

Doctoral (Ph.D.) Theses

Ádám Balog

INVESTIGATION OF THE OPTOELECTRONIC
PROPERTIES OF SEMICONDUCTOR ELECTRODES

SUPERVISOR:

Dr. Csaba Janáky

Associate Professor

Doctoral School of Chemistry



University of Szeged

Faculty of Science and Informatics

Department of Physical Chemistry and Materials Science

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1. Introduction and aims

One of the most critical challenges of the 21st century is to decrease the use of fossil fuels and to replace them with renewable energy sources. In this regard, solar energy plays a crucial role because it can provide the annual global energy demand in just 1 hour 20 minutes. This means the total amount of energy that reaches the entire Earth, which obviously cannot be fully utilized but the number indicates the importance of solar energy in the optimal energy management.

Semiconductors have a key role in the transformation of solar energy into electrical and chemical energy. The current generated by photovoltaic solar cells is often used to carry out an electrochemical reaction, while in the case of photoelectrochemical cells the light absorption and the chemical reaction can be performed in one technology. In photoelectrochemistry, the measured current shows the rate of the reaction where solar energy is used directly to create chemical bonds.

The development and application of efficient and stable photoelectrodes is one of the main research topics in the Photoelectrochemistry Research Group at the Department of Physical Chemistry and Materials Science, University of Szeged. Detailed mechanistic understanding of the optoelectronic features is a key factor in designing high performance photoelectrodes. The presence of trap states makes the task especially difficult.

Since the discovery of photoelectrochemistry, the investigation of trap states in semiconductors opened a new field of research. It was recognized early on that the presence of these states greatly influences the photoelectrochemical behavior and also affects the stability. If we search among the studies in the literature, in many cases, we encounter contradictions about the role of trap states in different processes. This is especially true for titanium dioxide (TiO₂) which is one of the most widely studied semiconductors. The first results about photoelectrochemical behavior of TiO₂ showed that the presence of trap states is detrimental to the utilization of sunlight, their amount should be minimized for optimal operation. Therefore, the problem seemed to be solved, however in 2011, the discovery of black TiO₂ made the situation complicated. In this case, the partial reduction increased the density of donor states within the bandgap, while the photoelectrochemical properties improved. Nowadays this also became questionable, so there is still no explanation, which accurately describes the effect of trap states.

The above-mentioned contradictions placed this topic in the forefront of research again, and the investigations have been extended to other semiconductors. It turned out that the type of the trap states and also their effect can be completely different in different materials. Because of

this, our first goal was to prepare TiO₂ electrodes with different amount of defect sites and examine the effect of these states on the (photo)electrochemical properties. We aimed to find an explanation for the exact role of trap states and evaluate their chemical composition. As the next step, we aimed to perform the passivation of these states.

Our second goal was to investigate the trap states in a p-type semiconductor as well, namely in CuI, both in dark and under irradiation. According to the literature, CuI is a promising candidate as a photoelectrode and also as a hole transporting material. Another special property of CuI lies in its excited state properties, where the charge carriers are in bound form as excitons. The large exciton binding energy of CuI makes it difficult to induce charge carrier separation. Because of this, we aimed to examine the effect of potential and the possible contribution of trap states on the lifetime of excitons.

Finally, we would have liked to scrutinize another p-type semiconductor, NiO which shows electrochromic behavior. This is the consequence of the potential dependent Ni(II)/Ni(III) ratio on the surface which changes the color of the material. Our goal was to separate the effect of trap states, which remain in the structure after the synthesis, from the Ni(III) centers created by the potential bias. We aimed to investigate their roles using electrochemical methods.

2. Experimental techniques

For the preparation of TiO₂ electrodes, fluorine doped tin oxide (FTO) coated glass substrates were used. The TiO₂ nanoparticles were spray-coated on preheated substrates (at 140 °C) from an ethanol-based Aeroxide P25 TiO₂ suspension (5 mg cm⁻³). The same loading was achieved by using the same number of spray-coating cycles (~80 μg cm⁻²). The exact amount of the material was always weighed with a Mettler-Toledo XPE-26 microbalance. After the spray-coating process, the electrodes were heat-treated in a tube furnace at 400 °C for 2 hours in air, argon, or hydrogen atmosphere using ~100 cm³ min⁻¹ flow rate.

