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Micro-Raman, photoluminescence and photocurrent studies on the photostability of quantum dot sensitized photoanodes

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ABSTRACT

Photoanode electrodes have been made by layer deposition of CdS, CdSe and ZnS quantum dots on nanocrystalline titania and were studied by micro-Raman and photoluminescence techniques or were assembled with a Cu_2S-on-brass cathode to make quantum dot sensitized solar cells. Spectroscopic characteristics of the photoanodes and electric characteristics of the cells were studied as a function of the illumination time and the photoanode material and structure. Combined semiconductor quantum dot sensitizers gave more stable photoanodes than simpler components. Stability increased by successive CdS, CdSe and ZnS deposition. ZnS was the most crucial component the presence of which on the top of the subsequent layers consolidated stability. Furthermore, analysis of the Raman spectra revealed the formation of CdS_xSe_{1-x} composites at the interface of the CdS/CdSe layers, which may be an additional stabilization factor. Thick cells were used in this work where the distance between anode and cathode electrodes was 5 mm. Despite this large distance, the cells produced high currents, thanks to the high ionic conductivity of aqueous polysulfide electrolyte and the liberty in configuring the active area of the cathode electrode.

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1. Introduction

Quantum dot sensitized solar cells (QDSSCs) have emerged as an interesting subject of research that enjoys increasing popularity. QDSSCs are excitonic solar cells characterized by low preparation cost and high power conversion efficiencies. They function under a similar concept as their dye-sensitized homologues but they also present many differences: semiconductor quantum dots (QDs) are used as sensitizers in the place of dye sensitizers; they employ aqueous polysulfide (S_n^{2-}/S^{2-}) electrolytes instead of corrosive organic-solvent-dissolved polyiodide (I_3^-/I^-) electrolytes; and they employ low cost metal sulfide electrocatalysts on the counter electrode instead of expensive Pt nanoparticles. Platinum nanoparticles cannot sustain themselves in the presence of polysulfide electrolyte [1,2] and lead to high charge transfer resistance [3,4]. The popularity of QDSSCs stems from the several favorable properties of QD semiconductors [5]: their absorption edge can be tuned by means of the quantum confinement effect; they have large extinction coefficients, therefore a thin layer can absorb sufficient quantity of photons; they have high excited state dipole moments and, since they match well the conduction band level of oxide semiconductors, they facilitate excited electron injection; they combine synergistically with other QDs offering panchromatic sensitization, etc. Most interesting is the presence of impact ionization effects resulting in their capacity for multiple electron generation per absorbed photon that could push cell efficiency beyond the 32% Shockley–Queisser limit [6,7]. In addition, synthesis of QD nanoparticles is easy and their sizes (a few nanometers) match well the mesoporous structure of oxide semiconductors, for which they are intended to act as sensitizers. Typical QD sensitizers are CdS, CdSe, ZnS, PbS and Sb_2S_3, however, it seems that only CdS, ZnS and CdSe are effective with liquid electrolyte solar cells [8–10]. Combined QD sensitizers have been shown to be more effective than single species [8]. A standard configuration comprises a bottom layer or CdS [9,10] (or a mixture of CdS with ZnS [8]) a middle layer of CdSe and a thin top layer of ZnS, which passivates [9,10] and protects the underlying layers, while its high lying conduction band level [11] discourages inverse electron leakage towards the electrolyte. Even though, ZnS passivation layers have been widely used in order to improve the stability of the QDSSCs, there is a lot of work currently being carried out to better understand the mechanisms of the chalcogenide QDs oxidation and photocorrosion, to optimize the ZnS thickness and to substitute ZnS with other inorganic layers,

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like $PbCl_2$ [12] or organic compounds bearing hole sequestering ligands [13].

In the present work, we have studied the stability of QD-sensitized nanoparticulate titania (nc-TiO_2) photoanodes by spectroscopic techniques, namely, by micro-Raman and Photoluminescence (PL), in order to demonstrate the importance of QD combination. For this purpose, we combined CdS, CdSe and ZnS QDs, which are standard semiconductors employed in QDSSCs and have also been previously employed by ourselves [8]. Combination of these QDs provides a substantial absorption cross section in the Visible as will be also shown in the present work. Nanocrystalline titania and QD sensitizers were deposited in a standard configuration on transparent electrodes and were studied during successive stages of materials deposition. Such photoanodes were tested in QDSSC devices and their performance was recorded instantaneously and as a function of time in order to elucidate the stability issues and correlate them with the spectroscopic properties of the films.

2. Experimental

2.1. Materials

Unless otherwise indicated, reagents were obtained from Aldrich and were used as received. Commercial nanocrystalline titania Degussa P25 was used in all cell constructions and Millipore water was used in all experiments. SnO_2:F transparent conductive electrodes (FTO, resistance 8 Ω/square) were purchased from Pilkington.

