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Microwave Assisted Chemical Bath Deposition of PbS Quantum Dots for Quantum Dot-Sensitized Solar Cells

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Abstract: A simple, rapid and effective method of microwave assisted chemical bath deposition (MACBD) has been adopted to deposit PbS quantum dots on the surface of TiO_2 film as a photoanode for quantum dot-sensitized solar cells. The photovoltaic performance of the as-prepared cell is investigated. The results show that the cell based on MACBD deposited TiO_2/PbS electrode achieves a power conversion efficiency of 0.15% at one sun (AM 1.5G, 100 $mWcm^{-2}$). The present synthetic strategy should be a promising fabrication technique for QDSSCs.

Keywords: Quantum dot-sensitized solar cells; PbS; TiO_2; Microwave assisted chemical bath deposition

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Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention throughout the world from both academic and industrial fields as a promising alternative to conventional solid-state photovoltaic devices since a report by O'Regan and Grätzel in 1991 [1-6], and the conversion efficiency of DSSCs could reach a maximum value of 12% [7]. The conventional DSSCs are made from nano-porous TiO_2 photoelectrode with dye as a light harvesting component. Recently, replacing the organic dye by inorganic quantum dots (QDs) has attracted a lot of attention due to the larger absorption coefficient of QDs and the tunability of the absorption spectrum by quantum size confinement [8-18]. The conversion efficiency of quantum dots-sensitized solar cells (QDSSCs) has achieved 5.1% recently [19].

QDSSCs are based on the photosensitization of semiconductor photoanode, typically TiO_2, by absorbed QDs sensitizers, such as CdS, CdSe, and PbS, and their working mechanism is depicted in Fig. 1 involving key processes (1)-(7). In brief, electrons, excited from valance band (VB) to conduction band (CB) of QDs by absorbing light (path (1)), are rapidly injected into the CB of TiO_2 particles (path (2)) and then transported to F-doped SnO_2 (FTO) (path (3)). The oxidized QDs are regenerated by accepting the electrons from counter electrode (CE) (path (5)) via redox pair (path (4)). However, the charge recombination (paths (6) and (7)) will happen in the meantime and deteriorate the cell performance. Therefore, the improvement of the performance of QDs and their interconnectivity with TiO_2 substrate will facilitate the electron transfer from QDs to TiO_2 and decrease the back transport electrons from TiO_2 to electrolyte, which is very important to the cell efficiency. Many studies have also devoted to explore different fabrication techniques to attach QDs onto TiO_2. So far, the QDs have been successfully sensitized on the surface of TiO_2 by self-assembled monolayer via linker assistance or direct adsorption [20],

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sequential chemical bath deposition (SCBD) [21,22], electrochemical deposition [23], and photodeposition [24] techniques.

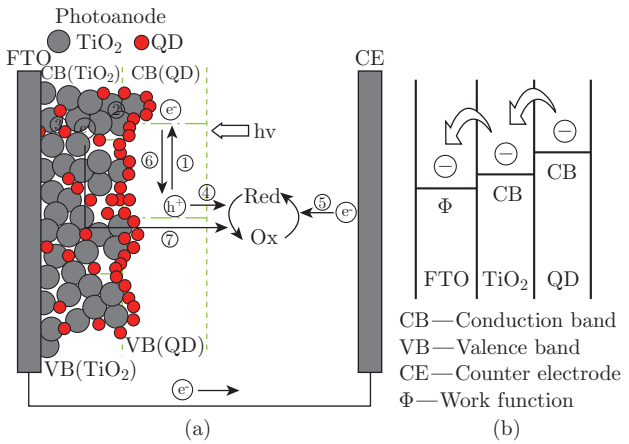

Fig. 1 Schematic diagram of (a) working mechanism and (b) energy-band structure of QDSSCs.