In the case of CuI, a 0.15 mol dm⁻³ CuI solution was prepared in acetonitrile (ACN). The CuI layers were deposited on the tin doped indium oxide (ITO) electrodes by spin-coating technique. A dynamic coating procedure was used and 50 μl stock solution was dropped on the surface of each electrode after reaching 1000 rpm spin speed, then the rotation continued for 1 minute. Immediately after spin coating, the layers were subjected to a drying step for 5 minutes at 50 °C on a hotplate. Afterwards the layers were annealed at 150 °C for 10 minutes. The average CuI loading was ~30 μg cm⁻².

The NiO layers were deposited on the ITO substrates by electrodeposition, using a galvanostatic procedure. The aqueous solution contained 0.13 M nickel sulfate, 0.13 M sodium acetate and 0.10 M sodium sulfate; and was stirred during the deposition. The same loading was achieved by setting 1 C cm⁻² charge density, applying 0.5 mA cm⁻² anodic current density. The formed nickel oxide hydroxide films were heat treated at 300 °C for an hour in air, which resulted in NiO on the electrode surface.

To evaluate the effect of heat treatment in the different atmospheres on the crystallinity of TiO₂, X-ray diffraction (XRD) measurements were carried out. The spectra were recorded with a Bruker D8 Advance instrument with a Cu K_α (λ= 1.5418 Å) X-ray source in the 20-60° 2 theta range with a scan speed of 0.25° min⁻¹. Rietveld refinement of the XRD patterns was performed to determine the ratio of the anatase and rutile phases using the GSAS-II software package.

X-ray photoelectron spectroscopy (XPS) was carried out to evaluate the chemical composition of the surface of the three differently treated TiO₂ samples. The measurements were performed with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical analyzer. The analyzer was in FAT mode with 20 eV pass energy. The Al K_α radiation (hν = 1486.6

eV) of a dual anode X-ray gun was used as an excitation source and operated at 150 W power. Ten scans were averaged to get a single high-resolution spectrum. For spectrum evaluation, CasaXPS commercial software package was used.

To determine the position and the electron density of the valence band (VB), He(I) ultra-violet photoelectron spectroscopy (UPS) measurements were performed with a He(I) excitation (21.22 eV) source. There was 10 V of external bias applied to the samples to accelerate secondary electrons to the analyzer.

To investigate the subsurface composition of TiO₂ samples, Ar⁺ bombardment was carried out with 2 keV energy for 5 minutes with a 5.0 μA cm⁻² sample current in all cases.

Scanning electron microscopic (SEM) images were captured to examine the morphology of different semiconductor electrodes using a Hitachi S-4700 instrument, operating at an accelerating voltage of 10 kV.

To determine the band energy diagrams of the semiconductors, Kelvin probe microscopy measurements were performed using a KP Technology APS04 instrument.

All electrochemical measurements were carried out with a Biologic VMP-300 type potentiostat/galvanostat in a classical three-electrode setup. The semiconductor coated FTO or ITO electrodes were used as the working electrode, a platinum foil functioned as the counterelectrode. In aqueous media a Ag/AgCl wire in 3 mol dm⁻³ NaCl, while in non-aqueous media a AgCl coated Ag wire was used as reference electrode. All currents were normalized to the geometric surface area of the electrodes. In the aqueous measurements performed with TiO₂ and NiO, 0.1 mol dm⁻³ Na₂SO₄ or 0.1 mol dm⁻³ Na₂SO₃ electrolytes were used, while the media for non-aqueous measurements was a 1 mol dm⁻³ LiClO₄ or 1 mol dm⁻³ Bu₄NClO₄ in ACN. In some measurements, the latter two solutions were diluted tenfold. In the case of CuI, the measurements were carried out in a 0.1 mol dm⁻³ solution of Bu₄NPF₆ in dichloromethane (DCM), except in the long-term photoelectrolysis experiment where 0.1 mol dm⁻³ NaNO₃ aqueous electrolyte was used.

Photoelectrochemical (PEC) experiments were carried out using a UV lamp (Hamamatsu L8251) or a solar simulator (Newport LCS-100, AM1.5) as the light source with a power density of 100 mW cm⁻².

For the spectroelectrochemical experiments, an Agilent 8453 UV– visible diode array spectrophotometer was used in the 300–1100 nm wavelength range.

In situ Raman spectroelectrochemical measurements were carried out by a Senterra II Compact Raman microscope, using 532 nm laser excitation wavelength with a laser power of 2.5 mW. The experiment was performed in an ECC-Opto-Std electrochemical cell (EL-CELL GmbH) equipped with a sapphire window. The spectra were recorded after a 100 s potentiostatic conditioning step at the given potential.

