Final report on OTKA-PD 105773 postdoctoral proposal

(2012.09.01.-2014. 06.30.)

Nowadays, scientists are inspired to find alternative „green" procedures for solving the problems with the source of energy predicted for the near future. One of these trends is the development of photoelectrochemical solar cells, in which promising semiconductors have been tested (TiO_2, ZnO etc.). One of the main hindrances of the applications is their decomposition under UV illumination (photocorrosion). This problem can be avoided by employing dyes on the surface of the oxides or certain conducting polymers (CPs) which are able to resist photocorrosion much more than some semiconducting oxides. Therefore the concept of organic/inorganic hybrid solar cells has been developed.

During the first period of the OTKA proposal (2012, 1 September–2013, 31 August), the following results have been achieved.

According to the previous plan for the first year, the acquisition of the small-sized, blutooth controlled DropSens potentiostat, a controlling notebook and all necessary chemicals were realised in 2012. New, temperature controlled electrochemical cells were developed in order to ensure the experimental conditions at higher temperature (25-90 C) for both chemical and electrochemical synthesis of ZnO nanostructures. The literature of the photovoltaic hybrids consisting of semiconducting inorganic oxides and conducting polymers was throroughly reviewed.

In the first part of the experimental work, the optimization of the conducting polymer layers was carried out in aqueous surfactant solution (0,05 M). This concentration was well above the critical micellization concentration of tenside used, it helps to solubilize the organic monomers in aqueous medium. Synthesis of polymers and co-polymers from pyrrole (py) and 3,4-ethylene-dioxy-pyrrole (edop) with different concentration ratio, as well as from 3,4-ethylene-dioxy-thiophene (edot) monomers were carried out by electrochemical methods. One of the key parameters in solar applications is the tunable thickness of the organic materials which cover the semiconducting nanostructures. The thickness of the polymer layer and the polymer domain size should be in the range of the exciton diffusion length. The thickness-charge density function was studied in case of the polymers and their redox behaviours were compared by cyclic voltammetry in base solution.

Beside the polymer depositions, the synthesis of nanostructured ZnO has also been started. The role of the nanostructured metal oxide electrode is crucial, as its morphology determines many physical processes that control the overall performance: the light-harvesting properties are directly dependent on the amount of interface available for polymer and/or dye grafting; the generation yield of free electrons is driven by the electronic configuration of the oxide. ZnO nanorods with controlled orientation onto the substrate allow a more efficient electrontransport. The length and the orientation of the vertically aligned ZnO nanorods were influenced by strict control of the experimental conditions (Zn^{2+} concentration, pH, dissolved O_2 content, temperature etc.). It is known from the literature, that in order to make nanostructured ZnOs, a base seed layer should be worked up on the substrates prior to the nanostructure synthesis. The base layers were constructed by chemical and electrochemical methods, too. First, nanorods were grown on indium-tin-oxide surface which was coated with ZnO nanoparticles (average diameter below 35 nm). Secondly, electrochemical buffer layer depositions have been tried. It was found that the synthesis was very sensitive to the oxygen content of the solution. If the concentration was not high enough, the preferred electrochemical reaction was the reduction of the substrate oxide (ITO) layer instead of oxygen reduction which was the first step in the ZnO evolution.

After the seed leayer deposition, hydrothermal synthesis of nanostuctured ZnO rods was the next step. It was also found that below 60-70 C ZnO nanorods could not be observed at all by SEM. Since the alignment and the length of the nanorods can be increased using additives (e.g. surfactants, poly-ethylene-imine (PEI), PEG etc.), we started to use branched PEI (Mw=2000). The morphology and chemical content of the synthesized ZnO and conducting polymers were studied by SEM-EDX and XRD.

During the second year the work on the ZnO/conducting polymer composite synthesis has been continued and photoelectrochemical characterization of the hybrids has been started. During photoelectrochemical studies of bare ZnO, significant decomposition of the oxide under UV illumination (photocorrosion) has been detected. This phenomena is one of the main hindrances of the ZnO applications. This problem can be avoided by employing dyes (very often rutheniumbipyridyl complexes) in conjunction with the semiconducting oxides, thus the energy of the excitation is lowered to the visible and near IR region (dye-sensitized solar cells, DSSC). Certain conducting polymers are able to resist photocorrosion much more than some semiconducting oxides. Therefore the concept of organic/inorganic hybrid solar cells was developed, in which the conducting polymer is responsible for both the light absorption and hole-transport. The literature of the photovoltaic hybrids consisting of semiconducting inorganic oxides and conducting polymers was throroughly reviewed.

