Pap, K Hernadi, The Effect of the Reducing Sugars in the Synthesis of Visible-Light-Active Copper(I) Oxide Photocatalyst, *Molecules* 26 (**2021**) 1149.

(I.F. 3.267)

Σ I.F.=10.763

5.2. PUBLISHED PAPERS NOT RELATED TO THE THESIS

1. G Kovács, **Sz Fodor**, A Vulpoi, K Schrantz, A Dombi, K Hernádi, V Danciu, Zs Pap, L Baia, Polyhedral Pt vs. spherical Pt nanoparticles on commercial titanias: Is shape tailoring a guarantee of achieving high activity?, *Journal of Catalysis* 325 (**2015**) 156–167.

(I.F. 7.354)

2. L Baia, E Orbán, **Sz Fodor**, B Hampel, E Zs Kedves, K Saszet, I Székely, É Karácsonyi, B Réti, P Berki, A Vulpoi, K Magyari, A Csavdári, Cs Bolla, V Coșoveanu, K Hernádi, M Baia, A Dombi, V Danciu, G Kovács, Zs Pap, Preparation of TiO_2/WO_3 composite photocatalysts by the adjustment of the semiconductors' surface charge, *Materials Sciencein Semiconductor Processing* 42 (**2016**) 66–7.

(I.F. 1.955)

3. **Sz Fodor**, Zs Pap, K Hernádi, G Kovács, L Baia, Pd és Pt nanorészecskék alakjának hatása fotokatalitikus hidrogénfejlesztés során, *Acta Scientiarum Transylvanica - Chimica* 25 (**2017**) 7-16. (ISBN/ISSN: 1842-5089)

4. **Sz Fodor**, G Kovács, K Hernádi, D Virginia, L Baia, Zs Pap, Shape tailored Pd nanoparticles' effect on the photocatalytic activity of commercial TiO_2, *Catalysis Today* 284 (**2017**) 137–145.

(I.F. 4.312)

5. E Bárdos, V A Márta, **Sz Fodor**, E-Zs Kedves, K Hernadi, Zs Pap, Hydrothermal crystallization of the bismuth oxychlorides (BiOCl) using different shape control reagents, *Materials* (**2021**).

(I.F. 3.057)

Σ I.F.=27.441

5.3. LECTURES, POSTERS, CONFERENCE PARTICIPATIONS

International / Foreign language first author lecture

1. **Sz Fodor**, G Kovács, Zs Pap, D Virginia, V Adriana, M Klára, A Dombi, K Hernadi, L Baia: *Kereskedelmi TiO_2 módosítása Pt nanokockákkal/gömbökkel: Pt nanorészecske alakjának hatása a szennyezők fotokatalitikus bontására, illetve a H_2 fejlesztésre*, XIX. Nemzetközi Vegyészkonferencia, Nagybánya, Romania, 2013. november 21-24.
2. **Sz Fodor**, Zs R Tóth, Zs Pap, L Baia, D Virginia, A Vulpoi, K Magyari, A Dombi K Hernadi, G Kovács: *The influence of Pt/Au nanoparticles' shape on activity of commercial TiO_2 photocatalysts*, E-MRS Spring Meeting, Lille, France, 26-30 May 2014.

3. G Kovács & Zs R Tóth & **Sz Fodor**, Zs Pap, D Virginia, A Dombi, K Hernadi, L Baia: *Differently shaped Pt/Au nanoparticles: activity enhancement of commercial* TiO_2 *photocatalysts,* 8th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, Thessaloniki, Greece, 25- 28 june 2014.
4. **Sz Fodor**, Zs Pap, G Kovács, L Baia, D Virginia, A Vulpoi, A Dombi, K Hernadi: *Pd nanorészecske alakjának hatása a szennyezők fotokatalitkus bontására*, *illetve* H_2 *fejlesztésre,* XX. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia, 2014. november 6-8.
5. **Sz Fodor**, K Saszet, B Hampel, T Makó, M Abrudbányai, H Vadas, D Virginia, L Baia, E Gál, G Kovács, Zs Pap, *Solar light activated photocatalysts in the service of the society: the sinergy of photocatalysis and sociology,* E-MRS Spring Meeting, Lille, France, 11-16 May 2015.
6. **Sz Fodor**, A Csavdári, Zs Pap: *Investigation of photocatalytic activity of Pd, Pt modified* TiO_2, XIIIth edition of International Conference Students for Students, Cluj-Napoca, Romania, 13-17 April 2016.
7. **Sz Fodor**, Zs Pap, K Hernadi, G Kovács, L Baia: Különböző alakú nemesfémekkel módosított TiO_2 fotokatalizátorok hatékonysága fotokatalitikus hidrogénfejlesztésben, 22nd International Symposium on Analytical and Environmental Problems, Szeged, Magyarország, 2016. október 10.
8. **Sz Fodor**, Zs Pap, K Hernadi, G Kovács, L Baia: *Pd és Pt nanorészecskék alakjának hatása* TiO_2 *fotokatalitikus aktivitására*, XXII. Nemzetközi Vegyészkonferencia, Temesvár, Románia, 2016. november 3-6.
9. **Sz Fodor**, Zs Pap, K Hernadi, G Kovács, L Baia: *Különböző alakú nemesfémekkel módosított* TiO_2 *fotokatalizátorok hatékonysága*

