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Inorganic photoelectrochemical solar cells based on nanocrystalline ZnO/ZnSe and ZnO/CuSe heterostructures

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ABSTRACT

Nanocrystalline FTO/ZnO/ZnSe were prepared from electrodeposited zinc oxide films and then converted into FTO/ZnO/CuSe heterostructures via complete substitution of zinc(II) in zinc selenide by copper(II). The starting FTO/ZnO films contain a 5–6- μm layer of porous zinc oxide microplatelets with the lateral size of up to 3 μm and the thickness of up to 200 nm which are formed by loosely aggregated ZnO nanocrystals. Partial conversion of such films into ZnSe and CuSe does not induce considerable changes in the film morphology allowing to use the FTO/ZnO films as a template defining the morphology and composition of resulting FTO/ZnO/ZnSe and FTO/ZnO/CuSe films. The FTO/ZnO/ZnSe heterostructures were found to be efficient photoanodes of model liquid-junction solar cells with sulfide/polysulfide redox-couple under illumination with white light ($\lambda > 400$ nm). The activity of FTO/ZnO/CuSe heterostructures as cathodes of such solar cells was demonstrated for the first time. A two-electrode solar cell based on the FTO/ZnO/ZnSe photoanode and the FTO/ZnO/CuSe cathode generates by an order of magnitude higher photocurrent density as compared with a similar cell based on a Pt foil cathode.

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Introduction

In recent 10–15 years solar cells based on nanostructured porous wide-band-gap oxide semiconductors (TiO_2 , ZnO, etc.) sensitized to visible light by dyes or metal complexes, for example, the well-known Grätzel cell [1–3], have achieved 11–12% efficiency of light conversion and emerged therefore as a feasible competitor to the silicon-based photovoltaic systems. The attractiveness of the so-called liquid-junction solar cells lies not only in their comparatively low cost but rather in multiple ways to design such systems by tailoring the morphology and properties of a wide-band-gap metal oxide component, the structure and light sensitivity range of a molecular sensitizer, the nature of interaction between the sensitizer and the oxide surface and electrolyte, the transport properties of a redox-couple, etc. [2,3].

Recently the combusive progress in the field of dye-sensitized solar cells has reached a certain saturation and an alternative research direction has emerged dealing with the all-inorganic liquid-junction solar cells where the nanocrystals of narrower-band-gap semiconductors, typically cadmium or lead chalcogenides are used as sensitizers of the wide-band-gap oxide

photoanodes [2,4–6]. The progress of this branch of the photovoltaics requires addressing several vital issues. The first one is searching for new efficient and at the same time “green” sensitizers free from cadmium or lead or other acutely toxic metals.

The second important subject is the search for new efficient counter electrodes because platinum cathodes typical for the Grätzel cells are inefficient for the $\text{S}^{2-}/\text{S}_x^{2-}$ redox-couple which is one of the most frequently used in the all-inorganic solar cells [5–8]. Recently high activity of many metal sulfide semiconductor as counter electrodes has been reported, for example Cu_xS [2,5,6,8–12], CoS [5,6,11,13], PbS [6,7], MoS_2 [14,15], Sb_2S_3 [2], Bi_2S_3 [16], etc.

Finally, design of the wide-band-gap components, typically TiO_2 and ZnO films, aiming at tailoring of their morphology, surface chemistry and electron transport properties still remains one of the key points at developing an efficient all-inorganic solar cell [2,6]. In this field the titania-based systems dominate by many reasons including higher stability of TiO_2 over zinc oxide in various electrolytes and in a broad pH range. At the same time, the very chemical activity of ZnO can be exploited to create various heterostructures—potential components of both photoanodes and counter electrodes of the all-inorganic solar cells. In particular, partial transformation of zinc oxide into zinc chalcogenides at immersion of the ZnO crystals into solutions of the corresponding salts is an easy way to ZnO/ZnX heterostructures, where X = S, Se, Te.

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A particular interest is drawn to ZnO/ZnSe heterostructures exhibiting a favorable combination of the band levels of the components with the sensitivity to the visible light. The ZnO/ZnSe heterostructures are currently explored as photodetectors [17], photocatalysts of dyes transformation [18–21] and photoelectrochemical water splitting [22], and as a visible-light-sensitive component of solid-state [23–25] and liquid-junction [12,19,26,27] solar cells. Formation of mixed layers on a ZnO–ZnSe interface often impart the ZnO/ZnSe heterostructures with the sensitivity in the range of up to 700–800 nm, where the separate components do not absorb [18–20,23,25].

Substitution of zinc(II) in zinc selenide component of ZnO/ZnX heterostructures with the metals ions giving less soluble chalcogenides (Cu_xS , Ag_2S , Bi_2S_3 , etc.) opens a way to a myriad of heterostructures which are of potential interest for the photovoltaics. A proof-of-concept experiment has recently been performed [28] in preparing $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ photoanodes by partial sulfidation of Cu_2O films.

The present work aims at testing the applicability of such method for preparation of both the photoanodes and counter electrodes from nanocrystalline zinc oxide films. The results show that the ZnO films can be easily transformed into the ZnO/ZnSe and then into ZnO/CuSe heterostructures. The ZnO/ZnSe films can be used as visible-light-sensitive photoanodes in a model solar cell in a tandem with ZnO/CuSe films. The latter serve as cathodes, by an order of magnitude more efficient than conventional platinum.

