



Ultrafast characterization of the electron injection from CdSe quantum dots and dye N719 co-sensitizers into TiO₂ using sulfide based ionic liquid for enhanced long term stability



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ARTICLE INFO

Article history:

Received 28 January 2013

Received in revised form 21 March 2013

Accepted 21 March 2013

Available online 28 March 2013

Keywords:

Quantum dot sensitized solar cells

Ionic liquid

TiO₂

CdSe

Dye

ABSTRACT

Combination of inorganic quantum dots (QDs) and organic/metallorganic dyes as supracollectors nanocomposites could have an important role on the development of efficient photovoltaic devices based on the synergistic action of the hybrid-sensitizers. Here we have analyzed the combination of CdSe QDs and polypyridil N719 ruthenium dye. By ultrafast transient grating measurements we show that the cascading structure (type II) of this system takes full advantage to augment electron injection and hole regeneration efficiencies. Co-sensitized TiO₂ electrodes lead to an improvement in charge separation, increasing the number of injected electrons from the CdSe QDs to the TiO₂ as a consequence of the suppression of back reaction, by fast regeneration of holes by the dye action. The potentiality of this supracollector system has been verified in a complete cell configuration. Sulfide/polysulfide based ionic liquid in which both sensitizers (QD and dye) are stable has been employed as hole conducting media. In spite of the limited efficiencies of the analyzed cells, the higher photocurrents measured for CdSe/N719 co-sensitization compared to the cells sensitized using a single sensitizer constitutes a valid proof of the concept. Impedance spectroscopy unveiled the recombination limitation of the analyzed cells. On the other hand, ionic liquid exhibits an enhanced cell stability maintaining cell efficiency after one week and keeping it at 80% after 21 days. The reported results highlight a huge potential of the synergetic combination of QD and dyes for improving solar cell performance and of novel sulfide/polysulfide ionic liquid-based electrolytes for enhancing long term stability and sustainability of QD sensitizers.

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1. Introduction

The increasing worldwide demand for clean energy and the limited fossil fuels reserves on the planet require development of reliable and renewable energy sources. Among the various technologies available nowadays quantum dot sensitized solar cells (QDSCs) have attracted a great deal of attention due to its extremely easy fabrication, and relatively low production cost [1–4]. Furthermore, the use of semiconductors as sensitizers has some unique

advantages as the high extinction coefficients due to the quantum confinement, tunable band gap from the infra-red to the ultraviolet by adjusting the size [5], large intrinsic dipole moments which may lead to a rapid charge separation, and the possibility of multiple electron generation (MEG) [6,7] which gives to QDSCs the capability to achieve quantum yields, or even external quantum efficiency, greater than 100% [8,9].

In addition, semiconductor QDs are excellent building blocks for the design of light supracollecting structures by the synergetic combination of different types of QDs [10,11], or QDs and dyes [12–20]. Different QDs and dye hybrid systems have been explored with the aim to exploit their interacting proprieties. In these heterostructures, performance can increase from the fast scavenging of photogenerated holes in quantum dots by a molecular dye. This process can outbalance the competition between the electron transfer into the TiO₂ and the internal relaxation of the

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quantum dot excited state, leading to a better charge separation and higher electron injection yields [15,19]. Simultaneously, the combined use of QD and dye enhances the light harvesting wavelength range due to the combined absorption of the two assembled sensitizers [12,17,18].

Although hybrid sensitized systems appear promising, only few examples have been reported showing clear synergistic effects due to the lack of an appropriate electrolyte, compatible with all individual chromophores. The well established I^-/I_3^- electrolyte cannot be used with quantum dot sensitizers due to the highly corrosive nature of the polyiodide species with most of the semiconductors [1,21,22]. On the other hand, the common electrolyte for chalcogenide QDSCs in liquid devices, polysulfide aqueous electrolyte [23], promotes the dye desorption from TiO_2 surface due to its high pH value (~ 13). Therefore, different redox couples such as iron (II/III) [24] and cobalt (II/III) [13] complex-based electrolytes with the ability of regenerating oxidized forms of QDs and dyes have been proposed as alternative systems. Besides, the use of TiO_2 [17] or Al_2O_3 [18] coatings has also been explored as alternative to protect one of the two light absorbing materials. Most recently, solvent-free ionic liquid based electrolytes containing sulfide/polysulfide redox couple compatible with inorganic sensitizers have been reported, being a promising alternative for this type of efficient supracollector nanocomposites, and adding the advantages of ionic liquid electrolytes, such as, non-volatility, non-flammability and high ionic conductivity, among others [25].

We have studied, in previous works, the charge separation in hybrid sensitized electrodes with surface photovoltage [15,19] (SPV) and photoluminescence [16] (PL). These studies are completed in this work. Here, we make a global approach to the synergistic interaction of QDs and dyes. We have studied the ultrafast injection of carriers with and without electrolyte in the ps timescale. These new data complements the recombination characterization, in the μs timescale, carried out previously [16]. On the other hand, QDSCs have been prepared using electrodes sensitized in the same way and sulfide/polysulfide-based ionic liquid (IL) electrolyte. The potentiality of QDs and dye supracollectors systems is demonstrated by higher photocurrent, J_{sc} , compared to the single sensitizers. We also report, to our best knowledge, the first results for a QD/dye hybrid sensitized systems working with an ionic liquid electrolyte in a regenerative cell showing the capability of this type of electrolytes for regenerating the oxidized form of both QDs and dyes, whereas other electrolytes work well only with one sensitizer. The cells exhibit no decrease in efficiency after one week and maintain 80% of the original performance after 21 days. In addition, a high recombination rate, especially with dye sensitization, has been identified limiting the final cell efficiency.

