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Theses of Doctoral (Ph.D.) Dissertation

**Synthesis and characterization of oxid-based complex
photoelectrodes**

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Introduction and objectives

Because of the increasing effects of climate change, several researches are focusing on the development of new, environment friendly energy sources as well as on the production of fuels by recycling the already produced CO₂. Photoelectrochemistry addresses both points, by using solar energy to generate fuels.

Oxides are the most studied photoelectrodes due to their remarkable stability and electrical conductivity. Their valence band position makes these materials capable for the photoelectrochemical reduction of water (H₂-generation) and CO₂.

Many monometallic oxide, such as Cu₂O, TiO₂, have already been used in photoelectrochemical reduction processes. However, these compounds alone cannot fulfill all the criteria required for a good photoelectrode (they can photocorrode, their band position is not appropriate for reduction processes, they can absorb only a small part of the visible light, or the charge transport in the semiconductor is not satisfying).

There are two main approaches to overcome the deficiencies of single-metal oxides. In the first one, the oxide is combined with another material to form a composite. In the other one, a complex oxide is formed by the combination of two single-metal oxides. In these materials, better charge transport can be achieved, greater stability can be gained and they absorb a bigger portion of the visible light than the simple oxides.

During my doctoral research, I have studied both pathways. First, we wanted to examine how the morphology of the semiconductor

and the co-catalyst affected the efficiency of the photoelectrochemical process of nanostructured semiconductor/metal photoelectrodes. We wanted to produce a p-type NiO by anodization, and improve the photoelectrochemical activity of the porous photoelectrodes by applying Pt nanoparticles of different sizes and quantities as co-catalyst. We also aimed to investigate these composites in photoelectrochemical reduction of water.

My other goal was to create a p-type bimetallic oxide with a nanostructured morphology that provides efficient charge carrier transport. We wanted to produce a complex oxide (CuCrO_2) by solution combustion synthesis, which was not used in photoelectrochemical CO_2 reduction process yet. We aimed to synthesize nearly phase pure material by this time and energy efficient method.

Finally, our aim was to combine the nanostructured CuCrO_2 with CuFeO_2 that can provide a higher absorption of visible light, and was already applied in photoelectrochemical CO_2 reduction process. We wanted to create single-phase alloys as well as two-phase composites from the two materials and we wanted to compare the structure and electrochemical behavior of these materials to the two starting materials.

Experimental section

The NiO was synthesized by anodization which is an electrochemical etching process. During this process in the solution of a complexing agent there is a competition between the

complexation and the oxide formation, which in turn results in the formation of a porous structure.

The CuCrO_2 , CuFeO_2 and their alloys/composites were synthesized by solution combustion (SCS). The SCS is a fast and simple process in which a nitrate salt of a metal (oxidizing agent) is mixed with a fuel (reducing agent) and a porous solid is formed in a highly exothermic reaction.

The CuCrO_2 and CuFeO_2 complex oxides, their composites and alloys were spray-coated to the preheated glass carbon electrode surface and the applied amounts were always checked by weight measurement.

Photoelectrochemical behavior of the pure materials and their composites were studied by using linear scanning photovoltammogram in a standard three-electrode cell. During the measurement, the electrodes were illuminated by UV or visible light, which were periodically interrupted.

The bandgap width of the semiconductors was determined by UV-Vis spectroscopy and Incident-photon-to-electron conversion efficiency (IPCE) measurements.

Electrochemical impedance spectroscopy measurements were performed on the NiO and Pt/NiO samples to determine the origin of the increased photoelectrochemical activity.

During the long-term photoelectrolysis, a closed cell was used. The products in the gas phase were detected by gas chromatography. To prove that the products were produced in the photoelectrolysis ^{13}C isotope-labeled measurements were performed. NMR

spectroscopic measurements were performed to analyze the liquid samples.

To investigate the formation of CuCrO_2 and CuFeO_2 and their alloys, Raman and infrared spectroscopy and X-ray diffraction measurements were performed. To quantify the composition Rietveld refinement was performed on the diffractograms.

Morphology of the nanocomposites was examined by scanning and transmission electron microscopy (SEM and TEM).

The specific surface area was determined by N_2 adsorption/desorption measurements whose isotherms were evaluated by the BET equation.

