Research Article

CdSe Quantum Dots Sensitized Mesoporous TiO₂ Solar Cells with CuSCN as Solid-State Electrolyte

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Mesoporous TiO₂ is functionalized by 3-mercaptopropyl trimethoxysilane (MPTMS) to anchor CdSe quantum dots (QDs). The resulting TiO₂/CdSe is combined with solid-state electrolyte (CuSCN) to form solar cells. It is found that the efficiency of electron injection from QDs to TiO₂ can be improved owing to the substitution of the long chains of organic capping agents at the surface of QDs with MPTMS. The hydrolyzate of MPTMS forms an insulating barrier layer to reduce the recombination at the TiO₂/CdSe interface, leading to the increase of open-circuit voltage (V_{oc}).

1. Introduction

As the supplies of fossil fuel are expected to decrease, energy conservation and alternative energy sources are actively investigated to achieve sustainable development [1]. Low-cost and high-efficiency dye-sensitized solar cells are regarded as an excellent candidate for exploiting solar energy, which is one of the most important alternative energies [2]. Semiconductor Quantum Dots (QDs) can also serve a sensitizer for light harvesting assemblies in solar cells [3]. The size quantization of QDs leads to the capability of tuning visible-spectrum response and varying band offsets to modulate the vectorial charge transfer across QDs with different sizes [4]. By anchoring different-sized QDs on mesoporous electrodes, researchers hope to prepare rainbow solar cells which took advantages of both the faster electron injection of small QDs and the greater absorption range of large QDs [5]. Among other benefits of the use of QDs in solar cells, hot electrons can generate carrier multiplication in QDs [6, 7]. Solar photon conversion with efficiency up to about 66% has been estimated [3].

Solar cells based on mesoporous TiO₂ sensitized by PbS [8], InP [9], CdS [10], and CdSe QDs [11] have been reported. However, it has been said that the surface capping of QDs is an integral part of its electronic system and can alter the energy levels position [12]. It has been shown in

the work on CdSe QDs-sensitized TiO₂ that bifunctional surface modifiers with shorter chains can assemble QDs on TiO₂ [4, 5]. Mainly, the effects of the modifiers are limited to reduce the spaces between QDs and TiO₂, increasing the electron injection efficiency. What is more, in most of QDs-sensitized solar cells liquid electrolytes are used as hole transfer media. Although solid-state electrolytes have been employed in solar cells with extremely thin absorbers (ETA) such as CdSe [13], CuInS₂ [14], CdS [15], In₂S₃ [16], Cu_{2-x}S [17], and Sb₂S₃ [18], they have been rarely used in QDs-sensitized solar cells. In this paper, we use 3-mercaptopropyl trimethoxysilane (MPTMS) as the surface modifier to link preprepared CdSe QDs and mesoporous TiO₂. Hydrolyzate of MPTMS (SiO₂) forms an insulating barrier layer to reduce the recombination at the TiO₂/CdSe interface [19]. In our QDs-sensitized solar cells, p-type CuSCN is the solid-state electrolyte, and all the processes are nonvacuum including electrode preparation.

2. Experimental Details

Mesoporous TiO₂ electrodes were prepared by use of a classical method [20]. In brief, commercial TiO₂ nanoparticles (P25, Degussa AG, Germany) were mixed with water, acetylacetone and detergent (OP10). The mixture was then ground for about 1 h to obtain TiO₂ paste which was painted

SCHEME 1: Structural sketch of our CdSe QDs sensitized mesoporous TiO_2 solar cell with CuSCN as solid-state electrolyte.

on a conduction FTO glass substrate as TiO_2 electrodes. On the substrate, two parallel adhesive tapes were covered to control the film thickness and shape of TiO_2 . After drying in air, the TiO_2 electrodes were annealed at 550°C for 1 h. After cooled in furnace to about 100°C , the TiO_2 electrodes were taken out and placed into a 1% MPTMS ethanol solution. It took at least 24 h to finish the immersion, which aimed to functionalize the surface of TiO_2 with bifunctional surface modifiers. The TiO_2 electrodes were subsequently washed with ethanol several times. They were finally blow-dried with N_2 .

CdSe QDs were prepared using a similar method to that used in [21]. Selenium powder and cadmium myristate were placed into a three-neck flask with adequate amount of octadecene (ODE). After 10-minute degassing, the mixture was heated to 240°C at a rate of 25°C/s while being stirred. The temperature was held at 240°C for 1 h. After washing with ethanol and n-hexane for several times, CdSe QDs with a mean size of about 5 nm were produced. These CdSe QDs might be well dispersed in hexane.

