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journal homepage: www.elsevier.com/locate/solmat

Thermal annealing of photoanodes based on CdSe Qdots sensitized TiO₂



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ARTICLE INFO

Article history:

Received 19 February 2016

Received in revised form

24 May 2016

Accepted 11 June 2016

Available online 17 June 2016

Keywords:

Quantum dots

Photoanode

Thermal annealing

Nanotubes

ABSTRACT

Thermal annealing of photoanodes made of TiO₂ nanotubes sensitized with CdSe quantum dots is studied. Heat treatment of these photoanodes in air can cause either an improvement or a serious drop in the photocurrent generation. Ligands or capping agents stabilize Qdots removing highly reactive dangling bonds on its surface but also they can act as a passivating layer that increases charge transfer resistance between Qdots and TiO₂ nanotubes; therefore optimal conditions of thermal annealing are needed to improve efficiency of the interfacial charge transfer avoiding as far as possible the decomposition of the sensitizers. As a corollary of this study, a 2.5-fold increase in photocurrent value was reached after thermal annealing at 200 °C during at least two hours; while thermal treatments at temperature values higher than 250 °C can produce a deleterious effect on the conversion efficiency if the annealing time extends over a long period of time. Photoelectrochemistry, thermogravimetry and SEM microscopy were used as tools to propose a mechanism able to explain the observed behaviour.

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1. Introduction

As a consequence of the climate change that is currently being developed mainly by greenhouse gases, especially CO₂ increased emissions, further advancement in research and development to exploit alternative energy sources such as sunlight is required. Photovoltaic (PV) cells are the most direct way to convert sunlight into electricity and nowadays efforts are targeted to enhance the sunlight to electric power conversion efficiency and to reduce the fabrication cost of such devices. Quantum dot sensitized solar cells (QDSSCs) are a type of third generation PV devices with potential conversion efficiencies and fabrication methods that would meet the required needs [1].

To build QDSSCs photoanodes, semiconductor quantum dots (Qdots) which act as optical sensitizers are deposited onto wide-bandgap semiconductor nanostructures such as TiO₂ nanotubes or mesoporous films. Semiconductor Qdots such as CdSe, CdS, PbS, PbSe, CdTe, InAs among others can be synthesized in-situ (directly into wide band gap nanostructures) through SILAR [2] (Successive ionic-layer adsorption and reaction) or CBD [3] (Chemical bath deposition) methodologies or synthesized prior to its deposition

Abbreviations: Qdots, Quantum dots; PV, Photovoltaic; QDSSCs, Quantum dot sensitized solar cells; IPCE, Incident Photon-to-Current Efficiency; TOP, Trioctylphosphine; VB, Valence Band; CB, Conduction Band

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<http://dx.doi.org/10.1016/j.solmat.2016.06.015>

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onto wide-bandgap nanostructures for example by "Hot injection method" [4]. The major advantage of pre-synthesized colloidal Qdots over those which are synthesized in-situ is the possibility of controlling their shapes and size distribution, features that are intimately related to their optical properties [5]. In this case attachment to wide-bandgap semiconductor can be achieved by the use of molecular linkers or simply by direct adsorption [6]. In order to obtain efficient photoanodes it is important to optimize charge transfer processes between Qdots and wide band gap nanostructures and to prevent recombination reactions of the photogenerated electrons.

Thermal annealing performed over photoanodes consisting of TiO₂ mesoporous films sensitized with Qdots has been reported to improve their efficiency when it is carried out in a certain range of temperatures by increasing the crystallinity of sensitizers and improving the interfacial charge transport dynamics [7–9]. Nevertheless thermal treatment at higher temperatures causes an efficiency decrease because the oxidation of the sensitizers occurs.

Pre-synthesized Qdots are covered by capping agents, which are usually organic molecules attached to the Qdots surface such as fatty acids or alkyl phosphines. These ligands prevent aggregation and also stabilizes Qdots removing highly reactive dangling bonds on its surface but they can affect the interaction of Qdots with the wide-bandgap semiconductor, acting as a passivating layer that increases charge transfer resistance [10]. It was shown previously in [11] that thermal annealing in Argon atmosphere at 300 °C during 30 min performed over a photoanode

consisting of CdTe presynthesized Qdots linked to TiO₂ nanotubes by mercaptopropionic acid (MPA) improved its efficiency as a consequence of the evaporation of MPA from Qdots surface enabling a better electron transfer. Thus, thermal annealing of the photoanodes is considered as a possibility to evaporate capping molecules from Qdots surface enabling a better interfacial contact between Qdots and TiO₂ when it is carried out in optimal conditions i.e. time and temperature of thermal treatment. Nevertheless is worth noting that massive evaporation of capping molecules in first place leaves Qdots surface in direct contact with the electrolyte phase surrounding the photoanode and recombination reactions of photogenerated electrons became more important, reducing the conversion efficiency. Also the stability of Qdots becomes lowered by leaving the surface dangling bonds free which can lead to the formation of an oxide layer in the presence of oxygen probably interfering in electron transfer reactions.

In order to analyze the thermal annealing effect on the photoanode, changes in the electrical/physicochemical properties of the photoanodes and in the kinetic of processes involved on photocurrent generation caused by thermal treatment were evaluated. In this work, we explored the effect of thermal annealing in air atmosphere carried out in a wide range of temperatures and annealing times on the efficiency of photoanodes consisting of TiO₂ nanotubes sensitized with CdSe pre-synthesized Qdots by direct adsorption.

2. Experimental section

2.1. Synthesis and characterization of TiO₂ nanotubes obtained by Titanium anodization

The chemicals used for TiO₂ nanotubes synthesis were Titanium foil, Ethylene glycol (Pro analysis, Dorwil), ammonium fluoride (NH₄F Pro analysis, Ciccarelli).

