

Doctoral (Ph.D.) Theses

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**PHOTOELECTROCHEMISTRY OF CONDUCTING
POLYMER-BASED NANOHYBRID ELECTRODES**

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1. INTRODUCTION AND AIMS

One of the most critical challenges of the 21st century is the shift in energy use from fossil fuels to renewable sources. Sunlight is undoubtedly one of the most valuable resources in the quest for a diversified and sustainable energy supply. While solar energy is the most abundant energy source on our planet, its intermittency necessitates the storage of the harvested energy. Photoelectrochemical (PEC) solar energy conversion, as a potentially attractive candidate, has gained an increased momentum during the recent years. Although both water-splitting (hydrogen evolution) and carbon dioxide reduction are promising avenues, they both have substantial shortcomings to be addressed. A common virtue of these two processes is that a good photoelectrode has to concurrently fulfill *many attributes* to drive these reactions efficiently. Although several inorganic semiconductors (SCs) have been tested in these PEC processes, still, there is no single material, which bears with all of these.

Conducting polymers (CPs) belong to the category of organic SCs. These materials are conceptually different alternatives to their inorganic counterparts. CPs are promising photoelectrode candidates due to their beneficial properties, namely:

- CPs can be prepared via *mild synthetic routes* (such as electrodeposition), which result in short energy payback time.
- Processing and fabrication of high surface area photoelectrodes is *convenient and cheap*.
- The polymer structure can be *tailored* to fit to the requirements of the given application (e.g., tunable bandgap, high CO₂-adsorption capacity).
- Several N-containing CPs showed *reasonable catalytic activity* toward the electrochemical reduction of CO₂, which implies that N-atoms play a key role in this process – note that polyimides are among the best CO₂ adsorbents.

The investigation of the synthesis and electrochemical properties of CPs and their nanocomposites in our research group and its predecessor one dates back to the end of the 1980s. However, the applicability of these materials in solar fuel generation processes were not studied, not just in our group, but in the literature in general. When I've started my PhD studies in 2013, our first goal was ***to study the fundamental PEC behavior of CP photocathodes and their applicability to the PEC reduction of CO₂***. After understanding the main factors dictating the enhanced PEC activity toward the reduction of CO₂, and identifying

the main drawbacks of using only the pristine CPs as photoelectrodes, our focus turned to CP-based nanocomposite electrodes. Such hybrids might eliminate some of the experienced disadvantages, thus resulting in improved PEC properties.

To improve the charge carrier transport properties, CP/nanocarbon (CNTs and graphene) electrodes were synthesized. Our goal was to develop a synthesis procedure through which the composition of the nanohybrids can be tuned. As a next step, we wanted to study the effect of composition on the PEC behavior and the applicability of these composites in PEC CO₂-, and H⁺ reduction processes. Our further object was to explore the effect of the nanocarbon network on the conductivity, light absorption properties and finally, on the amount and distribution of the formed products.

To improve the charge carrier transfer properties of SiC, polyaniline was studied as a co-catalyst, immobilized on the surface of the SiC nanoparticles. Our goal was to synthesize such nanocomposites by applying both photocatalytic-, and electrochemical deposition techniques, which result in an electroactive CP coating on the surface of SiC. As a next step we wanted to investigate the PEC properties of the synthesized nanocomposites, along with their applicability as photoelectrodes in the PEC reduction of CO₂.

2. EXPERIMENTAL TECHNIQUES

The CNT, graphene and SiC dispersions were spray-coated on a preheated glassy carbon (GC) electrode surface, employing an Alder AD320 type airbrush and a homemade spray-coater robot operated with 1 bar compressed air pressure. The precise amount of spray-coated materials was monitored by a Mettler Toledo XPE-26 type analytical microbalance. For the electrochemical characterizations the nanocomposite samples, prepared by photocatalytic deposition were spray-coated on a Au electrode surface.

All (photo)electrochemical measurements were performed on a Metrohm Autolab PGSTAT302 type potentiostat/galvanostat. The electropolymerization of CPs was carried out in a classical three-electrode cell setup, including a Ag/AgCl/3 M NaCl as reference electrode and a Pt sheet as a counter electrode.

CPs were deposited on the bare-, nanocarbon- or SiC-modified electrode surface potentiodynamically (polyaniline, poly(N-methylaniline), galvanostatically (polypyrrole) and potentiostatically (poly(3,4-ethylenedioxythiophene) using a classical three-electrode cell setup.