Experimental section

Electrodeposition of FTO/ZnO films was described in detail elsewhere [29] and is given in supporting information (SI). The ZnO/ZnSe composites were prepared by a partial substitution of oxygen with selenium at immersion of an FTO/ZnO film into Se(II)-containing solution. The solution was prepared by introducing 0.05 M NaBH_4 into 20 mL of 0.02 M boiling Na_2SeO_3 solution. The solution changes from colorless to red–brown and then again to colorless indicating successive reduction of Se(IV) to elemental selenium and Se(0) to selenide-anions. The FTO/ZnO films produced at a different electrolysis duration were immersed into this solution for 5 min, then extracted and washed with argon-saturated distilled water for 10 min, dried for 5 min in the argon flow at 70 °C and kept in dark.

The ZnO/CuSe composites were produced by substituting Zn(II) in the zinc selenide with Cu(II). For this, the FTO/ZnO/ZnSe films were immersed into 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution for 30 min, then extracted, washed with distilled water, dried for 5 min in argon flow at 70 °C and kept in vacuum.

Electrochemical and photoelectrochemical measurements were performed in three- and two-electrode schemes. The three-electrode cell with an inner diameter of 4 cm housed an FTO/ZnO/ZnSe film as a photoanode, Pt foil with the working area of 1 cm² as a cathode and an Ag/AgCl/KCl reference electrode. The two-electrode cell contained FTO/ZnO/ZnSe and FTO/ZnO/CuSe films as a photoanode and a cathode, respectively. The aqueous electrolyte (20 mL) with 0.1 M NaOH, 0.1 M Na_2S and 1×10^{-3} M Na_2S_x was constantly bubbled with the argon flow. The cells were illuminated with a white LED lamp ($\lambda > 400$ nm, intensity $I = 18$ mW/cm²) under magnetic stirring. In electrochemical and photoelectrochemical experiments a PC-programmed Keithley 2400 multimeter was used as a potentiostat/galvanostat. All the potentials in the paper are given relative to an Ag/AgCl reference electrode.

Absorption spectra of the films were registered using a Specord 210 spectrophotometer. Scanning electron microphotographies (SEM) were taken on Tescan Mira 3 microscope at an accelerating

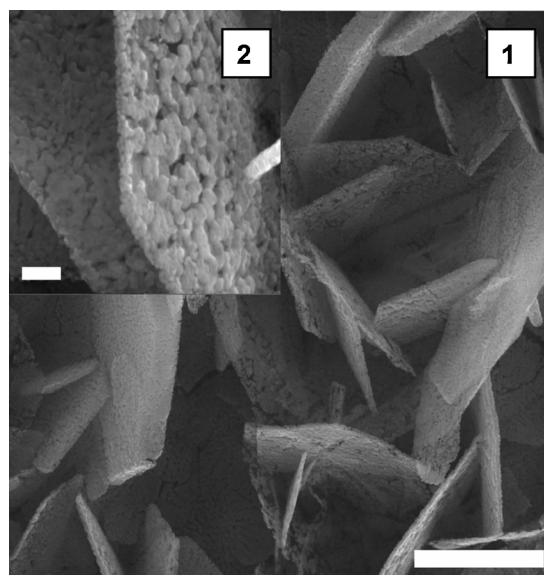


Fig. 1. SEM image of FTO/ZnO film. Scale is 1 μm (1) and 200 nm (2).

voltage of 10–20 kV. The energy-dispersive X-ray (EDX) spectra were registered using an Oxford X-max 80 mm² setup. The EDX spectra were recorded either from FTO-based films or from powdered samples produced by ultrasound-induced detachment of ZnO/CuSe particles from the surface of FTO/ZnO/CuSe films. The powdered samples were fixed on carbon films which is the origin of carbon signals in the EDX spectra.

Results and discussion

The FTO/ZnO films

Electrodeposition from aqueous zinc(II) nitrate solutions onto the optically transparent electrodes (ITO, FTO) results in formation of layered zinc hydroxychloride $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ films [29]. According to SEM, the hydroxychloride films are composed of $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ microplatelets with a lateral size of up to 3 μm and a thickness varying from 50 to 300 nm (SI, Fig. S1). Calcination of the films at 400 °C results, according to XRD [29], in complete conversion of $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ into ZnO. The ZnO microplatelets produced by the thermal treatment are characterized by the same lateral size, up to 3 μm , and a thickness of up to ~200 nm (Fig. 1; additional images are given in Fig. S2). The platelets are formed by ZnO nanocrystals up to ~50 nm in size that are loosely aggregated resulting in a porous structure of the platelets (it is clearly observed in Fig. 1, fragment 2 and Fig. S2, fragments 2, 3).

The extinction spectra of the FTO/ZnO films reveal a broad structureless halo from the light scattering with the intensity increasing smoothly to shorter wavelengths (Fig. 2a). After the thermal treatment a new absorption band appears on the background of the halo at $\lambda < 390$ nm belonging to ZnO nanocrystals. The band gap E_g of the FTO/ZnO films can be estimated from the absorption band edge position using the well-known Tauc equation (1) for the absorption coefficient α [30]:

$$\alpha = A \frac{(h\nu - E_g)^n}{h\nu} \quad (1)$$

where A is a constant; $h\nu$ is the quantum energy; n depends on the nature of interband electron transition [30].

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