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Fabrication of submicron/micron size cavities included TiO_2 photoelectrodes and optimization of light scattering to improve the photovoltaic performance of CdS quantum dot sensitized solar cells

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ABSTRACT

In this research sub-micron size carbon spheres were hydrothermally grown with sizes around 500–550 nm. TiO_2 nanocrystals (NCs) were also prepared through a hydrothermal approach with dominant size of 20 nm. The TiO_2 NCs and carbon spheres were applied to make carbon-TiO_2 pastes with different weight percents of the included carbon spheres. The different pastes were deposited on FTO glass substrates and annealed to remove the carbon spheres from the layers. As a result some nanocrystalline TiO_2 layers with included sub-micron and micron size cavities were fabricated. The density of cavities was higher and their corresponding size was larger for the layers formed of the carbon-TiO_2 pastes with higher included carbon spheres. CdS nanocrystals were grown on the surface of these different TiO_2 layers of various porosities as the light sensitizers. Finally these TiO_2 layers with included large cavities were applied as the photoelectrode of the quantum dot sensitized solar cells (QDSCs). The effect of density/size of the cavities on the light scattering level of the photoelectrodes and the photovoltaic performance of corresponding QDSCs was investigated. The results demonstrated that the maximum energy conversion efficiency was belonged to the QDSC with a photoelectrode made of carbon-TiO_2 paste with 8 wt% of the included carbon spheres. This efficiency was about 2.75% which was increased about 87% compared to that of the reference cell with cavity-free photoelectrode.

1. Introduction

Quantum dot sensitized solar cells (QDSSCs) have attracted a great deal of attention as a promising type of the third generation of photovoltaic devices [1–4]. Semiconductor quantum dots (QDs) demonstrate some prominent advantageous, for instance, tunable bandgaps [5,6], high molar extinction coefficient [6], multiple exciton generation [7] and hot electron injection [8], which make them suitable as the promising photon harvesters for the next generation solar cells. In these solar cells the incident photons are absorbed by semiconductor quantum dots and electron-hole pairs are generated. The electrons are commonly transferred to a meso-porous TiO_2 scaffold and external circuit and revival of quantum dots is carried out through the electrolyte [9,10]. Among the semiconductors, cadmium sulfide is an II–VI material with a direct band gap of about 2.4 eV at 300 K, having a wide range of applications. The typical Bohr exciton diameter of CdS is around 5.8 nm; consequently, CdS nanocrystals in the size range of 1–6 nm could show size-dependent quantum confinement effects with remarkably different optical properties [11,12]. This semiconductor could be considered as a moderate light absorber due to its value of the bandgap energy while it has similar crystal structure with TiO_2 and ZnO and could be simply over-grown on these scaffolds.

In the theory, the efficiency of QDSCs can reach to 42% due to the multiple electron-hole generation inside the quantum dots. That is while the corresponding laboratory efficiencies are quite lower and lower than those of similar dye sensitized solar cells [13]. Nevertheless, the energy conversion efficiency of QDSCs has been considerably increased in recent years [14–17].

As one knows, the nanostructured TiO_2 scaffold and its morphology play a key role in improvement of the efficiency of the QDSCs. The TiO_2 photoelectrode is generally consisted of a porous film of interconnected TiO_2 nanoparticles (around 10–20 nm). These small nanoparticles provide a large surface area, but lead to the formation of 5–15 nm pores within the layer [18,19]. This could create serious difficulties for QDs penetration which is deleterious for QDSCs performance [20]. In fact, the use of porous nanostructures with larger pore size and lower surface area could be a solution to overcome to this failure. As a result, nanotubes [21–23], nanowires [24,25], nanorods [26,27] and hollow spheres within the TiO_2 mesoporous layers [28,29] have shown very promising results.

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Another approach for improvement of the energy conversion efficiency of QDSCs is photon management. This could be performed through the enhancement of the photons path length inside the mesoporous electrode. This can increase the probability of light absorption by QDs sensitizers and enhance the light absorption. To perform this idea, one approach is to apply a light scattering layer of large TiO_2 particles or hollow spheres on the top of nanocrystalline TiO_2 scaffold [28,30–32]. Another approach could be the application of TiO_2 hollow spheres inside the nanocrystalline mesoporous TiO_2 layers or creation of submicron-size cavities within the layer [29,33,34]. Recently, polystyrene spheres have been embedded in the TiO_2 paste and created cavities in the deposited layers during the sintering process. The role of these sub-micron size holes in the efficiency improvement has been attributed to the increased light scattering and light absorption [33,35–36]. Other templates like carbon spheres could be applied to create micron/sub-micron size cavities in the photoelectrodes. Nevertheless, there is a problem due to the agglomerations in corresponding carbon powder and their controlled application [32,37]. Meanwhile, the carbon templates could be still attractive owing to the low cost applied materials for the synthesis and ease of fabrication [28–29,37].

In this research sub-micron size carbon spheres with sizes around 500 nm were synthesized by a facile hydrothermal method. Then they were mixed with specific amounts of a TiO_2 paste composed of nanoparticles with dominant size of 20 nm. The weight percent of carbon nanospheres in the final pastes was set in the wide range of 0–10%. The mixed pates were deposited on FTO glass substrates and annealed at specific temperature and time to form nanocrystalline TiO_2 layers with controlled porosity. The considerably higher porosities were achieved for the TiO_2 layers with higher amounts of included carbon spheres. These TiO_2 layers were applied as the photoelectrode of the CdS sensitized QDSCs. The photovoltaic parameters of corresponding cells were measured and demonstrated the best performance for the cell with photoanode made 8 wt% TiO_2 paste. The efficiency of this optimized cell was increased about 87% compared to the reference cell. The increase in the efficiency and optimization of the porosity was addressed based on the competition between the light scattering and sensitization.