In the last decade numerous new derivatives of thiophene and pyrrole have been studied. Unfortunately, the irreversible oxidation (also called overoxidation) of the polymer is one of the existing problems during the practical applications of such materials. By the modification of the five-member, nitrogen and sulfur containing monomers at the 3 and 4 positions, extremely stable polymers (e.g., poly(3,4-ethylenedioxy)thiophene, PEDOT, poly(3,4-ethylenedioxy)pyrrole, PEDOP) can be synthesized. These polymers have narrow bandgap (low redox potential) and moreover, they are resistant to overoxidation. Because of the above arguments, CP/inorganic oxide SC hybrids are in the focus of investigations. Moreover, effective photocorrosion inhibition and photoactivity enhancement for zinc oxide via hybridization with polymer layer can be obtained.

At the end of the second year, we reported about the successful optimization of the photoelectrochemical activity of CP covered ZnO nanorod composite electrodes. Results of the systematic study on the photocorrosion protection of PPy, PEDOT, and PEDOP are submitted and accepted in *Journal of Solid State Electrochemistry*. In this work, we investigated the structural, optical, and electrochemical properties of ZnO nanorod arrays and their hybrids with PPy, PEDOT and PEDOP polymers. In situ spectroelectrochemical measurements proved that the optical properties and redox activities of these covering polymer layers were preserved. Photoelectrochemical properties of the polymer-covered ZnO nanorods were masked by thicker layers, while thin films inhibited the photocorrosion of ZnO, preserving partially their photo-activity. If the polymer layer was too thick, the hybrid lost its photoelectrochemical activity in the anodic region, and its properties were determined mainly by the polymer. On the other hand, if the polymeric layer was too thin, the anticorrosion effect could not be evolved. More effective protection of PEDOP was evidenced in comparison with PPy and PEDOT, since the optimal performance was obtained by a thinner film, balancing properly between photoelectrocatalytic effect and protection against photocorrosion.

Publications:

1. Mágneses nanorészecske tartalmú vezető polimer nanokompozitok előállítása és jellemzése, Endrődi Balázs,* Kormányos Attila, Bencsik Gábor, Peintler-Kriván Emese, Janáky Csaba és Visy Csaba, Magyar Kémiai Folyóirat, accepted
2. Optimization of the photoactivity of conducting polymer covered ZnO nanorod composite electrodes, Emese Peintler Krivan*, Ditta Ungor, Csaba Janáky, Zoltán Németh, Csaba Visy*, Journal of Solid State Electrochemistry, accepted, online published http://link.springer.com/article/10.1007/s10008-014-2587-8

Poster presentation:

64th Annual Meeting of the International Society of Electrochemistry in Santiago de Queretaro, Mexico, 3-8 September, 2013), Synthesis and Characterization of Nanostructured ZnO/Conducting Polymer Composites for Photovoltaic Applications, Emese Peintler-Kriván*, Ditta Ungor, Balázs Endrődi, Zoltán Németh, Csaba Visy, poster number: s06-038.

Oral presentations:

XXXVI. Kémiai Előadói Napok, "ZnO nanostruktúrák és vezető polimerekkel alkotott kompozitjaik előállítása, jellemzése", 29 October, 2013, Szeged, (ISBN: 978-963-315-145-7)

XV. Eötvös Konferencia: "ZnO nanostruktúrák és vezető polimerekkel alkotott kompozitjaik előállítása, jellemzése", April 27, 2014, Budapest,

SZTE Diákköri Konferencia (2. helyezés), "ZnO nanostruktúrák és vezető polimerekkel alkotott kompozitjaik előállítása, jellemzése", Szeged, April 29, 2014

March 4, 2014, Szeged, Group Meeting, “Polipirrol/ZnO nanokompozitok”.

Szeged, 2014. 07. 30.

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