fotokatalitikus hidrogénfejlesztésben, XV. Erdélyi Természettudományi Konferencia, Kolozsvár, Románia, 2016. novenber 26.

10. **Sz Fodor**, K Mucsi, Zs Pap K Hernadi, L Baia: *Synthesis and characterization of different shape Cu_xO and Cu_xS nanocrystals,* 5th European Conference on Environmental Applications of Advanced Oxidation Processes, Prague, Czech Republic, 25-29 June 2017.
11. **Sz Fodor**, M Kata, Zs Pap, K Hernadi, L Baia: *Hőmérséklet hatása a réz-alapú fotokataliyátorok előállításában és hőkezelésében,* 23rd International Symposium on Analytical and Environmental Problems, Szeged, Hungary, 2017 október 9-10.
12. **Sz Fodor**, M Kata, Zs Pap, L Baia, K Hernadi: *Réz-alapú félvezetők előállításának és kalcinálásának befolyásolása hőmérséklet szabályozással*, XXIII. Nemzetközi Vegyészkonferencia, Déva, Románia, 2017. október 25-28.
13. **Sz Fodor**, Zs Pap, L Baia, K Hernadi: Investigation of photocatalytic activity of Pd, Pt modified TiO_2, 3rd International Symposium on Nanoparticles-Nanomaterials and Applications, Caparica, Portugal, 22-25 January 2018.
14. **Sz Fodor**, Zs Pap, L Baia, K Hernadi: *effect of the precursor and the temperature in synthesis of Cu_2O,* 12th International Conference on Physics of Advanced Materials, Heraklion, Greece, 22-28 September 2018.
15. **Sz Fodor**, Zs Pap, L Baia, K Hernadi: *Réz-alapú félvezetők előállítási paramétereinek szabályozása,* XXIV. Nemzetközi Vegyészkonferencia, Szováta, Románia, 2018 október 24-27.
16. **Sz Fodor**, Zs Pap, L Baia, K Hernadi: *Sinthesys and characterization of visible light active Cu_2S crystals,* 6th European Conference on Environmental Applications of Advanced Oxidation Processes, 26-30 June 2019, Portorose, Slovenia.

17. D Dusnoki, **Sz Fodor**, Zs Pap, K Hernadi: *Photocatalytic efficiency of copper(I) oxide-noble metal composite systems*, 6th European Conference on Environmental Applications of Advanced Oxidation Processes, Portorose, Slovenia, 26-30 June 2019.
18. **Sz Fodor**, Zs Pap, L Baia, K Hernadi: *Redukáló cukrok szerepe a réz(I)-oxid előállításában,* XXV. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia, 2019 október 24-26.

International / Foreign language co-author lecture

1. E Orbán, E Zs Kedves, K Saszet, **Sz Fodor**, B Hampel, Zs R Tóth, I Székely, G Kovács, Zs Pap, D Virginia, L Baia: *TiO_2/WO_3 kompozit fotokatalizátorok előállítása a félvezetők felületi töltésének módosításával,* XX. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia, 2014. november 6-8.
2. Zs Pap, G Kovács, I Székely, E Zs Kedves, K Saszet, B Hampel, **Sz Fodor**, Zs R Tóth, E Orbán, Z Kovács, K Hernadi, A Dombi, Zs Kása, K Vajda, É Karácsonyi, D Virginia, A Vulpoi, V Coșoveanu, L Baia: *Nanoszerkezetű fotokatalizátorok és kompozitjaik-alakszobrászat és aktivitás,* XX. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia, 2014. november 6-8.
3. Zs Pap, G Kovács, Zs R Tóth, K Vajda, É Karácsonyi, Zs Kása, **Sz Fodor**, E Zs Kedves, I Székely, K Saszet, B Hampel, Zs Czekes, E Orbán, Z Kovács, D Virginia, L Baia, A Dombi: *The Functioning Mechanism of Photocatalytic Systems from the Charge Transfer Point of View. "The Adventure of the Electron",* XXI. Nemzetközi Vegyészkonferencia, Csíksomlyó, Románia, 2015. november 23-25.
4. Zs Pap, **Sz Fodor**, T Gyulavári, G Kovács, Ys R Tóth, Kása Zsolt, E Bárdos, G Rózsa, G Simon, Zs Kozmér, M Rusu, K Hernadi, L Baia, M Baia, I