Summary of new scientific results in thesis points

T1. Nanoporous NiO was successfully obtained by electrochemical anodization from ethylene glycol solution containing NH_4F and KOH . After appropriate heat treatment, significant photoelectrochemical activity was achieved.

Nanoporous p-type NiO was produced by electrochemical anodization. The product was shown to have superior electrochemical and photoelectrochemical properties compared to other NiO electrodes. We successfully overcame the disadvantages of anodization conditions taken from literature examples. As a result, there was no F^- contamination in the layers that would have led to low photoelectrochemical activity. The rate of etching was appropriately slow to not prevent the formation of the nanostructure.

T2. The photoelectrochemical properties of NiO are greatly improved in the presence of Pt nanoparticles. We proved that NiO/Pt composites can be used in the water-splitting (H_2 production) process.

We have demonstrated that Pt nanoparticles of different diameters and sizes increase the photoelectrochemical activity of NiO layers to varying degrees. For samples with optimal Pt surface coverage, long-term measurements were performed with in-situ gas detection. These results confirmed that the water reduction is the main process during photoelectrolysis. In the examined time interval (4 hours), the electrochemical activity of the samples retained about 60% of their activity.

T3. We have demonstrated that both the size and loading of Pt nanoparticles significantly influence the photoelectrochemical activity.

We showed that Pt nanoparticles of different diameters (2.0; 4.8; 7.2; 8.6; 12.3 nm) had an optimum surface coverage, where the increase in photoelectrochemical activity reached a maximum value. The highest increase was achieved when the 4.8 nm nanoparticles were applied in an amount of 2 mg cm^{-2} . This was the size where the strongest interaction between NiO and Pt can be envisioned. The diameter of the nanoparticles was not too large, so they can partially infiltrate into the nanoporous NiO structure, which was ideal for facilitating better charge transfer. The smaller particles were located in the deeper parts of the pores where the reinforcing effect was inadequate. In addition, the ideal surface quantity was important because too much of the nanoparticles resulted in an optical shielding effect.

T4. Nearly phase-pure CuCrO_2 can be prepared by solution combustion synthesis. The resulting product formed an interconnected network of nanoparticles.

The CuCrO_2 was prepared by solution combustion synthesis. The composition and purity of the prepared CuCrO_2 samples were determined by X-ray diffraction and Raman spectroscopy, confirming that near-phase pure material was produced. Evaluation of X-ray diffraction patterns with Rietveld refinement showed that 90% of the product were CuCrO_2 even before heat treatment. TEM

and SEM images showed that the resulting semiconductor particles were closely linked, which is advantageous for efficient charge transport.

T5. CuCrO_2 showed greater photoelectrochemical activity and stability than Cu_2O . We proved that the bimetallic oxide could be used in the photoelectrochemical CO_2 reduction process.

We showed that in the case of the same layer thickness and illumination, notably higher photoelectrochemical activity was observed for CuCrO_2 , compared to Cu_2O . In addition, in the case of CuCrO_2 , less pronounced photocorrosion was observed. H_2 , CO , and CH_4 were detected in the gas phase, and HCOOH and CH_3OH from the liquid phase as photoelectrolysis products. The chemical nature of the products were independent of the applied potential of the photoelectrolysis, but their distribution changed with the the applied potential. Furthermore, we proved that the products are derived from the photoelectrochemical reduction of CO_2 by means of ^{13}C isotope-labeling measurements.

T6. The bandgap of the CuCrO_2 can be significantly influenced by alloy formation ($\text{CuFe}_x\text{Cr}_{1-x}\text{O}_2$).

The CuCrO_2 bandgap was reduced when the precursor solution contained $\text{Fe}(\text{NO}_3)_3$ during the combustion synthesis. An alloy with $\text{CuFe}_x\text{Cr}_{1-x}\text{O}_2$ composition was formed. Tauc plots calculated from UV-visible spectroscopy showed that the greatest change in the bandgap occurred when only a very small amount of Fe was

incorporated into the CuCrO_2 matrix (5% Fe content). For each composition ($X=0.05; 0.1; 0.25; 0.5; 0.75; 0.9; 0.925; 0.95; 0.975$), the measured absorption edge was located between the spectrum of the pure materials. The lattice parameters calculated from XRD showed a linear relationship with the change in composition, which was a good match with the Vegard's law.