Surface-modified TiO_2 electrodes were immersed in CdSe/hexane solution for approximately 15 h. After drying in air, TiO_2 /QDs electrodes were preheated to 80°C . Dilute CuSCN/ $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{S}$ solution was dropped on TiO_2 /QDs electrodes to reach certain thickness at 80°C [22]. Conducting carbon paste was then coated on CuSCN films with a simple doctor-blade method. The solar cells were defined by a mask in the drop-cast deposition of carbon paste. The uncovered films by carbon electrodes were scraped away to delimit the working areas. The complete structure of solar cells was illustrated in Scheme 1 and labeled as SC-modified (C/CuSCN/CdSe(modified)/ TiO_2 /FTO). To find out the effect of surface modifier on the performance of solar cells, solar cells with the same preparation procedure as described before except that TiO_2 electrodes were not treated with MPTMS were also prepared and labeled as SC-unmodified (C/CuSCN/CdSe(unmodified)/ TiO_2 /FTO). What should be noted was that since the wettability between oil-chelating QDs and TiO_2 particles was poor, QDs solutions were dropped directly onto TiO_2 films instead of absorption. For comparison, solar cells made by use of TiO_2 electrodes without MPTMS treatment and CdSe QDs sensitization were also prepared and labeled as SC-refer (C/CuSCN/ TiO_2 /FTO).

The morphology of TiO_2 electrodes was investigated by use of an atomic force microscopy (AFM) AFM, nanoscope

III). Absorption spectra were recorded using a UV-Vis spectrophotometer (Hitachi Model U-4 100). A homemade platform based on Keithley 4200S was employed to study the current-voltage (I - V) characteristics of solar cells under the illumination of a tungsten halogen lamp (intensity of 50 mW/cm^2 by photometer).

3. Results and Discussion

Figure 1 shows the differences in surface morphology between an as-grown TiO_2 and CdSe QDs-sensitized TiO_2 characterized by AFM. It can be seen that the as-grown TiO_2 is porous with a mean particle size of about 20 nm, the same as previously reported in [2]. It should be noted that the porosity and grain size are crucial to electron transport in nanocrystalline TiO_2 electrodes [23]. After sensitized by CdSe QDs, the TiO_2 becomes rougher. The root-mean-square (RMS) roughness increases by about 5 nm, from 12 nm to 17 nm. It may be a coincidence that the roughness increment is close to the diameter of CdSe QDs applied (mentioned in the following). However, we assume monolayer absorption of CdSe QDs at the surface of TiO_2 , as reported in [5]. The monolayer absorption facilitates the penetration of CdSe QDs to the porous network of TiO_2 , whereas some pores may be too cabined for the QDs to transport. The additional roughness enhancement could be due to the absorption of QDs or not in different areas.

The absorption spectra for a TiO_2 electrode and CdSe QDs-sensitized TiO_2 electrodes (modified and unmodified) are shown in Figure 2. Due to the large bandgap of TiO_2 (3.2 eV), we ascribe this apparent absorption in visible wavelength range mainly to scattering effect. It is seen that the CdSe QDs sensitized TiO_2 films absorb photons more efficiently in the wavelength range of 400–650 nm, due to the limitation of CdSe QDs absorption edge. The absorption peak at about 600 nm corresponds to the 1S transition of CdSe QDs. By comparing the 1S transition peak position to that reported by Yu et al. [24], we estimate that the CdSe QDs are about 5 nm. The absorbance of modified TiO_2 films shows little increase as the exposure time in QDs solution increases, indicating monolayer absorption of CdSe QDs at the surface of TiO_2 . In this mode of absorption, it is assumed that QDs can be anchored onto both exterior and interior surfaces of mesoscopic TiO_2 films through molecule linkers [4]. We find higher absorbance in unmodified TiO_2 films which are prepared directly by drop-casting QDs than that of modified TiO_2 films. This indicates that more CdSe QDs are deposited on the films, however packed in a multilayer form possibly.