Recently, we reported that preparation of CdS, CdSe and CdS/CdSe QDSSCs via using a simple, rapid and effective microwave assisted chemical bath deposition (MACBD) method [25-27]. This method can synthesize rapidly these QDs and form a good contact between QDs and TiO_2 layer. Importantly, MACBD avoids repetitive immersing operation, organic linker or high temperature heating required in other conventional methods while the cells fabricated using MACBD exhibit comparable photovoltaic performances as those using other methods. In the work, we further explore the application of MACBD method in the fabrication of PbS QDs sensitized TiO_2 photoanode for QDSSCs. The as-synthesized PbS QDSSC shows a short-circuit current density of 0.42 mA cm^{-2} and conversion efficiency of 0.15% under one sun illumination.

Experimental

TiO_2 electrode was prepared by screen printing of TiO_2 paste on FTO (resistivity: 14 Ω/, Nippon Sheet Glass, Japan). The electrode configuration was a transparent layer of nanocrystalline TiO_2 (P25, Degussa) with a mean size of 25 nm and a scattering layer microcrystalline TiO_2 with a mean size of 200 nm (Dalian HeptaChroma SolarTech Co., Ltd.). The as-prepared electrodes were sintered at 500℃ for 30 min.

Subsequently, the as-prepared TiO_2 electrodes were sensitized by PdS QDs by MACBD process [25-27], as shown in Fig. 2. In brief, the TiO_2 electrode was immersed into a vessel with precursor aqueous solution consisting of 0.05 M $Pb(NO_3)_2$ and 0.05 M CH_4N_2S (Sinopharm Chemical Reagents Co. Ltd.), and then the vessel was put into an automated focused microwave system (Explorer-48, CEM Co.) and treated at 150℃ with a microwave irradiation power of 150 W for 20 min.

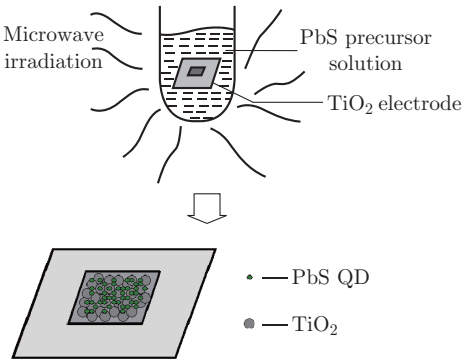

Fig. 2 Schematic diagram of MACBD deposition of PbS QDs.

The CdS QDSSCs were sealed in a sandwich structure with a 25 μm spacer (Surlyn) by using thin Pt counter electrode. The redox electrolyte was composed of 1 M DMII, 50 mM LiI, 30 mM I_2, 0.5 M *tert*-butylpyridine, and 0.1 M GuNCS in a solvent mixture of 85% acetonitrile with 15% valeronitrile by volume [28]. The active area of the cell is 0.2 cm^2. Photocurrent-voltage measurement was performed with a Keithley model 2440 Source Meter and a Newport solar simulator system (equipped with a 1 kW xenon arc lamp, Oriel) at one sun (AM 1.5G, 100 mW cm^{-2}).

Results and discussion

The UV-vis absorption spectra of pure TiO_2 and TiO_2/PbS electrodes were detected using a UV-vis spectrophotometer (Hitachi U-3900) and shown in Fig. 3. The inset of Fig. 3 shows the photo images for pure TiO_2 and TiO_2/PbS electrodes. After PbS QDs are deposited, the color of electrode changes from white to gray. Compared with the absorption spectrum of pure TiO_2 film, the absorption edge, obtained from the

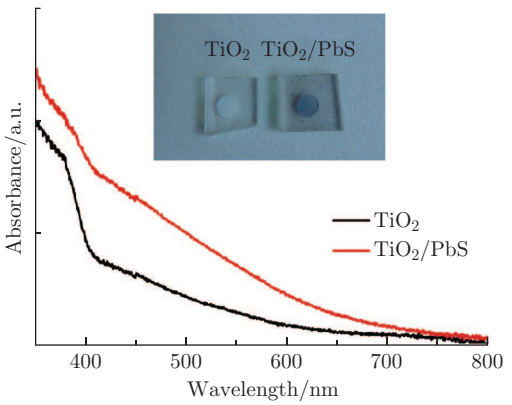

Fig. 3 UV–vis absorption spectra of TiO_2 and TiO_2/PbS electrodes. Inset is the photographs of TiO_2 and TiO_2/PbS electrodes.

intersection of the sharply decreasing region of the spectrum with its baseline, is about 750 nm for TiO_2/PbS electrode. The band gap corresponding to the absorption edge is about 1.65 eV, which is higher than the value of PbS in the bulk (0.42 eV) [29], indicating that the size of these PbS particles is withwin the scale of QDs.