Linear sweep photovoltammograms were recorded in a sealed, custom-designed one-compartment, three-electrode quartz cell. The working electrode was always covered with the CP or nanocomposite to be examined, while a Pt sheet and Ag/AgCl/3M NaCl were employed as the counter-, and reference electrodes respectively. Two different light sources were applied during these measurements:

- A Newport LCS-100 type *solar simulator*, operated at full output. The solar simulator source was placed 5 cm away from the illuminated working electrode surface (200 mW cm⁻² flux), which was irradiated through a quartz window.
- A Hamamatsu L8251 300 W *Hg-Xe arc lamp*, operated at full output. The lamp was placed 5 cm away from the illuminated working electrode surface (180 mW cm⁻² flux), which was irradiated through a quartz window.

Incident photon-to-current efficiency (IPCE) measurements were performed on a Newport Quantum Efficiency Measurement System in a single compartment, three-electrode quartz electrochemical cell.

Electrochemical impedance spectra of all investigated photoelectrodes were recorded in the 10 Hz to 100 kHz frequency range, using a sinusoidal excitation signal (10 mV RMS amplitude). Modulus weighted fitting was performed using the Nova Software of the Autolab Instrument.

Long-term PEC measurements were carried out in a sealed two-compartment cell where the compartments were separated by a Nafion117[®] membrane. During the reaction, gas samples were taken via an on-line detection system, which was coupled to the cathode compartment of the cell. Liquid and gas phase aliquots were taken from the cathode compartment of the cell at the same time. Gas samples were analyzed by a Shimadzu GC-2010 Plus gas chromatograph, utilizing a dielectric barrier ionic discharge detector. To quantify the products, calibration measurements were performed, using a gas mixture containing H₂, CO, CH₄ and C₂H₄, in concentrations, ranging from 0.1 V/V% up to 10 V/V%. The liquid aliquots were injected into the Shimadzu GC-MS 2010SE chromatograph coupled with a MS QP2010 detector. Qualitative detection was afforded by selective ion monitoring (SIM)-MS, while the total ion chromatogram was used for the quantification of methanol and ethanol.

Raman spectra were recorded using a DXR Raman microscope (Thermo Scientific, Waltham, USA) using a $\lambda = 532$ nm green laser, operating at typically 5 - 10 mW laser power.

ATR-FT-IR studies were performed using a Bio-Rad Digilab Division FTS-65A/896 FT-IR spectrometer. Vibrational spectroscopic changes upon CO₂ adsorption were monitored by FT-IR spectroscopy using an Agilent 670 Fourier-transform infrared spectrometer equipped with a Harrick's Praying Mantis™ Diffuse Reflection Accessory. The background spectra were recorded at room temperature after a 60 min pretreatment in He, at 200 °C.

Morphology of both the constituents and the nanocomposites was studied by scanning-, and transmission electron microscopy (SEM and TEM). A Hitachi S-4700 field emission scanning electron microscope was used for the SEM measurements, operating at an accelerating voltage of 10 kV. TEM images were taken by using a FEI Tecnai G² X-Twin type instrument, operating at an accelerating voltage of 200 kV.

Carbon dioxide adsorption on the polymer films was monitored by quartz crystal microgravimetry (QCM) technique using a Stanford Research Systems QCM 200 instrument.

Thermoanalytical measurements (TG & dTG) were performed on a TA Q800 TGA instrument. In a typical experiment, 3-5 mg of samples were heated in synthetic air (20.5 % O₂ in N₂) from room temperature to 800 °C with a heating rate of 10 °C/min.

Kelvin probe microscopy-coupled ambient UV photoelectron spectroscopy measurements were performed using a KP Technology APS04 instrument. First, the contact potential difference (CPD) was measured between the sample and the Kelvin-probe after electric equilibrium was reached. Ambient pressure UV photoelectron spectroscopy (UV-APS), measurements were carried out with a stationary Kelvin-probe tip.

3. SUMMARY OF NEW SCIENTIFIC RESULTS

Photoelectrochemical behavior of conducting polymer electrodes

T1. Polyaniline, polypyrrole, poly(N-methylaniline) and poly(3,4-ethylenedioxythiophene) behave as p-type semiconductors in their reduced form.

This statement was justified by both the positive photopotential and the cathodic photocurrents. The highest harvested photocurrents in a N₂-saturated electrolyte were 80 $\mu\text{A cm}^{-2}$ in the case of polyaniline and 110 $\mu\text{A cm}^{-2}$ in the case of poly(3,4-ethylenedioxythiophene) and notably inferior to the other two studied polymers.

