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Spray-assisted silar deposition of cadmium sulphide quantum dots on metal oxide films for excitonic solar cells

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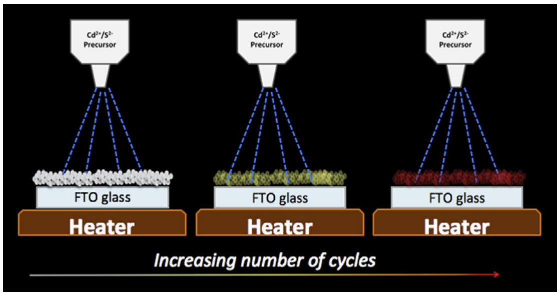
HIGHLIGHTS

- Application of spray deposition to SILAR quantum dots generation is presented.
- Enhanced optical density of CdS quantum dots on TiO_2 is achieved.
- Smaller nanocrystal sizes were systematically obtained.
- Improved functional features of quantum dot sensitized solar cells were recorded.

GRAPHICAL ABSTRACT



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ABSTRACT

The proof of principle of the successful application of spray deposition to the SILAR (successive ionic layer absorption and reaction) technique, one of the most effective strategies to sensitized TiO_2 scaffold with QDs, is demonstrated. Systematically improved optical features of the materials (higher optical density together with reduced nanocrystal sizes) as well as of the functional performances of QD solar cells (photoconversion efficiency, fill factor, short circuit current, open circuit voltage) sensitized via SD-SILAR, with respect to traditional SILAR sensitization based on impregnation, are demonstrated.

1. Introduction

Inorganic semiconductor nanocrystals (NCs), also known as quantum dots (QDs) have attracted a remarkable interest over the last two decades as appealing materials to be exploited in a variety of domains [1–3]. This attention is especially motivated by their optical and electronic properties, easily tunable through the modulation of their dimensions. The first paper dealing with their preparation appeared in 1993 [4] and since then many efforts have been carried out devoted to both increase the basic knowledge on these systems and the ways to exploit them.

In particular, in the field of third generation photovoltaics (PV), semiconductor QDs appear as the ultimate frontier as light harvesters [3], since they have band gap easily tunable with sizes, they can energetically sensitize metal oxides, they can expand the solar spectrum region in which light is collected [5] and they could in principle overcome the Queisser–Shockley limit, thanks to the claimed multiexciton generation effect, the presence of intraband transitions and other processes, which are not present in single

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junction cells [6]. Unfortunately, up to now the performances provided by quantum dot sensitized solar cells (QDSCs) are still lower as compared with those shown by classical dye sensitized solar cells [7]; QDSCs are indeed photoelectrochemical systems very different from their homologues DSCs, although taking advantage from a very similar architecture, and many things are to be learnt from the very beginning [8,9]. However, this has not reduced the tremendous interest for QDSCs and many efforts are currently carried out to understand these systems and building up devices with improved performances. Very recently, a remarkable 5.4% photoconversion efficiency has been obtained with Mn-doped CdS/CdSe QDs [10]. From the technological viewpoint, the same research group set-up a one-step coating approach to design relatively high efficiency semiconductor-sensitized solar cells, based on QD-sensitized TiO_2 paint [11].

Over the last three years, the technique known as SILAR (successive ionic layer adsorption and reaction) has emerged as an effective strategy to directly generate and grow semiconductor QDs on a host surface. This approach is particularly promising in the field of QDSCs for which increased photoconversion efficiencies (PCEs) have been obtained [12–14].

SILAR technique presents several appealing advantages as compared with the classical synthetic approaches, based on the well-known hot injection method. It is indeed a very simple and fast strategy to generate semiconductor nanocrystals, envisaging a certain number of immersion/washing/drying cycles into ionic solutions of selected precursors. According to the number of cycles and the chosen precursors, it is also easily possible growing QDs of various sizes and building up networks of different materials, thus opening the path towards the so-called rainbow QDSCs. SILAR approach provides for polydisperse QDs and allows an intimate contact between them and the metal oxide surface used as host (typically, a thin film of nanoparticulate TiO_2).

On the other hand, some limits related to the SILAR technique in the field of PV have also been highlighted: a faster recombination with respect to colloidal QDs and a decrease in the rate of photogenerated electron injection with the number of SILAR cycles [15]. Despite the mentioned limits, SILAR remains an interesting way to easily exploit QDs for PV.

A real scenario technological exploitation of these materials asks for development of synthetic routes able to provide low cost, high production yield, high reproducibility, precise control of composition and size, low by-products amount. This latter point is of particular relevance, taking into account that the chosen materials are often composed of heavy metals (such as cadmium) and, in view of the possibility to scale up the production, waste should be as reduced as possible.

