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Effects of passivation treatment on performance of CdS/CdSe quantum-dot co-sensitized solar cells

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ABSTRACT

Carrier recombination can greatly reduce the efficiencies of quantum-dot sensitized solar cells (QDSSCs). This work aims to find a general preparation route to reduce carrier recombination in QDSSCs. The effects of a series of passivation treatments on CdS/CdSe quantum-dot (QD) co-sensitized solar cells are investigated. The QDs were synthesized on a nanoporous TiO_2 electrode by the successive ionic layer adsorption and reaction processes. The different types of treatment included a blocking layer, a fluoride-ion coating, a ZnS coating, annealing, a TiO_2 scattering layer and an Au counterelectrode. The power conversion efficiency was observed to become three times larger after treatment. The effectiveness of each treatment method is as follows in descending order: blocking layer≅TiO_2 scattering layer > Au counterelectrode > F^- ions and ZnS coatings > annealing. The best cell yields a current density of 14.6 mA/cm^2 and a respectable power conversion efficiency of $\eta = 3.11\%$ under AM 1.5 sun. The passivation procedure makes a useful general guide for researchers for the preparation of QDSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied as a low cost alternative to silicon-based photovoltaics. A DSSC comprised a photoanode, an electrolyte and a counterelectrode. The photoanode (or photoelectrode) consists of a nanoporous TiO_2 film coated onto a transparent conductive oxide glass substrate (usually fluorine-doped tin oxide-FTO). The TiO_2 nanoparticles are sensitized by adsorbing a monolayer of organic dye molecules onto their surface. Upon solar illumination, the photoexcited electrons of the dye molecules are injected into the conduction band (CB) of the TiO_2 nanoparticles, then injected into the FTO substrate, finally producing a photocurrent. The highest efficiency achieved has been ~11% in 2005 [1], and ~13% in 2011 [2]. High efficiency is due to the three-dimensional nanoporous network of TiO_2 nanoparticles, which greatly increases the surface area for dye adsorption, in turn, enhancing light harvesting. The most commonly used organic dyes are the ruthenium complex dyes, N3 and N719. These dyes have strong optical absorption in the visible spectral range, but weak absorption in the infrared range. This leads to an incomplete overlap with the solar spectrum and a loss of more than 50% of the incident solar power. In addition, organic DSSCs have problems of long-term stability at high temperatures under full illumination from the sun.

In recent years, inorganic nanomaterials have emerged as alternative light harvesters for solar cells. Thin film semiconductor absorbers have been employed as sensitizers for solar cells. Semiconductor quantum dots, such as CdS, CdSe [3–5], PbS, PbSe [6,7] and InP [8], have also been used in solar cells. Quantum-dot (QD) sensitizers have several advantages over organic dyes such as tunable absorption bands due to the quantum confinement effect [9], higher absorption coefficients than most organic dyes [10], and the generation of multiple electron-hole pairs by a single incident photon [11]. Quantum-dot sensitized solar cells (QDSSCs) typically have power conversion efficiencies of ~2–5% [12–16]. By combining two types of QDs, the õabsorption spectral range can be increased. Double-layered (or co-sensitized) QD CdS/CdSe-based systems have been investigated by several groups. The efficiencies achieved for double-layered QDSSCs are higher than those from single-layered QDSSCs [17–23]. However, these efficiencies are still lower than those of organic DSSCs. A major problem limiting the efficiency of QDSSCs is that not all photoelectrons can reach the collecting electrode. Several back reactions can lead to the recombination of a photoelectron with a hole in the electrolyte. Fig. 1(a) shows four electron-hole recombination routes: (1) electrons in the CB of the QD recombine with the oxidized redox couples; (2) electrons injected into the CB of TiO_2 can transport quickly to the electrolyte, a process similar to recombination; (3) electrons injected into the FTO glass recombine with the oxidized redox couples; and (4) electrons in the CB of TiO_2 recombine with holes in the valence band of the QD. Carrier recombination reduces the photocurrent, open-circuit voltage and fill factor, resulting in lower power conversion efficiencies.