Figure 4 displays the current density-voltage (J-V) curve of PbS QDSSCs fabricated by MACBD method. It can be observed that the cell exhibits a short-circuit current density (J_{SC}) of 0.42 mA cm^{-2}, an open-circuit voltage (V_{OC}) of 0.58 V, a fill factor (FF) of 63.4% and a power conversion efficiency (η) of 0.15%.

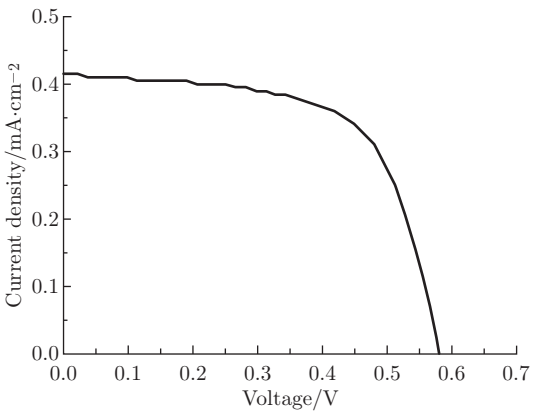

Fig. 4 J-V curve of prepared PbS QDSSCs.

To further understand the effect of MACBD method on PbS QDSSCs, the mechanism of PbS QDSSCs prepared by MACBD method has been discussed. PbS deposition on the surface of TiO_2 via MACBD method is a three-step process (as shown in Fig. 5) [25]. In the first step, positively charged Pb^{2+} ions form a complex with TiO_2 film. In the second step, thermal decomposition of CH_4N_2S in the presence of microwave irradiation releases S^{2-} which reacts with Pb^{2+} to produce PbS nuclei. The PbS nuclei grow, crystallize and stabilize on the TiO_2 under microwave irradiation [30], leading to a good contact between PbS and TiO_2. Therefore, a good contact between PbS QDs and TiO_2 layer is formed due to rapidly elevated temperature during microwave irradiation, leading to a higher FF (63.4%). In addition, microwave irradiation can heat up the aqueous solution homogeneously and fast due to the penetration characteristic of microwaves and high utilization factor of microwave energy [31,32]. Therefore, the nucleation and growth of PbS can be finished in an extremely short period of time, which is extraordinarily beneficial for reducing the concentration of surface defects of QDs [33,34]. The carrier recombination at surface defects of QDs is correspondingly suppressed and thus the cell performance is increased [35,36].

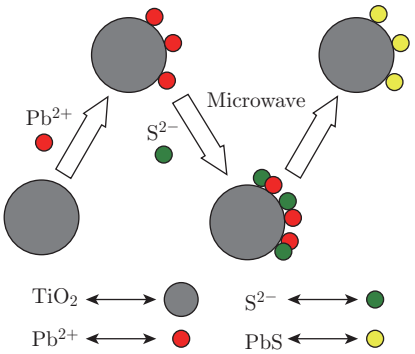

Fig. 5 Schematic diagram of the process of PbS deposition on TiO_2 film under microwave irradiation.

Conclusions

In summary, PbS sensitized TiO_2 film as photoanode for QDSSCs has been prepared by using a simple, rapid and effective MACBD technique. This technique can synthesize PbS QDs rapidly and suppress their surface defects as well as form a good contact between QDs and TiO_2 film. A short-circuit current density of 0.42 mA cm^{-2} and conversion efficiency of 0.15% under one sun illumination has been achieved for prepared PbS QDSSCs. The present synthetic strategy should be a promising fabrication technique for highly efficient QDSSCs.

Acknowledgments

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