T2. Photoelectrochemical reduction of CO₂ was performed on polyaniline electrodes, 500-700 mV less negative potential than the thermodynamic potential of most of the CO₂-reduction processes (e.g., methanol formation). H₂, methanol and ethanol were detected as reduction products during the long-term photoelectrolysis.

The cathodic photocurrents originated from the reduction of H⁺ ions and CO₂ at the polyaniline/electrolyte interface. A two-fold increase was seen in the photocurrents in the plateau region in the presence of CO₂ compared to the measurements, carried out in N₂-saturated electrolytes. According to GC-BID and GC-MS measurements in the CO₂-saturated case, 20% of the transferred charge (Faradaic efficiency) accounts for H₂ formation, while the rest is responsible for the alcohol formation. On the other hand, H₂ was the only detectable product in the N₂-saturated case.

T3. We identified the set of physical-chemical properties which has to be met by a conducting polymer photoelectrode, to be able to drive the CO₂ reduction process.

Photoelectrochemical CO₂ reduction can be driven on CPs, if (i) their conduction band energy levels are negative enough to reduce CO₂, (ii) their valence band energy levels are positive enough to make the conducting polymer behave as a semiconductor at the potential where the photoelectrochemical experiment is performed, and (iii) it must contain N–H groups in its structure to ensure the chemisorption of CO₂.

T4. Both polyaniline and poly(3,4-ethylenedioxythiophene) showed limited photostability, evidenced in the substantial decrease in the photocurrent values during the long-term photoelectrolysis experiments.

During the long term photoelectrolysis experiments, an initial decrease in the photocurrents was always observed. At the same time, the intrinsic *electroactivity* of the films did not change significantly. This fact confirms that not a molecular or supramolecular degradation is the process behind the decrease of the PEC performance. In the case of polyaniline, the experienced decrease in the photocurrents was correlated to the charge carrier recombination-induced local heating, which resulted in the melting of the polymer film, thus in a decreased active surface area.

Synthesis and photoelectrochemical behavior of conducting polymer/nanocarbon electrodes

T5. Enhanced photoelectrochemical activity was observed in the case of both polyaniline/nanocarbon and poly(3,4-ethylenedioxythiophene)/nanocarbon photoelectrodes compared to the bare polymer, caused by the efficient transport of the photogenerated charge carriers via the interconnected nanocarbon matrix.

A maximum of four times higher photocurrents were harvested in the case of the poly(3,4-ethylenedioxythiophene)/CNT system, compared to the pristine polymer, while the increase was two and a half times in the case of the poly(3,4-ethylenedioxythiophene)/graphene electrodes. Similar observations were made in the case of polyaniline; however, the enhancement was not as striking as in the poly(3,4-ethylenedioxythiophene) case. According to the electrochemical impedance spectroscopy results, both nanocarbons significantly enhanced the electric conductivity of the nanocomposites compared to the bare CP layers.

T6. Light absorption properties, the formed products and the photostability were not affected by the nanocarbon networks in the case of poly(3,4-ethylenedioxythiophene)/nanocarbon electrodes.

The characteristics of the photoaction spectra were identical (along with the wavelength-range of light-absorption), while the order of the maximum incident photon-to-current-efficiencies were in line with the photovoltammetry data (highest values were obtained for the CNT-containing layers). H₂ was the only detectable product in the case of both the pristine poly(3,4-ethylenedioxythiophene), and the poly(3,4-ethylenedioxythiophene)/nanocarbon electrodes, which evolved with a Faradaic efficiency close to 100%.

Synthesis and photoelectrochemical behavior of polyaniline/SiC electrodes

T7. Polyaniline layers can be deposited on the surface of SiC nanoparticles by both photocatalytic-, and electrochemical polymerization. The thickness of the deposited CP can be regulated by the time of either the illumination-, or the electrochemical polymerization.

The thickness of the polymer shell can be varied between 1.0 – 2.5 nm during the photocatalytic process, simply by varying the irradiation time. Polyaniline was also successfully electrodeposited on the surface of SiC nanoparticles by potentiodynamic cycling, which resulted in a 2 – 10 nm thick polymer coating.

T8. The wavelength of illumination has a significant effect on the electroactivity of the photocatalytically deposited polyaniline.

As gleaned from vibrational spectroscopic and electrochemical studies, it was a key factor to filter out the irradiation below 300 nm during the synthesis. Formation of polyaniline with conjugated structure was only witnessed if this high energy component was filtered.

T9. Higher and more stable photocurrents were registered for the polyaniline/SiC nanocomposite photoelectrodes, compared to the pristine polymer.

