Co-sensitization of microporous TiO$_2$ electrodes with dye molecules and quantum-sized semiconductor particles

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Abstract

The microporous titanium dioxide (TiO$_2$) film has been prepared on a conducting glass substrate. A seven-fold enhancement in energy conversion efficiency of the dye-sensitized solar cell was achieved by pre-depositing a closely packed TiO$_2$ thin film on the surface of the conducting glass. Moreover, FeS$_2$ particles were coated on TiO$_2$ electrode by chemical reaction of iron pentacarbonyl with sulfur in xylene. Both atomic force microscope (AFM) and photoelectric studies suggest that the FeS$_2$ quantum-sized particles play a dominate role in the photoelectric conversion of FeS$_2$/TiO$_2$ electrode, while the FeS$_2$ large particles have less or even no contribution to the photo-current. Furthermore, the TiO$_2$ electrode has been co-modified with phthalocyanine dye molecules and quantum-sized semiconductor particles. Co-sensitization of the TiO$_2$ electrode with CdSe particles and ZnTCPc dye molecules not only extends the photoresponse of CdSe/TiO$_2$ electrode further into red region, but also improve the quantum efficiency of photoelectric conversion. We believe that such a co-sensitization technique should be of general importance in designing novel solar energy conversion devices. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Titanium dioxide; Co-sensitization; Dye molecule; Photoelectric conversion

1. Introduction

Sensitization of wide-bandgap semiconductor electrode with organic dye has been investigated intensively for a long time due to its potential applications in solar energy conversion. Recently impressive solar-to-electrical energy conversion efficiency has been achieved by using a highly porous TiO$_2$ substrate electrode with organic dye as sensitizer [1,2]. In the configuration, organic

dye coated on the TiO$_2$ surface was used to harvest incident light. Light absorption of the dye was followed by an electron injection from the excited state of the dye molecule into the conduction band of the semiconductor. The remaining positive hole was scavenged by a redox couple in electrolyte. The main feature of this work was the preparation of 'microporous' TiO$_2$ electrode with a high specific surface area, which is defined as the ratio of the effective surface area to the geometric area of the electrode. The microporous TiO$_2$ electrode is made of quantum-sized TiO$_2$ particles, and it has such a high surface area that even a dye monolayer coating could completely absorb the

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incident light in the respective spectral region of the dye molecule. Therefore the energy conversion efficiency was improved.

In our laboratory, microporous TiO_2 electrodes with a specific surface area over 150 has been fabricated [3,4]. It has been shown that both organic dye molecules and semiconductor quantum-sized particles can be used as sensitizer to extend the photoresponse of the TiO_2 electrode into visible region [3–8]. Wahi et al. [9] studied in details the photoresponse of the TiO_2 electrode in the presence of PbS quantum dots. Very recently we have shown [10–12] that the energy conversion efficiency of dye-sensitized TiO_2 solar cell can be greatly improved by co-sensitization of TiO_2 electrode with two different dye molecules such as tetrasulfonated zinc porphyrin (ZnTsPP) and tetrasulfonated gallium phthalocyanine (GaTsPc). The improvement in conversion efficiency is attributed to the formation of the ZnTsPP–GaTsPc heteroaggregates on the co-sensitized TiO_2 electrode resulting from charge–transfer interaction between GaTsPc and ZnTsPP. The obvious question is whether this enhancement effect will also appear in a coupled system composed of dye molecules and semiconductor particles. We report here detailed studies of sensitization and co-sensitization of microporous TiO_2 electrodes with dye molecules and semiconductor quantum-particles.

2. Experiment

A transparent TiO_2 electrode was prepared by spreading a colloidal solution of TiO_2 particles with an average size of 8 nm on a conducting glass substrate (ITO), followed by annealing for about one hour at 450°C in air after drying. After heat treatment, the TiO_2 film adhered strongly to the glass support. Atomic force microscope (AFM) revealed that the film is composed of interconnected TiO_2 particles and pores [3].

The TiO_2 electrode was coated with Zinc tetrasulfonated phthalocyanine (ZnTsPc) dye by immersing the TiO_2 electrode in ZnTsPc solution (10^{-3} M, in ammonia) for a few hours at the temperature of 20°C. The transparent TiO_2 electrode became green after coating with dye molecules.