Székely, E Zs Kedves, B Boga, A Ravasz, B Hampel, Z Kovács, K Saszet, D Virginia, V Coșoveanu, K Vajda, É Karácsonyi, L C Pop, Zs Czekes, Zs Nagy, K Magyari, T Milica, A Vulpoi, G Veréb, E Orbán, A Dombi: *Új nanokompozitok és nanoszerkezetek a víztisztításban*, XXII. Nemzetközi Vegyészkonferencia, Temesvár, Románia, 2016. november 3-6.

5. D Dusnoki, **Sz Fodor**, Zs Pap, K Hernadi: *Réz(I)oxid-nemesfém rendszerek előállítása és jellemzése*, XXIV. Nemzetközi Vegyészkonferencia, Szováta, Románia, 2018 október 24-27.
6. Z Kovács, **Sz Fodor**, L C Pop, Zs Pap: *A ZnO/Pt/redukált grafit-oxid hármas kompozit fotokatalizátorok előállítása és összehasonlítása kémiai redukciós és impregnálás módszerrel*, XXIV. Nemzetközi Vegyészkonferencia, Szováta, Románia, 2018 október 24-27.
7. A Ravasz, E Zs Kedves, Zs R Tóth, E Bárdos, **Sz Fodor**, Z Kovács, Zs Pap, K Hernadi, L Baia: *MoO_3 hatása az AgBr, BiOI, Cu_2O és ZnO fotokatalizátorok aktivitására*, XXIV. Nemzetközi Vegyészkonferencia, Szováta, Románia, 2018 október 24-27.
8. D Dusnoki, **Sz Fodor**, Zs Pap, K Hernadi: *Réz(I)-oxid-titán dioxid kompozitok fotokatalitikus aktivitásának vizsgálata*, XXV. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia 2019 október 24-26.
9. A Ravasz, E Zs Kedves, Zs R Tóth, E Bárdos, **Sz Fodor**, Z Kovács, Zs Pap, K Hernadi, L Baia: *α-MoO_3 tartalmú bináris kompozitrendszerek fotokatalitikus aktivitásának vizsgálata*, XXV. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia, 2019 október 24-26.

First author's lecture in Hungarian / Hungarian

1. **Sz Fodor**: *Pd-al módosított TiO_2 nanokompozitok előállítása, jellemzése és szerepük környezetünk tisztaságának megőrzésében*, Balassi Intézet, Márton Áron Szakkollégiumi Zárókonferencia, Budapest, Magyarország, 2016. május 27-29.
2. **Sz Fodor** & Zs R Tóth: *Különböző geometriájú nemesfém nanorészecskékkel módosított TiO_2 fotokatalizátorok hatása fenol bontásában,* V. Környezetkémiai Szimpózium, Tihany, Magyarország, 2016. október 6-7.
3. **Sz Fodor**, K Mucsi, Zs Pap, K Hernadi: *Cu_xS félvezető katalizátorok előállítása és anyagszerkezeti vizsgálata,* PhD – konferencia - Külgazdasági és Külügyminisztérium - Szegedi Tudományegyetem, Szeged, Magyarország, 2017. március 4.
4. **Sz Fodor:** *Cu_xO félvezetők előállítása, anyagszerkezeti vizsgálata és fotokatalitikus aktivitásának vizsgálata***,** Külgazdasági és Külügyminisztérium - Márton Áron Kutatói Program Zárókonferencia, Budapest, Magyarország, 2017 június 16.
5. **Sz Fodor**, Zs Pap, K Hernadi: *Cu_2O/CuO mikrorendszerek morfológiai szobrászata*, ELTE MÁSZ PhD-konferencia, Debrecen, Magyarország