Ultrafast transient spectroelectrochemistry measurements were carried out in collaboration with the group of Dr. Prashant Kamat (University of Notre Dame) using a Clark MXR-2010 laser system. Helios software package from Ultrafast Systems was used for data collection.

Electrochemical impedance spectra were recorded at different potential values in the 100 kHz to 0.1 Hz frequency range, using a sinusoidal excitation signal (10 mV RMS amplitude). Before each measurement, a pretreatment step was applied at the given potential for two minutes. To determine the charge transfer resistance (R_{ct}) values, the first semicircle was fitted in the Nyquist plot with a simple R(RC) circuit. To determine the flatband potential of the semiconductors and the donor density of different TiO₂ electrodes, Mott-Schottky analysis was carried out. The Mott-Schottky plots were constructed for the given frequency using the impedance spectra.

3. Summary of new scientific results

The effect of trap states on the optoelectronic properties of TiO₂

T1. The structure of black TiO₂ consists of a disordered but stoichiometric shell and a defective crystalline core. The presence of Ti(III) sites in the core causes a decrease in the bandgap energy compared to white TiO₂.

The bandgap energy slightly decreased with the increasing reducing ability of the heat-treatment atmosphere, while the chemical composition of the surface was not changed (the XPS spectra showed only the presence of Ti(IV) in all cases). On the high resolution Ti2p spectra of black TiO₂, however, a significant shift was observed towards higher binding energies. This alteration in the peak position can be assigned to structural distortions on the surface of the black TiO₂ sample. This was confirmed by UPS measurements which showed non-zero electron density in the bandgap, proving the extension of the VB. Ar⁺ bombardment experiments revealed that under the disordered shell Ti(III) defects are also present and these states are responsible for the visible light absorption which is the reason of the color change.

T2. With the increasing number of trap states, the achievable photocurrent maximum decreases, but the electrocatalytic and charge storage properties improve.

Based on the decreasing bandgap energies with the increasing number of trap states, we expected to achieve the highest photocurrent in the case of black TiO₂. In contrast, the opposite trend was observed which indicates that the excitation is possible with lower light energies, however most of the created electrons will be trapped without generating photocurrent. The capacitance, however, enhanced with the number of defect sites, which can be explained with the increased charge carrier density in the semiconductor. In terms of electrocatalytic properties, the presence of trap states was also beneficial which suggests that these filled energy levels play an important role in reduction processes.

T3. The trap states in black TiO₂ can be passivated by the intercalation of cations, which can only be achieved using small size cations. This passivation is a two-step process, while the first step is a spontaneous uptake, the second step can only be performed through proper electrochemical polarization.

In tetrabutylammonium ion containing solution the photocurrent of white TiO₂ is more than three times higher compared to the black sample (3.4 mA cm⁻² vs. 1.0 mA cm⁻²). When the electrodes were immersed in a lithium ion containing electrolyte, we could observe that the photocurrent difference between the two electrodes became significantly lower (3.4 mA cm⁻² vs. 2.5 mA cm⁻²). This can be explained by the fact that the passivation of surface defects takes place even if the black TiO₂ electrode is immersed into the solution. When the PEC measurement was started from more negative potential (-1.0 V instead of -0.4 V) the photocurrent of black TiO₂ became equal to the white sample. This passivation step affects the deeper regions, namely the Ti(III) sites which can only be achieved through proper electrochemical polarization. The first step was found to be spontaneous and irreversible, and caused the reorganization of the disordered surface. In contrast, the second step was reversible when a potential more positive than the open circuit potential (OCP) is applied to the electrode.

T4. The population of trap states with electrons can be performed by changing the potential in the negative direction and these electrons are responsible for the catalytic activity of black TiO₂.

In principle, the electrons can reach the semiconductor/electrolyte interface only at more negative potentials than the flatband. Based on our measurements, however, the onset of the oxygen reduction reaction can be observed at much more positive potentials, especially in the case of black TiO₂. Spectroelectrochemical experiments showed a simultaneous absorbance increase with the increasing cathodic current. The maximum of the absorbance change can be measured at the wavelength, which corresponds to the energy that needed to excite electrons from the valence band to the defect states. This signals that the electron filled trap states can act as a catalyst and lower the overpotential of the reduction processes.

The effect of trap states on the optoelectronic properties of CuI

T5. The originally hole-containing trap states in CuI can be populated and depopulated by the applied electrode potential. The population level of these states influences the optical and electronic properties.