Approximately two times higher photocurrents were detected for the best performing polyaniline/SiC nanocomposite sample compared to the pristine polyaniline. The enhanced photoelectrochemical activity of the hybrids is rooted in: (i) the higher electrochemically active surface area, (ii) photoelectrons originated from the SiC counterpart (due to the 0.2 eV lower bandgap of the nanocomposites compared to the bare polyaniline) and (iii) the catalytic effect of polyaniline, facilitating electron transfer from SiC to the substrates.

4. SCIENTIFIC PUBLICATIONS

Hungarian Scientific Bibliography (MTMT) identifier: 10039524

Publications related to the scientific topic of the dissertation

1. **A. Kormányos**, B. Endrődi, R. Ondok, A. Sápi, C. Janáky, Controlled photocatalytic synthesis of core-shell SiC/polyaniline hybrid nanostructures, *Materials* 9 (2016) 201-214.
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3. **A. Kormányos**, A. Thomas, K. Rajeshwar, C. Janáky Synthesis and characterization of p-type semiconductor inorganic nanocrystals for photoelectrochemical fuel generation *250th ACS National Meeting* 2015. August 16 - 21., Boston USA
4. **A. Kormányos**, M. S. Hossain, F. W. Foss, K. Rajeshwar, C. Janáky Electrochemistry of Synthetic

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5. **A. Kormányos**, D. Hursán, C. Janáky, E. Kecsenovity, K. Rajeshwar Photoelectrochemical reduction of CO₂ on organic/inorganic nanocomposite photoelectrodes *253rd ACS National Meeting*, 2017 April 02 - 06. San Francisco, USA
6. **A. Kormányos**, D. Hursán, C. Janáky, E. Kecsenovity, K. Rajeshwar Photoelectrochemical reduction of CO₂ on organic/inorganic nanocomposite photoelectrodes *21st Topical Meeting of ISE*, 2017 April 23 - 26., Szeged, Hungary

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7. C. Janáky, **A. Kormányos**, D. Hursán, K. Rajeshwar Photoelectrochemical reduction of CO₂ on hybrid organic/inorganic photocathodes *248th ACS National Meeting*, 2014 August 10 - 14. San Francisco, USA
8. C. Janáky, A. Varga, **A. Kormányos**, G. F. Samu, K. Rajeshwar – Hybrid organic/Inorganic assemblies with tailored photoelectrochemical activity: from synthetic aspects to energy applications - *7th Forum on New Materials (CIMTEC)*, 2016 June 5 - 9., Perugia, Italy
9. G. F. Samu, **A. Kormányos**, A. Thomas, K. Rajeshwar, C. Janáky – Rapid and sustainable synthesis of metal oxide photocatalyst nanostructures - *9th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA9)*, June 13 - 17, 2016, Strasbourg, France
10. D. Hursán, C. Janáky, T. Kiss, **A. Kormányos**, R. Ondok Photoelectrochemistry of organic semiconducting polymers: fundamentals and implications in solar fuels generation *21st Topical Meeting of ISE*, 2017 April 23 - 26., Szeged, Hungary
11. D. Hursán, C. Janáky, T. Kiss, **A. Kormányos**, R. Ondok Photoelectrochemistry of conducting polymers and opportunities in solar fuel generation *254th ACS National Meeting*, 2017. August 20 - 24., Washington DC, USA
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4. **A. Kormányos**, A. Thomas, K. Rajeshwar, C. Janáky Synthesis and Characterization of p-type semiconductor inorganic materials for photoelectrochemical fuel generation *Workshop on the Electrochemistry of Electroactive Materials*, 2015. May 31 - June 05. Bad Herrenalb, Germany
5. **A. Kormányos**, A. Thomas, M. N. Huda, P. Sarker, J. Ping Liu, N. Poudyal, K. Rajeshwar, C. Janáky Solution combustion synthesis, characterization and photoelectrochemistry of CuNb_2O_6 and ZnNb_2O_6 nanoparticles, *7th Forum on New Materials (CIMTEC)*, 2016 June 5 - 9, Perugia, Italy
6. **A. Kormányos**, B. Endrődi, R. Ondok, A. Sápi, C. Janáky Controlled Photocatalytic Synthesis of SiC/polyaniline core-shell nanostructures *9th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA9)*, June 13 - 17, 2016, Strasbourg, France
7. R. Ondok, **A. Kormányos**, C. Janáky Controlled synthesis and CO_2 photoelectroreduction activity of conducting polymer/SiC hybrid nanostructures *21st Topical Meeting of ISE*, 2017 April 23 - 26., Szeged, Hungary