The TiO_2 electrode was modified with FeS_2 particles by a similar procedure described before [13]. The clean TiO_2 electrode was dipped in the solution of sulfur (0.02 M) in xylene, followed by immersion in a solution of iron pentacarbonyl (0.01 M) in xylene at the temperature of 139°C. The transparent TiO_2 electrode became black after this procedure was repeated several times, indicating that FeS_2 particles were coated on the electrode.

CdSe particles were coated on the TiO_2 electrode by a chemical bath deposition method, which is an attractive, low cost and simple method for large area deposition onto various substrate with various materials as well as complex geometry [14,15]. Then the $CdSe/TiO_2$ electrode was modified with zinc tetracarboxyl phthalocyanine (ZnTcPc) dye molecules to fabricate a $ZnTcPc–CdSe/TiO_2$ electrode, by immersing $CdSe/TiO_2$ electrode in ZnTcPc solution (10^{-3} M, in ammonia) for a few hours. The color of the electrode changes from red to green indicating the ZnTcPc molecules were coated on the electrode.

The morphology of the TiO_2 film was examined by an atomic force microscope (AFM) (DI Co., Nanoscope III). The film thickness was measured with a scanning electron microscope (SEM) (JEOL, JSM-6300). The absorption spectra were recorded with a Shimadzu UV-2201 UV-visible spectrometer. In photoelectric studies we used a two-electrode photoelectrochemical cell, which is composed of a sensitized TiO_2 electrode and a platinum electrode separated by an electrolyte containing 0.1 M Na_2S and 0.01 M Na_2SO_4. The photocurrent was measured with a potentiostat (model CMBP-1). Monochromatic illumination was obtained using a 500 W xenon arc lamp in combination with a grating monochromator (model CP130-II). The light intensity was calibrated using a model LM-5 laser power meter (National Institute of Metrology).

3. Results and discussions

3.1. Effect of pre-deposition layer of TiO_2 electrode

Fig. 1 shows the voltage–current characteristics of the liquid junction cell based on the ZnTsPc/TiO_2 electrode under an illumination of 35 mW cm^{-2}. The total photoelectric conversion efficiencies without and with the pre-deposited TiO_2 thin layer are 0.25 and 1.7%, respectively. A seven-fold
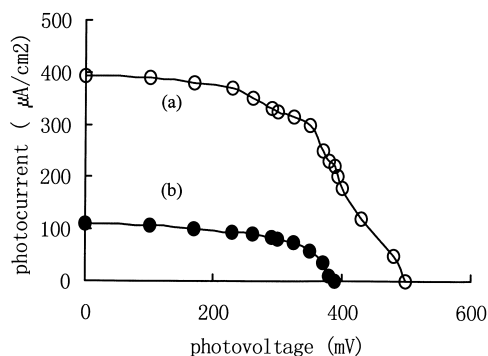

Fig. 1. The voltage-current characteristics of a liquid junction solar cell based on ZnTsPc/TiO_2 electrode under an illumination of 35 mW cm^{-2} with (A) and without (B) the pre-deposition of the conducting TiO_2 thin layer on an ITO conducting glass.
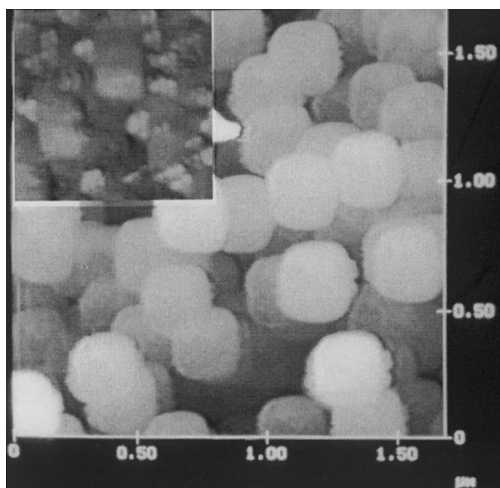

Fig. 2. AFM picture of TiO_2 microporous electrode, the inset (up-left) shows the morphology of TiO_2 electrode in the presence of FeS$_2$ particles.

improvement in the energy conversion efficiency is achieved through the pre-deposition of a closely packed TiO_2 thin layer on an ITO conducting support. The fill factor of the cell, defined as the maximum output power of the cell divided by short-circuit current and open-circuit voltage, reaches 0.625. This indicates that loss mechanisms such as recombination have been minimized. The role of TiO_2 in the liquid junction cell based on the ZnTsPc/TiO_2 electrode is merely to conduct the injected majority charge carriers (here it refers electrons). There are no minority carriers involved in the photo-conversion process. Surface and bulk recombination losses due to lattice defects, encountered in conventional photovoltaic cells, are not observable in such a device. The quantum-sized TiO_2 particles in the TiO_2 electrode allow efficient transport and rapid separation of the photogenerated charge carriers and minimize surface and bulk recombination. The conversion efficiency reaches 1.7% under an illumination of 35mW cm^{-2} at 700 nm, which presents one of the highest values reported for phthalocyanine photoelectric device.