In CuI, acceptor levels, namely hole-containing trap states can be found close to the valence band edge. After the heat treatment of the layer, a sharp peak appeared on the UV-visible spectrum which corresponds to the exciton absorption of CuI. The size of this peak can be reversibly modulated by the applied bias potential. In the negative potential regime, the number of excitons and the related absorbance increases. When the hole-containing trap states are filled with electrons by the potential, there is a higher probability to form excitons. This is the reason for the higher absorbance at negative potentials. If we remove the electrons from these states using positive potentials, the mentioned absorbance decreases. The population level also affects the electronic properties of CuI. When the trap states are filled, the number of free charge carriers is lower, which causes an increase in the charge transfer resistance. We have found that the deeper traps are primarily responsible for the electronic properties, while the shallow traps dictate the optical absorption at the excitonic peak.

T6. The photoelectrochemical stability of CuI is better compared to Cu₂O, even though the thermodynamic driving force for the cathodic corrosion of CuI is much higher. The reason for this is the dissimilar structure of the corrosion product, which makes the process kinetically sluggish.

Based on the band positions of CuI, only the cathodic (reductive) photocorrosion is possible. There is a higher thermodynamic driving force for this process in the case of CuI (2.01 eV) compared to its oxide counterpart, Cu₂O (1.26 eV), which suffers from rapid photocorrosion under similar circumstances. However, we could not observe any decrease in the performance of CuI during an 8 hours photoelectrolysis. The reason for this is to be found in the kinetics of the corrosion process which can be explained by solid-state chemistry considerations. Cu has a face-centered cubic crystal structure, which is very similar to cubic Cu₂O. In contrast, the studied CuI has a wurtzite structure, which has a completely different symmetry. The structural similarity of Cu₂O and the corrosion product Cu facilitates the corrosion process, whereas the dissimilar structure in the case of CuI makes the corrosion process kinetically sluggish.

T7. The lifetime of the excitons in CuI decreases with the increasing population level of trap states, which can be explained with the acceleration of the recombination process.

While the number of excitons in CuI increases with the decreasing potential (the exciton absorption is higher at negative potentials), their lifetime decreases. When trapping of charge carriers is possible on the trap states within the bandgap, the recombination is always slower. This is because the direct (band-to-band) recombination is faster than the trap state mediated process. With the increasing number of electrons on these states, the possibility of hole trapping gradually decreases. This is manifested in an increase in the rate of the exciton recombination and thus a decrease in their lifetime. The change of the lifetime is reversible; however, it shows a small hysteresis. This is due to the residual accumulation of charges caused by the pretreatment at different potentials.

The effect of trap states on the optoelectronic properties of NiO

T8. The population and depopulation of trap states in NiO can be distinguished from the surface oxidation, and the effect of the two separate processes can be detected by electrochemical methods.

Based on the UV-visible spectroelectrochemical measurements the population of the trap states cannot be separated from the Ni(II)/Ni(III) surface reaction. The reason is that the color change caused by the mentioned Faradaic event covers all other changes in the absorption spectrum. Using electrochemical impedance spectroscopy and Raman spectroelectrochemistry, the two processes can be distinguished. With the increasing potential, a gradual decay of the first phase angle minimum (at high frequencies) can be observed in the Bode plot. This process related to the depopulation of electrons from the trap states, which causes an abrupt decrease in the charge transfer resistance. From a given potential (-0.1 V), the appearance of a new phase angle minimum can be noticed which corresponds to Ni(III) on the surface. The intensity increase of the Raman peak originated from Ni-O stretching vibrations also confirms the existence of two separate processes. The depopulation of trap states causes a smaller, while the appearance of Ni(III) results in a higher intensity increase in the Raman spectra.

T9. The number of electrons on the trap states can be controlled with the applied electrochemical bias, which can be followed by measuring the electron density within the bandgap.

Kelvin probe microscopy measurements provide an opportunity to detect the electrons on the trap states after the pretreatment at different potentials. The potential change influences the population level of these states, which can be tracked by measuring the electron density within the bandgap. In the case of NiO, the originally hole-containing trap states close to the valence band can be filled with electrons by a treatment at -0.4 V, which causes a simultaneous increase in the electron density. After polarizing the electrode at potentials more positive than the valence band position (0.6 V), the previously filled states can be depleted resulting in the disappearance of the electron density in the bandgap.

4. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10070762

Publications related to the scientific topic of the dissertation:

Á. Balog, G. F. Samu, P. V. Kamat, C. Janáky: Optoelectronic properties of CuI photoelectrodes
The Journal of Physical Chemistry Letters, **2019**, 10, 259–264. **IF=6.710**

Á. Balog, C. Janáky: The effect of trap states on the optoelectronic properties of nanoporous nickel oxide

Journal of the Electrochemical Society, **2019**, 166, H3265–H3270. **IF=3.721**

G. F. Samu, R. A. Scheidt, **Á. Balog**, C. Janáky, P. V. Kamat: Tuning the excited state dynamics of CuI films with electrochemical bias

ACS Energy Letters, **2019**, 4, 702–708. **IF=19.003**

Á. Balog, G. F. Samu, S. Pető, C. Janáky, The mystery of black TiO₂: insights from combined surface science and in situ electrochemical methods

ACS Materials Au, accepted. (DOI: 10.1021/acsmaterialsau.1c00020)

ΣIF=29.434

Other publications:

A. M. Ismail, G. F. Samu, **Á. Balog**, E. Csapó, and C. Janáky, Composition dependent electrocatalytic behavior of Au–Sn bimetallic nanoparticles in carbon dioxide reduction
ACS Energy Letters, **2019**, 4, 48–53. **IF=19.003**

G. F. Samu, **Á. Balog**, F. De Angelis, D. Meggiolaro, P. V. Kamat and C. Janáky, Electrochemical hole injection selectively expels iodide from mixed halide perovskite films

Journal of the American Chemical Society, **2019**, 141, 10812–10820. **IF=14.612**

Á. Vass, B. Endrődi, G. F. Samu, **Á. Balog**, A. Kormányos, S. Cherevko, C. Janáky, Ni vs. Ir anode catalysts: challenges in zero-gap CO₂ electrolyzers

ACS Energy Letters, submitted.

ΣΣIF=63.049

Oral presentations

Presenting author:

Á. Balog, A. Kormányos, A. Berényi, C. Janáky: Rapid and selective detection of dopamine on molecularly imprinted polypyrrole/carbon nanotube polymer electrodes
8th Szeged International Workshop on Advances in Nanoscience, Szeged (Hungary), 7-10, October, 2018.

Á. Balog, G.F. Samu, C. Janáky: Optoelectronic properties of semiconductor photoelectrodes
American Chemical Society National Meeting & Exposition, Orlando (FL, USA), 31 March – 4 April, 2019.

Á. Balog, B. Endródi, Á. Szűcs: C₆₀ és szén nanocső kompozit filmek elektrokémiai vizsgálata
IV. Kárpát-medencei Szakkollégiumi Konferencia, Budapest (Hungary), 12-15, July, 2017.

Á. Balog, G.F. Samu, C. Janáky: Félvezető elektródok optoelektronikai tulajdonságainak tanulmányozása
XLII. Kémiai Előadói Napok, Szeged (Hungary), 28-30, October, 2019.

Á. Balog, G.F. Samu, C. Janáky: Félvezetőkben lévő hibahelyek tanulmányozása és azok hatása az elektrokémiai tulajdonságokra
„A nemzeti összetartozás jegyében” online konferencia, 7, November, 2020.

Co-author:

C. Janáky, G.F. Samu, **Á. Balog**: Optoelectronics, charge carrier dynamics, and photoelectrochemistry of metal halide photoelectrodes
American Chemical Society National Meeting & Exposition, Orlando (FL, USA), 31 March – 4 April, 2019.

G.F. Samu, R.A. Scheidt, **Á. Balog**, C. Janáky, P.V. Kamat: Modulation of excited state dynamics in lead halide perovskite films with electrical bias
International Conference on Hybrid and Organic Photovoltaics, Rome (Italy), 12-15, May, 2019.

G.F. Samu, **Á. Balog**, R.A. Scheidt, P.V. Kamat, C. Janáky: Modulation of excited state dynamics in semiconductor electrodes with electrical bias
235th ECS Meeting, Dallas (TX, USA), 26-30, May, 2019.

Poster presentations:

Á. Balog, A. Kormányos, C. Janáky: Selective and rapid detection of dopamine on molecularly imprinted polymer electrodes
The 69th Annual Meeting of the International Society of Electrochemistry, Bologna (Italy), 2-7, September, 2018.

Á. Balog, G.F. Samu, C. Janáky: The effect of trap states on the optoelectronic properties of semiconductor photoelectrodes

International Workshop on Electrochemistry of Electroactive Materials, Borovets (Bulgaria), 16-21, June, 2019.