Anodization was carried out following a procedure previously reported in [12] with slight changes. Briefly, prior to anodization, Ti foils were polished and ultrasonically cleaned in isopropyl alcohol, acetone, ethanol, deionized water (MILLI-Q) and dried in nitrogen atmosphere. Anodization was performed in a two-electrode cell with Ti foil as working electrode and Au foil as counterelectrode. A voltage of 40 V was applied between both electrodes during 2 h. The electrolyte solution was 4%w/w deionized water and 0.3%w/w NH₄F in ethylene glycol. Anodization was carried out at 24 °C and under constant stirring. After anodization was finished, the Ti/TiO₂ nanotube surface was rinsed with ethanol, ultrasonically rinsed for 2 min in ethanol and left drying in air. Finally, to convert TiO₂ crystalline structure to anatase, thermal annealing treatment in a furnace was carried out in air at 400 °C during 4 h.

TiO₂ nanotubes were morphologically characterized by Scanning Electron Microscopy (FE-SEM, Sigma).

2.2. CdSe Qdots synthesis and characterization

The chemicals used for CdSe Qdots synthesis were Cadmium oxide (CdO 99.5%, Aldrich), Selenium powder (99.5%, Sigma Aldrich), Trioctylphosphine (TOP 90%, Technical grade, Sigma Aldrich), Myristic Acid (98%, Fluka), 1-Octadecene (90%, Technical grade, Aldrich).

CdSe Qdots, capped with myristic acid and trioctylphosphine (TOP) were synthesized by the "Hot injection method", following a methodology previously described in [4] except that myristic acid was used instead of oleic acid to prepare the Cd precursor. Briefly, the Se-precursor (TOP-Se) dissolved in 1-octadecene at room temperature was rapidly injected into a flask containing the Cd-

precursor (Cadmium myristate) dissolved in 1-octadecene previously heated at ~230 °C under N₂ atmosphere; after 75 s the reaction vessel was removed from the hot plate and cooled down to quench the reaction. In this way a Qdots dispersion with good quality, small size distribution, with a Qdot diameter of 3.3 nm was obtained, as determined from the absorbance and fluorescence emission. After synthesis, the Qdot sample was purified by several washing cycles dispersing it in ethanol, centrifugation and extraction of the ethanolic phase which became enriched with excess precursors and 1-octadecene. Finally, CdSe Qdots were dispersed in toluene for later use.

Dispersions of synthesized Qdots in toluene were characterized by UV-vis absorption (UV 1700, Shimadzu) and fluorescent emission. Thermogravimetric analysis of CdSe Qdots samples were performed in a Shimadzu TGA/DTA-50 in the temperature range from 25 to 600 °C at a heating rate of 2 °C/min under flowing air.

2.3. Preparation and characterization of photoanodes

Photoanodes were prepared with TiO₂ nanotubes which were modified with CdSe Qdots by direct adsorption. TiO₂ nanotubes were immersed into a dispersion of CdSe Qdots in toluene for time periods ranging from 5 to 7 h. Photocurrent produced by illuminating with white light as it is described in the next paragraph was measured until a stationary value was reached in each case.

Phototelectrochemical experiments were performed in a three electrode cell built in a standard spectrophotometric cuvette with 10 mm pathlength. Photoanode was the working electrode, a Pt wire the counterelectrode and Ag₂S/Ag the reference electrode (see Fig. 1). An aqueous 1 M sodium sulfide (Na₂S · xH₂O 60–62%, Riedel-de Hæn) solution was used as electrolyte.

The cell was illuminated using a focused beam from a 150 W Xe lamp and photocurrent/photovoltage was measured using a potentiostat (PGSTAT-101, Autolab). Incident photon to charge efficiency (IPCE) measurements were performed employing the same

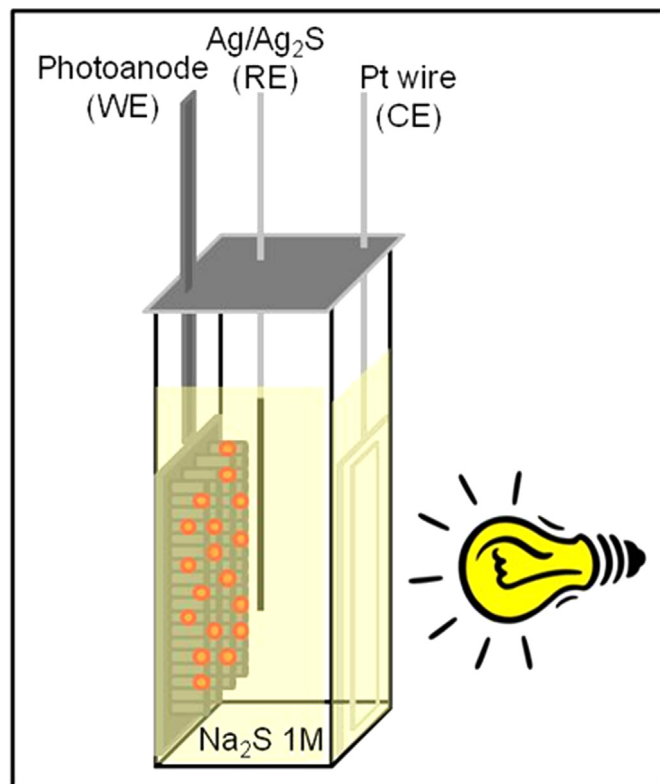


Fig. 1. Electrochemical cell assembly used to characterize the photoanode.

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