3.2. Sensitization of TiO_2 electrode with FeS$_2$ particles

Fig. 2 shows the AFM picture of the surface morphology of TiO_2 electrode on a conducting glass substrate. The TiO_2 film is microporous, composed of interconnected particles and pores. It can also be seen that the TiO_2 particles in the film are uniform with an average height of 50 nm and a width of 250 nm, which is larger than the size of the TiO_2 particles in colloidal solution. Probably the annealing increases the connectivity of the particles and makes them collapse to from much larger crystalline. The inset (up-left) of Fig. 2 shows the surface morphology of the FeS$_2$/TiO_2 electrode. It is clear that FeS$_2$ particles exist on the surface of TiO_2 electrode in two different forms: one is in quantum-sized FeS$_2$ particle, and another is in large aggregation of FeS$_2$ particles.

In order to study the photoelectric properties of TiO_2 electrode modified with FeS$_2$ particle, the short-circuit photo-current was measured at various wavelengths. The incident photo-to-current conversion efficiency (IPCE) was then determined
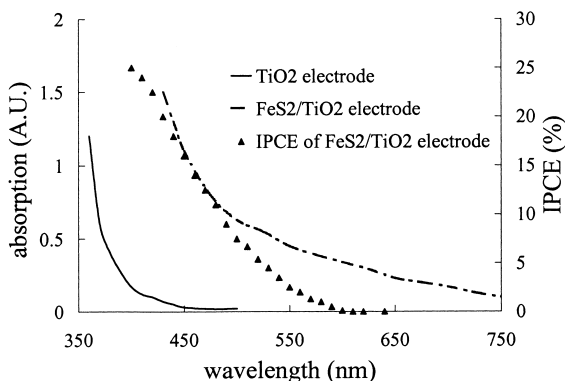
Fig. 3. Optical absorption spectra of TiO_2 (A) and FeS_2/TiO_2 (B) electrodes. Curve (C) is the photo-current action spectrum of FeS_2/TiO_2 electrode.
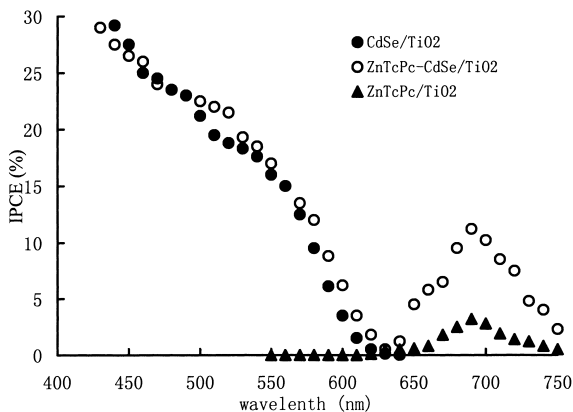

Fig. 4. Photo-current action spectra of $CdSe/TiO_2$, $ZnTcPc/TiO_2$ and $ZnTcPc–CdSe/TiO_2$ electrodes.

from: $IPCE = (i_{sc}/I_{inc})·(1241/\lambda)·100\%$, where i_{sc} is the short-circuit current ($\mu A\ cm^{-2}$), I_{inc} is the incident light intensity ($\mu W\ cm^{-2}$), and λ is the excitation wavelength (nm). The action spectra representing IPCE versus excitation wavelength for FeS_2/TiO_2 electrode is measured and shown in Fig. 3. For comparison, the absorption spectra of the electrodes with and without modification of semiconductor FeS_2 particles are also shown in Fig. 3. A conducting glass substrate is used as a reference in optical spectral measurement. The bare TiO_2 electrode exhibits the fundamental absorption edge of rutile, which has a bandgap of 3.2 eV. The FeS_2/TiO_2 electrode displays the characteristic absorption of FeS_2 in the visible range

with an apparent shoulder around 580 nm and a weak absorption tail. The low-energy tail comes from the large particles while the high-energy absorption edge comes mainly from the small FeS_2 particles. A significant blue shift in the absorption spectrum of the FeS_2/TiO_2 electrode compared with the bulk crystalline FeS_2 semiconductor is observed, which is similar to the absorption shift reported for colloidal FeS_2 particle [8]. A blue shift in the photo-current action spectrum similar to that of absorption spectrum is apparent which could also be explained as quantum size effect.

