NON-STOICHIOMETRIC Cu-In-S@ZnS NANOPARTICLES PRODUCED IN AQUEOUS SOLUTIONS BY A "GREEN" METHOD AS LIGHT HARVESTERS FOR LIQUID-JUNCTION PHOTOELECTROCHEMICAL SOLAR CELLS

O. Stroyuk[a], A. Raevskaya[a], O. Rosovik[a], A. Kozytskiy[a], V. Dzhagan[b,c], D. Zahn[b]

[a] L.V. Pysarzhevsky Institute of Physical Chemistry of Nat. Acad. Sci. of Ukraine, prosp. Nauky 31, Kyiv 03028, Ukraine
[b]Semiconductor Physics, Technische Universität Chemnitz, Reichenhainer Str. 70, 09107 Chemnitz, Germany
[c]V.E. Lashkaryov Institute of Semiconductor Physics of Nat. Acad. Sci. of Ukraine, prosp. Nauky 41, 03028, Kyiv, Ukraine

A direct "green" aqueous synthesis of mercaptoacetate-stabilized copper indium sulfide (CIS) nanoparticles (NPs) and core-shell CIS@ZnS NPs is reported. The NPs can be easily deposited onto the surface of nanocrystalline FTO/TiO_2 films yielding the visible-light-sensitive photoanodes for the liquid-junction solar cells.

Systematic variation of the NP composition, that is the content of copper, indium and sulfur, as well as the amount of ZnS deposited as a protective shell on the surface of CIS NPs showed that the highest photoelectrochemical activity was demonstrated by a TiO_2/CIS@ZnS photoanode with a molar Cu:In:S ratio of 1:5:10 and a ZnS shell produced as a molar Zn:Cu ratio of 1:1.

The photoelectrochemical activity of TiO_2/CIS@ZnS heterostructures and the photoluminescence (PL) intensity of original colloidal CIS@ZnS NPs were found to change is a similar manner at the variations of copper and indium content allowing to use PL as an indicative parameter when designing CIS-based absorbers for the solar cells. The Raman spectra of CIS NPs revealed a set of features typical for stoichiometric and copper-poorer chalcopyrite phases that is preserved after the ZnS shell formation and deposition of the CIS@ZnS NPs onto the titania surface. The X-ray photoelectron spectroscopy confirmed the copper and indium present as Cu(I) and In(III) and succesfull formation of a ZnS shell in the case of CIS@ZnS NPs.

The optimized TiO_2/CIS@ZnS photoanodes with Cu:In:S and Zn:Cu ratios of 1:5:10 and 1:1 were tested in two-electrode solar cells with aqueous polysulfide electrolyte and TiO_2/Cu_2S heterostructures produced by an original photo-assisted method as counter-electrodes. The cells revealed good stability providing steady photoelectrochemical parameters during more than 2-h continuous illumination and at least a week period of intermittent illumination as well as the excellent reproducibility of the light conversion efficiency that varied in the studied sequence of six identical solar cells not higher than by 1%. Under illumination by a xenon lamp with an intensity of 30 mW/cm^2 lamp the optimized cells showed the average light conversion efficiency of 8.2% with the average open-circuit voltage close to 0.6 V and the average fill factor of 0.42. Similar solar cells based on CIS NPs that were not covered with a ZnS shell demonstrated a far inferior activity with the light conversion efficiency around 5.8% indicating a crucial role of the passivation of surface defects of CIS NPs for achieving efficient charge collection from the TiO_2/CIS photoanodes.

The work is supported by the Volkswagen Foundation (project "New functionalities of semiconductor nanocrystals by controllable coupling to molecules").