2. Experimental

2.1. Preparation of co-sensitized TiO_2 -CdSe-N719 nanoporous electrodes

A double TiO_2 layer configuration was employed as working electrode. On a FTO conducting glass (Pilkington TEC15, $\sim 15 \Omega/sq$ resistance) a $8 \mu m$ -thick transparent layer (Dyesol, 18NR-T, 20 nm average particle size) was first screen-printed and then coated by a $4 \mu m$ -thick second layer of scattering titania particles (Dyesol, WERO-4, 300–400 nm particle size distribution). The resulting photoelectrodes were sintered at $450^\circ C$ for 30 min to obtain a good electrical contact between the nanoparticles. The $SnO_2:F$ (FTO) coated glass was previously covered by a compact layer of TiO_2 deposited by spray pyrolysis (thickness ~ 150 nm).

For the time-resolved measurements nanocrystalline transparent TiO_2 thin films were prepared by using a method reported

by Shen et al. [26,27] In this case, a TiO_2 paste was prepared by mixing 15 nm nanoparticles (SuperTitania, Showa Denko; anatase structure) and poly(ethylene glycol) (PEG) in pure water. After deposition onto FTO glass, the TiO_2 film was sintered in air at $450^\circ C$ for 30 min. The thickness of the film was $11 \mu m$.

The mesoporous TiO_2 electrodes were sensitized in situ by CdSe QDs grown by Successive Ionic Layer Adsorption and Reaction (SILAR). For this purpose, two solutions of 0.03 M $Cd(NO_3)_2$ dissolved in ethanol and another one containing the *in situ* generated 0.03 M selenide (Se^{2-}) in ethanol were used [28,29]. A single SILAR cycle consisted of 30 s dip-coating of the TiO_2 working electrode into the metal precursor (Cd^{2+}) and subsequently into the selenide solution, also during 30 seconds. The SILAR was carried out inside a glove box under N_2 atmosphere. After each precursor bath the photoanode was thoroughly rinsed by immersion in ethanol in order to remove the chemical residues from the surface and then dried with a N_2 gun. This procedure was repeated seven times. For dye sensitization a squared TiO_2 electrode (~ 0.25 cm^2) was stained by immersing it into a N719 dye solution 0.3 M in a mixture of acetonitrile and tert-butanol ($v/v = 1/1$) for 16 h. The same procedure was used for co-sensitization but using electrodes previously sensitized with CdSe. At least two samples were prepared with each kind of sensitization.

2.2. Preparation of sulfide/polysulfide ionic liquid-based electrolytes

Firstly, 1-butyl-3-methylimidazolium sulfide ionic liquid was synthesized following the procedure reported elsewhere [25,30]. In brief, 28 mmol of 1-butyl-3-methylimidazolium chloride (Solvionic) and 7.5 g (31 mmol) of $Na_2S \cdot 9H_2O$ were dissolved in 50 ml of methanol at $50^\circ C$. A white precipitate (NaCl) formed immediately. Methanol and water were removed in vacuo and more dry methanol was added in order to remove traces of water. This procedure was repeated several times keeping the solution at low temperatures, i.e. $\sim -20^\circ C$ in between each step and finally adding acetonitrile to remove last traces of NaCl and Na_2S by filtration followed by in vacuo removal of the solvent in order to purify the final product.

Secondly, an equimolar amount of molecular sulfur was dissolved in the 1-butyl-3-methylimidazolium sulfide ionic liquid, leading to formation of the ionic liquid 1-butyl-1-methylimidazolium S^{2-}/S_n^{2-} redox couple.

Finally, the electrolyte was prepared by mixing 1-butyl-3-methylimidazolium sulfide/polysulfide ionic liquid and a valeronitrile:acetonitrile mixture ($v/v = 1:1$) in 1:2 weight/volume ratio [25].

2.3. Electrode and cell characterization

The incident photon to current efficiency (IPCE) measurements were performed by employing a 150 W Xe lamp coupled with a computer controlled monochromator, photocurrent was measured by using an optical amperimeter 70310 from Oriol Instruments using a Si photodiode to calibrate the system. Current-Potential ($J-V$) curves and impedance spectroscopy (IS) measurements were obtained using a FRA equipped PGSTAT-30 from Autolab. The cells were illuminated using a solar simulator at AM 1.5 G, where the light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter to 1 sun intensity (100 $mW\ cm^{-2}$). Impedance spectroscopy (IS) measurements were carried out in dark conditions at forward bias, applying a 20 mV AC sinusoidal signal over the constant applied bias with the frequency ranging between 400 kHz and 0.1 Hz. Measurements were carried out using mask and without antireflective layer.

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