In this work we propose an innovative synthetic route to fabricate semiconductor quantum dots of CdS on polycrystalline TiO_2 scaffold via SILAR technique mediated by spray deposition (SD-SILAR). The approach has been recently attempted in literature for generation of CdS QDs, exploiting secondary sulphide sources (such as thiourea), needing thermal decomposition to provide for S^{2-} ions [16]. This mandatory treatment requires temperatures as high as 400–450 °C and in some cases a post-growth annealing devoted to either eliminate big CdS aggregates or improve QD attachment on TiO_2 scaffold [17], resulting in undesired CdO formation.

In the present study, growth dynamics at low temperatures (RT to 60 °C) and QD features obtained by applying the two SILAR approaches are systematically studied and compared, demonstrating improved functional features of the QDs obtained via SD-SILAR with respect to traditional SILAR technique based on impregnation and reaction in a hot application such as a QDSC. Moreover, we will show that the SD-SILAR approach uses quite reduced amount of precursor materials, without any waste.

CdS QDs have been chosen as system models, since they are easily generated and grown on metal oxide surface with simple procedures, without any need for operating in inert atmosphere, and they are among the most exploited semiconductor sensitizers in QDSCs.

2. Experimental

2.1. Preparation of photoanode

The photoanodes were prepared by tape casting commercial TiO_2 pastes (from Dyesol) on FTO glass (sheet resistance $\sim 10\ \Omega\ \square^{-1}$), followed by 30 min annealing at 450 °C in air. Substrates with various thicknesses were applied, ranging from 2 μm up to 11.5 μm. In the case of thin substrates (up to 5 μm) transparent TiO_2 layer was applied (Dyesol 18 NR-T, composed of anatase nanoparticles 20 nm in diameter). The 11.5-μm thick layers have a bi-layered structure in which a 4-μm thick scattering layer (Dyesol WER2-O, composed of anatase particles 150 nm to 250 nm in diameter) is added to the 7.5 μm thick transparent one.

2.2. Deposition and optical characterization of QDs

A 0.05 M ethanolic solution of $Cd(NO_3) \times 4H_2O$ (Sigma Aldrich) and a 0.05 M solution of $Na_2S \times 9H_2O$ (>99.99%, Sigma Aldrich) in H_2O/MeOH (50/50) were used as sources of Cd^{2+} and S^{2-}, respectively. Bidistilled water (Carlo Erba), ethanol (>99.5%, Sigma Aldrich) and methanol (>99.9%, Sigma Aldrich) were used as solvent. All chemicals were used as received without any further purification. Traditional bath-SILAR was carried out by immersing the TiO_2 photoanode into the suitable precursor solution for 1 min, followed by washing the substrate and drying it with a slight nitrogen flux.

SD-SILAR was carried out by using a two-guns apparatus, working with nitrogen (6 psi) as carrier gas (nozzles-to-sample distance: 10 cm). Cd^{2+} and S^{2+} precursor solution were loaded in the respective gun reservoir and sprayed for a given time, according to the chosen volume to be deposited. When needed, the substrate was placed on a hot plate and heated at the desired temperature. Cadmium and sulphide precursors were then alternatively sprayed. After each precursor spraying, sample was washed and dried with the same procedure as adopted for traditional bath-SILAR. All photoanodes were capped with ZnS (1 SILAR cycle), using 0.1 M aqueous solutions of $Zn(CH_3COO)_2 \times 2H_2O$ (99.999% Sigma Aldrich) and $Na_2S \times 9H_2O$.

UV–Vis spectra of the sensitized photoanodes were recorded on a TG80 PG Instrument (1 nm resolution). QD sizes are calculated from UV–Vis absorption spectra on the basis of Eq. (1) [18]:

$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + (13.29) \quad (1)$$

2.3. XPS measurements

XPS measurements were run on a Perkin-Elmer PHI 5600ci spectrometer. The spectrometer was calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line to be 84.0 eV with respect to the Fermi level. Both extended spectra (survey – 187.85 eV pass energy, 0.5 eV/step, 0.025 s/step) and detailed spectra (for Cd 3*d*, S 2*p*, O 1*s*, Ti 2*p* and C 1*s* – 11.75 eV pass energy, 0.1 eV/step, 0.1s/step) were collected with a standard Al-Kα source (1486.6 eV) working at 250 W. The reported binding energies (BEs, standard deviation = ±0.1 eV) were corrected for the charging effects by considering the adventitious C1*s* line at 285.0 eV. The atomic