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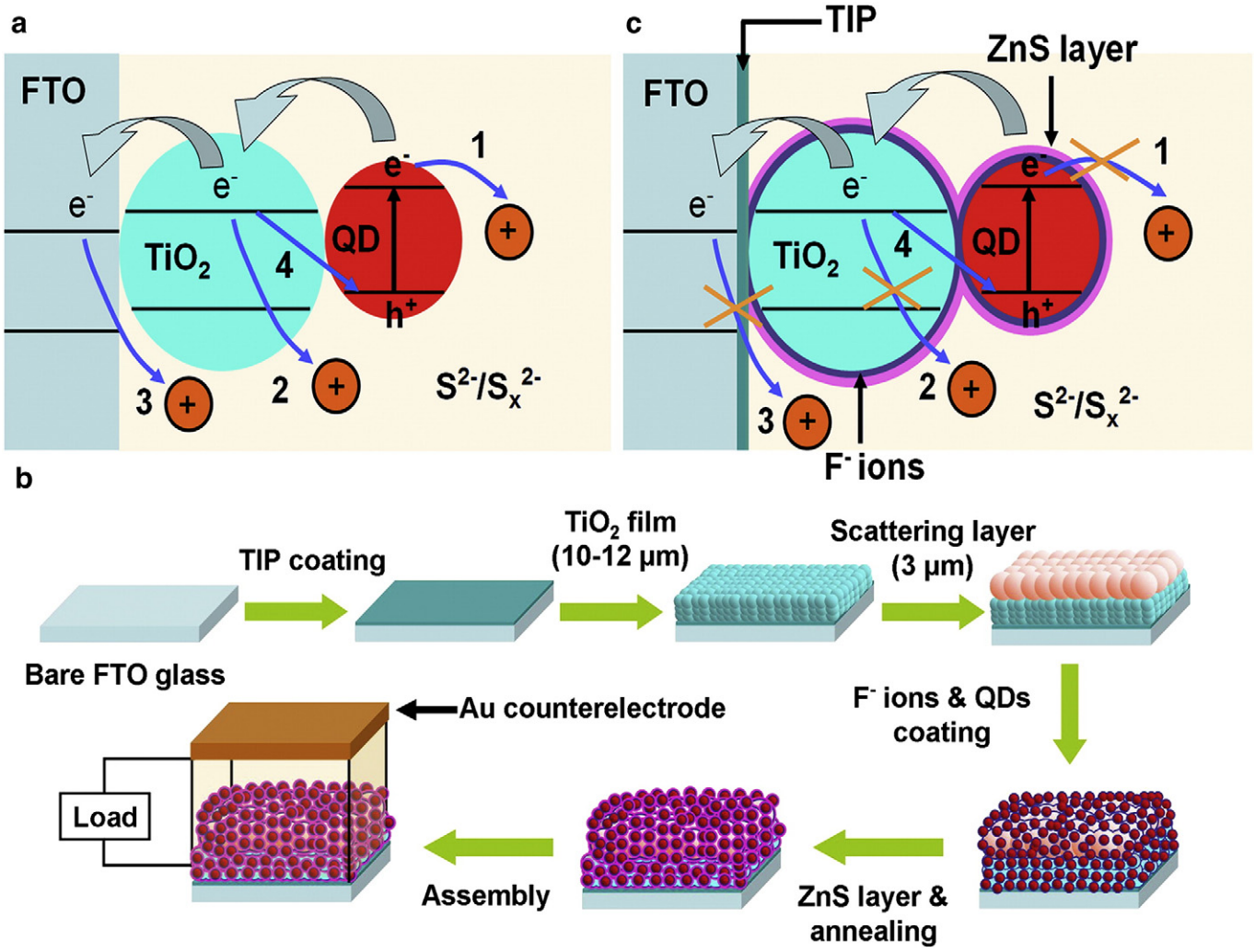

Fig. 1. (a) Diagrams of four recombination routes for photoelectrons, (b) preparation procedure for various passivation treatments and fabrication of QD-DSSCs, (c) diagrams of various passivating coatings and suppression of recombination routes.

To reduce recombination, researchers have discovered that the applications of various types of coating to the TiO_2 electrode can passivate the QD surfaces and suppress the recombination process [24,25]. Typically, one or two types of passivation coatings are applied to the electrode during the fabrication process. However, there is no consensus on what is the best procedure to perform the various passivation coatings. This work presents the complete passivation treatment that includes most of the passivation methods available to date. We investigate the effects of different passivation coatings in a double-layered CdS/CdSe QD system. Additional treatment methods, including annealing, the utilization of a TiO_2 scattering layer and the use of an Au counterelectrode have also been applied to the QDs. The effects of the passivation treatment are studied from the optical absorption, external quantum efficiency (EQE) and photovoltaic performance. The contribution to the efficiency due to each treatment is determined qualitatively. Large enhancement in power conversion efficiency is observed after treatment. The enhancement in efficiency due to each treatment method is compared.

2. Experimental details

Fig. 1(b) illustrates the sequence of sample preparation and various passivation treatments. The details are as follows.

2.1. Preparation of TiO_2 photoelectrodes

The TiO_2 electrodes are prepared by spreading a commercial transparent TiO_2 paste (Dyesol DSL-18NR-T, particle size ~20 nm) onto fluorine-doped tin oxide (FTO) glass (15 Ω/sq) using the doctor-blade technique described previously [26]. Prior to the TiO_2 coating, the FTO glass was coated with a titanium isopropoxide (TIP) film (for details please see the Section in Passivation treatments). The thickness of the TiO_2 films, determined from cross-sectional field emission scanning electron microscopic images, was ~10–12 μm. Finally, a 3 μm-thick TiO_2 scattering layer was coated on the top of the film.

2.2. Synthesis of CdS/CdSe QDs

The CdS/CdSe double-layered QDs were synthesized using the successive ionic layer adsorption and reaction deposition (SILAR) process. For efficient injection of photoelectrons, the CB of the top layer QD should lie above the CB of the underlayer QD. It has been revealed in previous work that the CdS QD should be the underlayer and the CdSe QD the top layer [17]. The TiO_2 electrode was first immersed into a 0.50 M, 25 °C $Cd(NO_3)_2$ ethanol solution, rinsed thoroughly in ethanol, immersed again in a 0.50 M Na_2S methanol solution and finally rinsed again in methanol. Each immersion step