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Preparing ZnO nanowires in mesoporous TiO_2 photoanode by an in-situ hydrothermal growth for enhanced light-trapping in quantum dots-sensitized solar cells

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ABSTRACT

This paper describes a solution-processed method for preparing TiO_2 nanoparticles (NPs) and ZnO nanowires (NWs) hybrid photoanodes, which includes two steps: the preparation of mesoporous (m) TiO_2/ZnO NPs hybrid films and the growth of ZnO NWs in the m-NPs hybrid films by an in-situ hydrothermal growth. This novel hybrid structure not only retains high surface areas of conventional TiO_2 NPs photoanodes in favor of photosensitizers adsorption, but also improves the light-trapping due to the strong light scatting effect of ZnO NWs with large size and facilitates the electron collection and transfer in hybrid photoanodes by a continuous NWs pathway. Herein, we used hybrid structured films as photoanodes in CdSe-sensitized solar cells. Due to the repeating reflections of injected light in hybrid films, the transmission of visible light was greatly reduced and the injected light was effectively confined in photoanodes. Thus, the incident photon-to-electron conversion efficiency (IPCE) and short-circuit current density (Jsc) were greatly improved. The results exhibited a remarkably enhanced Jsc of 18.2 mA cm^{-2} and the power conversion efficiency (η) of 2.8% (i.e., 134% enhancement in Jsc and a 47.4% enhancement in η as compared to the pure TiO_2 NPs-based cell with Jsc of 7.79 mA cm^{-2} and η of 1.9%).

1. Introduction

Recently, a great deal of attention was focused on renewable energy resources due to the increasing demand for energy, the shortage of fossil fuels and the deterioration of the human environment. In the field of renewable energy, sunlight is an unlimited and clean energy source, so solar cells have been regarded as a promising candidate. In recent years, quantum dots-sensitized solar cells (QDSSCs) have attracted a wide spread attention due to the large absorption coefficient of QDs and the tunability of the absorption spectrum based on quantum confinement effect. Various QDs, such as CdSe, CdS and CdTe [1–3], have been developed for QDSSCs. In order to improve the performance of QDSSCs, many efforts have been made. Apart from the researches for QDs (lower band gap QDs (PbS, PbSe) [4,5], alloy QDs[6] and core-shell QDs[7]), electrolyte [8] and counter electrode [9], many researches were focused on the nanostructure of photoanodes, whose purpose was to improve the light trapping or harvesting and facilitates the electron transport. For the conventional QDSSCs based on m-TiO_2 NPs film, the optimal thickness of TiO_2 film is 10–15 μm [10]. Because of the low light scattering ability of small-sized NPs (10–20 nm) [11], some of the light passing through the NP films will loss. In view of the intrinsic limitations associated with the effective diffusion length of charge-carriers in the films and the charge-carrier recombination occurring at the surfaces of active material. Although increasing films thickness can decrease the transmittance loss, it is not always an effective way to improve the cell efficiency. Generally, the light absorbance decreases with a decrease of the thickness of the light-absorbing layer, resulting in the low photoelectric conversion efficiency. In order to compensate for the lack of light absorption due to the reduction in the thickness of active layer, there are many ways to harvest light efficiently. That is, the light-trapping strategy could be quite useful to improve the power conversion efficiency for the limited active layer thickness of solar cells. Some light trapping or harvesting technologies have been explored, for example, inverse opal nanostructures [12,13], light scattering layers of large-size particles on top of active layer [14,15], photonic crystals with interesting multiple scattering and slow photon

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effect [16], and plasmonics with metallic nanostructures [17] have been developed for trapping incident light in the photoanodes of solar cells.

One dimension (1D) ZnO (TiO_2) nanostructure has also been widely investigated as photoanodes for solar cells. They can offer a continuous pathway for photogenerated electrons to transport along the long axis of 1D, as well as high light scattering and trapping. Besides, the electron diffusion coefficient in single crystalline is more than 2 orders of magnitude higher than that in 0D NPs [18]. Despite of many advantageous characteristics as noted above, the efficiency of QDSSCs based on 1D nanostructured photoanodes is low because the specific surface area of 1D nanostructure films is roughly an order of magnitude lower than NP films [19,20], which results in limited sensitizer loading. For 0D TiO_2 and 1D ZnO films, if their drawbacks can be overcome and the advantages can be inherited, the efficiency of cells could be greatly improved by a NPs/NWs hybrid structure. In previous works [21], we first synthesized ZnO NWs, and then filled TiO_2 paste in ZnO NW arrays, the hybrid structure was obtained. But the density-controlled synthesis of ZnO NWs was difficult and it was also difficult to completely fill TiO_2 NPs in the gap among NWs.

In this paper, we reported a simple preparation process, by which ZnO NWs were grown in the m-TiO_2 NP films, and the perfect TiO_2 NPs/ZnO NWs hybrid photoanode was obtained, which was composed of the crisscross hexagonal wurtzite ZnO NWs and small size of TiO_2 NPs. This novel hybrid structure not only retains high surface areas of NP films to adsorb sensitizers but also improves the light-trapping based on the high light scatting effect of ZnO NWs and facilitates the electron collection and transfer by a continuous pathway. The resulting hybrid films were subsequently exploited as photoanodes in QDSSCs, the test results exhibited a remarkably enhanced Jsc of 18.2 mA cm^{-2} and η of 2.8% (i.e., 134% enhancement in Jsc and a 47.4% enhancement in η as compared to the device prepared by using pure TiO_2 NPs with Jsc of 7.79 mA cm^{-2} and η of 1.9%).