T7. Two-phase $\text{CuFeO}_2/\text{CuCrO}_2$ and $\text{CuCrO}_2/\text{CuFeO}_2$ electrodes showed enhanced photoelectroactivity compared to their single-component counterparts.

Two-phase electrodes were synthesized by solution combustion synthesis, which was proved by XRD measurements. SEM images have shown that either CuCrO_2 or CuFeO_2 encapsulates the other composite oxide. In both cases, when CuCrO_2 was on the CuFeO_2 surface or CuFeO_2 was on the surface of CuCrO_2 , there was an optimal surface coverage on the electrode where larger photocurrents could be measured with visible light compared to the individual components separately.

List of Publications

Hungarian Scientific Bibliography (MTMT) identifier: 10054958

- **A. Varga**, G. F. Samu, C. Janáky, „Rapid Synthesis of Interconnected CuCrO_2 Nanostructures: A Promising Electrode Material for Photoelectrochemical Fuel Generation” *Electrochimica Acta*, 272 (2018) 22-32 (IF₂₀₁₇: 5.116)
- K. Rajeshwar, M. K. Hossain, R. T. Macaluso, C. Janáky, **A. Varga** and P. J. Kulesza, „Copper Oxide-Based Ternary and Quaternary Oxides: Where Solid-State Chemistry Meets Photoelectrochemistry” *Journal of the Electrochemical Society*, 165 (2018), 3192-3206 (IF₂₀₁₇: 3.662)
- A. Sági, **A. Varga**, D. Dobó, K. L. Juhász, G. F. Samu, B. Takács, E. Varga, Á. Kukovecz, Z. Kónya, C. Janáky; „Photoelectrochemistry by design: Tailoring the Nanoscale Structure of Pt/NiO Composites Leads to Efficient Photoelectrochemical Hydrogen Evolution” *Journal of Physical Chemistry C*, 121 (2017) 12148-12158 (IF₂₀₁₇: 4.484)

$$\sum IF = 13.262$$

Other Publications:

- M. K. Hossain, E. Kecsenovity, **A. Varga**, M. Molnár, C. Janáky „Solution Combustion Synthesis of Complex Oxide Semiconductors,, International Journal of Self-Propagating High-Temperature Synthesis, 27 (2018), 129–140 (IF₂₀₁₇: 0.55)
- L. Janovák, Á. Dernovics, L. Mérai, Á. Deák, D. Sebők, E. Csapó, **A. Varga**, I. Dékány, C. Janáky „Microstructuring of poly(3-hexylthiophene) leads to bifunctional superhydrophobic and photoreactive surfaces” Chemical Communications, 54 (2018) 650-653 (IF₂₀₁₇: 6.290)
- **A. Varga**, B. Endrődi, V. Hornok, C. Visy, C. Janáky: ”Controlled Photocatalytic Deposition of CdS Nanoparticles on Poly(3-hexylthiophene) Nanofibers: a Versatile Approach to Obtain Organic/inorganic Hybrid Semiconductor Assemblies”, Journal of Physical Chemistry C, (2015), doi: 10.1021/acs.jpcc.5b09029 (IF₂₀₁₅: 4.509)

$$\sum IF = 11.349$$

Conference lectures:

- **A. Varga**, C. Janáky B. Endrődi, O. Berkesi, C. Visy „Egy dimenziós Poli(3-hexiltiofén)/CdS kompozitok előállítás és vizsgálata” Kémiai előadói napok, Szeged, Hungary, 2013

Posters:

- **A. Varga**, B. Endrődi, C. Visy, C. Janáky, „Photocatalytic deposition and characterization of CdS/P3HT nanofiber composites” Workshop on the Electrochemistry of Electroactive Materials Bad Herrenalb, Germany, 2015
- **A. Varga**, C. Janáky, ”Challenges of the electrodeposition of CuMO₂ delafossites,, 11th International workshop on electrodeposited nanostructures, Balatonfüred, Hungary, 2015
- **Varga**, G.F. Samu, C. Janáky, „Synthesis and characterization of CuCrO₂ for CO₂ reduction” 5th International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Porto Heli, Greece, 2016
- **A. Varga**, G.F. Samu, C. Janáky, „Solution combustion synthesis of CuCrO₂ and application for CO₂ reduction”, 21st Topical Meeting of the International Society of Electrochemistry, Szeged, Hungary, 2017