Figure 3 shows the I - V curves for the SC-refer in the dark and light. In the dark, it is evident that the TiO_2 /CuSCN interface gives rise to a rectification effect since $\text{SnO}_2/\text{TiO}_2$ and CuSCN/graphite junctions are both considered to be ohmic contact [25]. It can also be concluded from the curve that a weak built-in electric field points from CuSCN to TiO_2 since applying positive bias to CuSCN layer leads to a positive current, which indicates that our CuSCN layer is p type and can serve as a hole transport layer. Though we obtain a rectification ratio of about 30, the numerical fitted

FIGURE 1: AFM images of (a) an as-grown TiO_2 electrode and (b) a CdSe QDs sensitized TiO_2 electrode.

FIGURE 2: Absorption spectra of a TiO_2 electrode and CdSe QDs sensitized TiO_2 electrode.

reverse saturation current is about 0.0065 mA/cm^2 , which is much higher than the data reported in the literature [20]. We ascribe the poor performance of the diode to the weak filling of CuSCN into porous TiO_2 films, resulting in a reduced working area. Under illumination, photovoltaic effect can be observed although the open voltage (V_{oc}) is rather low. This is not hard to understand since only ultraviolet light can be absorbed by the high bandgap materials of TiO_2 and CuSCN.

Figure 4 illustrates the I - V characteristics of the SC-unmodified. Compared with the SC-refer, it unexpectedly shows that the photocurrent is even smaller. Although CdSe QDs between CuSCN and TiO_2 electrodes improve light absorption and consequently lead to more light-induced carriers and higher current, it has been recently reported that the organic capping agent of QDs remains on the surface [26]. Therefore, we assume that organic residuals could form a high series resistance of the device and lower

FIGURE 3: I - V curves of an SC-refer (C/CuSCN/ TiO_2 /FTO) under dark and light (inset is the enlarged image).

the photocurrent. In addition, the multilayer pileup of QDs and much weaker filling of CuSCN into porous TiO_2 films because of this layer can make this even worse. On the other side, the long organic chain between TiO_2 and QDs could serve as barrier layer, increasing the shunt resistance and the V_{oc} afterwards.

In contrast to the drop casting method, both the V_{oc} and J_{sc} of SC-modified increase when CdSe QDs are modified as demonstrated in Figure 5. As a short chain surface modifier, MPTMS reduces the space between QDs and TiO_2 . As mentioned above, there exist organic capping agents with long chains at the surface of QDs. By substituting these long chains with short ones, the carrier injection efficiency can be improved [4]. In addition, hydrolyzate of MPTMS is SiO_2 , forming an insulating barrier between QDs and TiO_2 . The insulating layer is a “tunnel barrier”, reducing the pseudo-first-order recombination rate, as indicated in [27].

FIGURE 4: I - V curves of a SC-unmodified (C/CuSCN/ CdSe(unmodified))/TiO₂/FTO under dark and light.

FIGURE 5: I - V curves of a SC-modified (C/CuSCN/ CdSe(modified))/TiO₂/FTO under dark and light (inset is the enlarged image).

Generally speaking, the insulating layers increase the shunt resistance of devices and suppress shunt current. This leads to the increase in V_{oc} compared with SC-unmodified. What is more, the monolayer absorption mode of QDs lowers the series resistance and increase the J_{sc} consequently. Since the electron transfers from excited QDs to electrodes by tunneling through the insulating layer, the thickness of it should not be too large [19, 26].

Although the performances of our devices are relatively not as good as that reported in the earlier works [4, 5], we successfully employ solid-state electrolyte of CuSCN in QDs-sensitized solar cells and indicate the beneficial effects of MPTMS. In addition, considering the all nonvacuum process during the preparation of our solar cells (including

electrodes preparation) and the low energy density of our light, there can be great promoting potentials for our devices. Probable technology routes are the growth of p -type layers or TiO₂ electrodes to enhance the junction area, surface engineering to reduce the recombination in the QDs/TiO₂ interface, and QDs control to improve light absorption and electron injection.

4. Conclusions

CdSe QDs sensitized mesoporous TiO₂ solar cells with CuSCN as solid-state electrolyte have been prepared. The effect of MPTMS as a surface modifier on the I - V characteristics of solar cells is investigated. The surface modifier substitutes the long chains of organic capping agents at the surface of QDs, shortening the space between QDs and TiO₂ and improving the electron injection efficiency from QDs to TiO₂. In addition, the hydrolyzate of MPTMS forms an insulating barrier layer, leading to the increase of shunt resistance and open-circuit voltage of the devices.

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