2. Experimental

2.1. Preparation of TiO_2 NPs/ZnO NWs hybrid films

1.64 g of $Zn(CH_3COO)_2{\cdot}2H_2O$ and 0.96 g of KOH were dissolved in 84 ml and 46 ml of methanol, respectively. Then KOH solution was added into $Zn(CH_3COO)_2$ solution in a flask and the system reacted under constant stirring for 2 h at 60 °C. The obtained ZnO NPs were separated by centrifugation, washed thoroughly by ethanol and dispersed in ethanol (50mgml^{-1}).

According to the mass ratio between ZnO NPs and TiO_2 NPs required in the experiment, a certain volume of as-prepared ZnO NPs in ethanol (50 mgml^{-1}) was diluted in 20 ml of ethanol by ultrasonic dispersion; the diluted colloidal ZnO NPs was used as dispersion instead of pure ethanol to prepare ZnO/TiO_2 paste. Via this method, ZnO NPs can be evenly mixed into TiO_2 paste to achieve a uniform distribution of ZnO NWs. Commercial P_{25} TiO_2 NPs (Degussa) in the form of powder were used as a raw material. The detailed preparation process of a viscous TiO_2 paste was stated in a previous paper [22]. Meanwhile, we prepared the pure TiO_2 paste by the same method.

Prior to the fabrication of m-ZnO/TiO_2 NPs film, FTO glass plates (Pilkington TEC 15, sheet resistance: 15 Ωsq^{-1}) were cleaned in a detergent solution using an ultrasonic bath for 30 min and rinsed with deionized water and ethanol. Mesoporous ZnO/TiO_2 NPs films were prepared through three circular screen printing of paste on the FTO glass with TiO_2 compact layer, the first and second printing used the ZnO/TiO_2 NPs hybrid paste, and the last printing used pure TiO_2 NPs paste. Next the printed films were sintered in air by heating gradually to 325 °C and holding for 5 min, then 375 °C for 5 min, and finally at 450 °C for 30 min. The active area of the TiO_2 films was 0.5 × 0.5 cm^2.

At last, the growth of ZnO NWs was performed in a procedure similar to that in our previous paper [21,23]. Briefly, 15 ml of 0.05 M $Zn(NO_3)_2$ and 0.025HMTA (hexamethylenetetramine) aqueous solution were prepared, respectively, and $Zn(NO_3)_2$ solution was added into HMTA solution. Then 0.08 ml PEI and 0.71 ml NH_4OH were added into the mixture drop by drop. The pH of obtained solution was adjusted to 9.3 with HNO_3. The as-prepared mesoporous ZnO/TiO_2 NP films were placed in a sealed container and then the growth was performed at 93 °Cwater bath for 5, 10 or 15 h.

2.2. QDSSCs fabrication

The deposition of CdSe QDs was achieved by the successive ion layer adsorption and reaction (SILAR) method [23]. Briefly, 40 ml of 30 mM SeO_2 aqueous solution was reduced with KBH_4 as Se^{2-} source in inert atmosphere. Meanwhile, 40 ml of 30 mM $Cd(NO_3)_2$ aqueous solution was prepared as Cd^{2+} source. The SILAR process was repeated for 12 cycles. After the deposition of CdSe, a ZnS passivation layer was deposited by two SILAR cycles while being soaked in an aqueous solution containing 0.05 M zinc nitrate and 0.05 M sodium sulfide. A 45 μm-thick hot-melt ionomer film (Surlyn) under heating (120 °C) was then sandwiched between the sensitized photoanode and a 100 nm thick Pt counter electrode. A polysulfide electrolyte of 1 M Na_2S, 2 M Sand 0.2 M KCl in a

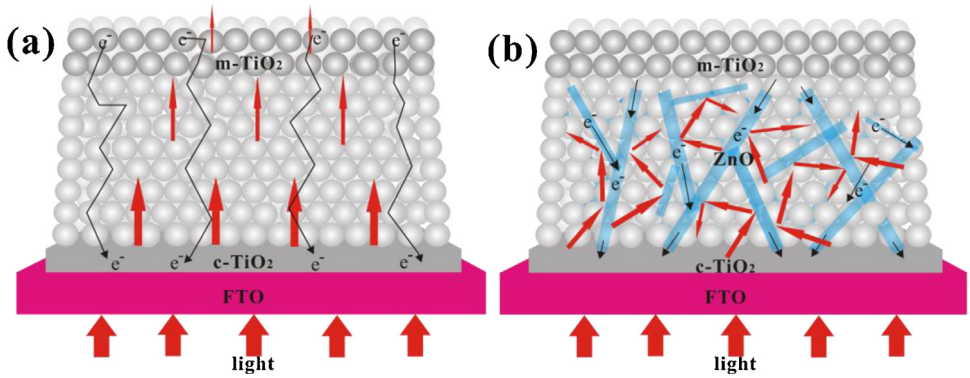

Fig. 1. Schematic illustration of electron (e−) diffuse transport and light transmission in a) pure TiO_2 NPs photoanodes and b) TiO_2 NPs/ZnO NWs hybrid photoanodes.