2.2. Construction of nc-TiO_2 films on FTO electrodes

The following procedures, similar to a previous publication [8], were undertaken in order to construct photoanode electrodes. First, the nc-TiO_2 film was synthesized. It was deposited in two layers, a bottom compact layer and a top open structure. The bottom layer facilitates attachment to the FTO electrode and enhances electric connectivity with the FTO layer. It also helps suppress charge recombination as it has been recently demonstrated [14]. This layer was synthesized by the sol–gel method while the top layer was deposited by using a paste made of Degussa P25 nanoparticles. Thus a densely packed nanocrystalline titania layer was first deposited on a patterned FTO electrode, which was cleaned by sonication in acetone, isopropanol and ethanol: 3.5 g of the non-ionic surfactant Triton X-100 was mixed with 19 mL ethanol. Then 3.4 mL glacial acetic acid and 1.8 mL of Titanium Tetraisopropoxide were added under vigorous stirring. After a few minutes stirring, the film was deposited by dipping and then it was left to dry in air for a few minutes. Finally, it was calcined at 550 °C. The temperature ramp was 20° min^{-1} up to 550 °C and the sample was left for about 10 min at that temperature. Then the above procedure was repeated once more to obtain a final compact film, about 300–350 nm thick. On the top of this compact nanostructured layer, commercial Degussa P25 was deposited. For this purpose, we used a paste [8], which was applied by screen printing. It was finally calcined again at 550 °C. This last sequence was repeated in order to obtain a top layer of about 10 μm thick. The thickness of the films was measured by their SEM profiles. The geometrical area of the film was 1 cm^2 (1 cm × 1 cm).

2.3. Formation of the CdS layer

CdS nanoparticles were deposited on the nc-TiO_2 film by Successive Ionic Layer Adsorption and Reaction (SILAR method) [8,15]. For this purpose, two aqueous solutions were used, one containing $Cd(NO_3)_2.4H_2O$ and the second containing $Na_2S.9H_2O$. The total concentration of cadmium ions and the corresponding concentration of sulfur ions were 0.1 mol L^{-1}. The freshly prepared titania electrode was immersed for 3 min in the metal salt solution, then copiously washed with triple-distilled water, then immersed for 3 min in the $Na_2S.9H_2O$ solution and finally washed again. This sequence corresponds to one SILAR cycle. 10 SILAR cycles were performed in all studied cases. Finally, the electrode with deposited CdS–nc-TiO_2 film was first dried in a N_2 stream and then for a few minutes in an oven at 100 °C. This electrode was used as a substrate for the next stage of CdSe deposition or was employed either for spectroscopic measurements or for cell assembly.

2.4. Formation of the CdSe layer

CdSe was deposited by Chemical Bath Deposition (CBD) on the above CdS layer. The procedure was similar to that previously employed by us and by other researchers [5,8,16] and involves the following steps: An aqueous solution of 0.08 mol L^{-1} Se powder was first prepared in the presence of 0.2 mol L^{-1} Na_2SO_3 by continuous stirring and refluxing at 80 °C. The procedure lasted about 15 h and was carried out overnight. The obtained solution, denoted in the following as sol A, actually aimed at the formation of sodium selenosulphate (Na_2SeSO_3), which is a precursor for slow Se^{2-} release. Two more aqueous solutions were then prepared, containing 0.08 mol L^{-1} $CdSO_4{\cdot}8/3H_2O$ (sol B) and 0.12 mol L^{-1} nitrilotriacetic acid trisodium salt (sol C), respectively. Sol B was mixed with an equal volume of sol C and the obtained mixture was stirred for a few minutes. The combination of sol B with sol C leads to the formation of a complex, which is used as precursor for slow release of Cd^{2+}. Finally, two parts of this last mixture were mixed with one part of sol A and the thus obtained final mixture was used for CBD. The final concentration of Se^{2-} and Cd^{2+} ions was 0.08/3 mol L^{-1}. The idea of the above procedure is to make a mixture of precursors, which slowly release selenium and cadmium ions so as to make them react after adsorption on the substrate. Thus the electrodes with substrate films were dipped in this final solution. Subsequently, they were put in a refrigerator at 5 °C for 4 h. Finally, the electrode with deposited CdSe–CdS–nc-TiO_2 film was first dried in a N_2 stream and then for a few minutes in an oven at 100 °C. This new electrode was used as a substrate for the next stage of ZnS deposition or was employed either for spectroscopic measurements or for cell assembly.

2.5. Formation of the top ZnS layer

A passivation ZnS layer was added on the top of the CdSe layer by 2 SILAR cycles as above, using 0.1 mol L^{-1} aqueous precursor solutions of the respective Zn^{2+} ($Zn(NO_3)_2{\cdot}6H_2O$) and S^{2-} ions. Finally, the film was first dried in a N_2 stream and then for a few minutes in an oven at 100 °C.

2.6. Construction of the counter electrode

A brass foil was cleaned, first by rubbing with a sand paper, washing with soap and acetone and then by sonication in ethanol. Subsequently, it was treated in a HCl 37% solution at 70 °C for 5 min and then it was immersed for 10 min in a polysulfide electrolyte made of aqueous 1.0 mol L^{-1} $Na_2S.9H_2O$ and 1.0 mol L^{-1} S. The polysulfide electrolyte solution was prepared by first dissolving Na_2S then heating solution up to 70–80 °C and finally dissolving S by continuous stirring at that temperature for about 20 min. The same electrolyte was also used to fill the cell. When the brass slide was taken out of the polysulfide electrolyte, it was covered by a thin black Cu_2S film [17]. After drying at 100 °C, the electrode with deposited material was annealed at 450 °C in an inert (N_2)

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