2. Experimental

2.1. Synthesis of carbon nanospheres

The synthesis of carbon nanospheres was carried out through a polycondensation reaction of glucose under a hydrothermal condition. Briefly, a 50 ml aqueous solution of glucose with 1 M concentration was prepared in the first stage. Then it was transferred to a Teflon lined stainless steel autoclave and heated at 175 °C for 12 h. The black/brown precipitate of carbon nanospheres were centrifuged and washed with ethanol and water for three times and dried at 80 °C for 4 h.

2.2. Synthesis of TiO_2 nanocrystals and preparation TiO_2 pastes

TiO_2 nanocrystals were synthesized by a hydrothermal method in acidic autoclaving pH. In the first stage, a quantity of 0.014 mol of acetic acid was mixed with 0.014 mol of titanium tetraisopropoxide (TTIP) and vigorously stirred. Then 19.6 ml of DI water was added and stirring was continued by 1 h for the hydrolysis process. A quantity of 0.26 ml HNO_3 was mixed with this solution and heated at 80 °C for 75 min. This was carried out for the peptization and resulted in formation of a pale blue TiO_2 solution. This final sol with pH of 1.4 was transferred to a teflon lined stainless steel autoclave and heated at 230 °C for 12 h. The hydrothermally grown TiO_2 nanoparticles were centrifuged and washed with ethanol for several times. Then they were applied in a TiO_2 paste preparation process.

The precipitate of hydrothermally grown TiO_2 NCs was sonicated by an ultrasonic horn (240 W, 120 × 0.5 s) in the first stage. Then it was heated at 40 °C and concentrated to form a 13 wt% sol of TiO_2 NCs in water. The solution was centrifuged and washed with ethanol for several times. This was carried out to obtain a 40 wt% white precipitate of NCs in ethanol. The total precipitate (about 1.9 g) was quite dispersed in proper amount of ethanol by sonication in an ultrasonic bath for 20 min. Another solutions containing terpineol in ethanol and ethyl cellulose in ethanol were separately prepared. Two kinds of ethyl cellulose (EC) powders i.e. the EC (5–15 mPas, #46070, Fluka) and EC (15–30 mPas, #46080, Fluka) were applied in this stage. The weight percents of these components in total applied EC powder (0.25 g) were about 56% and 44%, respectively. This powder was mixed with about 30 ml of ethanol and stirred. 2.027 g of terpineol was also added to 20 ml of ethanol and homogenized. These solutions were slowly added to the TiO_2 NCs sol in ethanol and stirred. The final solution was sonicated with an ultrasonic horn (240 W, 120 × 0.5 s) for three times for well-dispersion. The ethanol was completely removed from the solution through a vacuum evaporation process. The result was a semi-transparent paste composed TiO_2 NCs, terpineol and ethyl cellulose with final weight percents of 18%, 73% and 9%, respectively.

The reference photoelectrode of the QDSCs was fabricated by deposition of a monolayer of the prepared TiO_2 paste on the FTO glass substrates. This was performed through the standard doctor-blade deposition method. The layer was finally heated at 325, 375, 450 and 500 °C for 5, 5, 15 and 15 min to achieve a pure nanocrystalline TiO_2 layer [38].

2.3. Preparation of the carbon-TiO_2 pastes and TiO_2 porous layers

For preparation of the carbon included TiO_2 (carbon-TiO_2) pastes, specific amount of submicron size carbon spheres were desolved in ethanol and well-dispersed. Another, specific amount of the TiO2 paste prepared in the previous stage was taken and diluted by ethanol. Then the ethanol solution of carbon spheres was added to the TiO_2 nanocrystals solution and stirred. The ethanol solvent was finally removed by a rotary evaporator to make a concentrated carbon-TiO_2 paste. The amount of carbon spheres in this process was as selected to make the final pastes with different carbon spheres weight percents of 0–10%. These different pastes were deposited on FTO glass substrates and annealed through a similar procedure as mentioned in Section 2.2. The only difference was about the annealing time at 450 °C which was changed to 2 h for complete removal of the included carbon spheres. The TiO_2 layers with different porosities were named as TiO_2-CX% where x is the weight percent of the carbon spheres in the applied pastes. Based on this naming rule, the deposited layers in the experiments are mentioned as TiO_2-C2%, TiO_2-C4%, TiO_2-C6%, TiO_2-C8%, TiO_2-C10%.

2.4. Fabrication of CdS quantum dot sensitized solar cells

To make the photoelectrodes, different porous TiO_2 layers were sensitized with CdS quantum dots. This was carried out through a SILAR process using two solutions of Cd^{2+}, S^{2-} With 0.1 and 0.1 Concentrations. The photoelectrodes were dipped in a solution containing 0.1 M Cd $(CH_3COO)_2{\cdot}2H_2O$ in methanol for 1 min and rinsed with methanol. Subsequently, the photo-electrodes were dipped in a methanol/DI water solution containing 0.1 M $Na_2S{\cdot}9H_2O$ for another 1 min and wished with methanol. All these steps were one SILAR cycle. The sensitization was repeated for 6 SILAR cycles for effective sensitization. The fabricated photoelectrodes were named as TiO_2-CX%/6 CdS in the experiments. Provided CdS sensitized photoelectrodes were assembled with a CuS counter electrode. The photoelectrodes and counter electrodes were sealed by a 60 μm thermal-plastic spacer. The polysulfide electrolyte consisting of 1 M Na_2S, 2 M S and 0.2 M KCl in 3:7 water/methanol solutions was injected into the cells and cell was fabricated.