Although the FeS_2/TiO_2 electrode shows a visible absorption in wavelength longer than 580 nm, no photo-current could be measured at these wavelengths. This suggests that small quantum-sized FeS_2 particles play a dominant role in the spectral sensitization of TiO_2 electrode, while the larger FeS_2 particles have less even no contribution to the photo-current. It should be pointed out that pyrite (FeS_2) is a favorable photosensitization semiconductor material due to its advantages such as environmental compatibility, high stability towards photo-corrosion as well as very high optical absorption in the visible range of the solar spectrum. Ennaoui et al. [8] firstly reported a solar cell based on FeS_2-sensitized TiO_2 electrode. The quantum efficiency reported here is higher than previous result due to the fact that a highly porous TiO_2 electrode was used here and that the FeS_2 particles were modified not only at the surface but also inside the TiO_2 film.

3.3. Co-sensitization of TiO_2 electrode with ZnPc molecules and CdSe particles

In order to evaluate the photoelectric response of modified electrode, the action spectra representing IPCE versus excitation wavelength for $CdSe/TiO_2$ and $ZnTcPc–CdSe/TiO_2$ are shown in Fig. 4. It is obvious that modification of TiO_2 electrode with CdSe particles extends the photoresponse of the TiO_2 electrode into visible region. Note that the onset of the action spectrum shifts to shorter wavelength as compared to that of the bulk CdSe materials. This shift is also understood in terms of quantum-sized effect.

The photo-current spectrum of ZnTcPc–CdSe/TiO$_2$ electrode shown in Fig. 4 is different from the absorption spectrum [3] in that the maximum of the curve changes from 620 to 700 nm. The absorption peak at 620 nm is due to the ZnTcPc molecule in aggregation from, while that at 700 nm is due to monomeric ZnTcPc molecule. Thus the monomeric molecules contribute to the spectral sensitization effect on the coupled CdSe/TiO$_2$ electrode, while the contribution of ZnTcPc molecules in aggregation form is negligibly small.

It should be noted that both ZnTcPc/TiO$_2$ and ZnTcPc–CdSe/TiO$_2$ electrodes show significant IPCE in Fig. 4 in the absorption spectral range of the monomeric ZnTcPc dye molecule. The IPCE of ZnTcPc–CdSe/TiO$_2$ electrode is four times higher than that of ZnTcPc/TiO$_2$ electrode at the excitation wavelength in the red region. Deng et al. [9–11] reported a six to ten fold improvement in the photoelectric conversion efficiency for TiO$_2$ electrode co-sensitized with porphyrin and phthalocyanine dye molecules. The quantum yield improvement at 700 nm is attributed to the fact that most of the CdSe particles are directly in contact with TiO$_2$ electrode to form a coupled CdSe/TiO$_2$ semiconductor system. The coupling of the CdSe particles with TiO$_2$ particulate film possesses beneficial electrochemical rectification and results in the suppression of electron flow toward the electrolyte as well as recombination with holes of dye molecules. In addition, the presence of CdSe quantum-sized particles in TiO$_2$ electrode makes more ZnTcPc molecules exist in monomeric form, which contribute to the spectral sensitization effect on the coupled CdSe/TiO$_2$ electrode, as has been shown above. We believe that such co-sensitization technique should be of general importance in designing novel solar energy conversion devices.

4. Conclusion

We can conclude that: (1) A seven-fold enhancement in energy conversion efficiency of the dye-sensitized solar cell was achieved by pre-depositing a closely packed TiO$_2$ thin film on the surface of the conducting glass. (2) Quantum-sized FeS$_2$ particles were coated on TiO$_2$ electrode by chemical reaction of iron pentacarbonyl with sulfur in xylene. STM study revealed that FeS$_2$ particles exist on the surface of TiO$_2$ electrode in two different forms: one is in quantum-sized FeS$_2$ particles and another is in larger FeS$_2$ clusters. Both STM and photoelectric studies suggest that the quantum-sized FeS$_2$ particles play a dominate role in the photoresponse of FeS$_2$/TiO$_2$ electrode, while the large FeS$_2$ particles on the surface of the electrode have less or even no contribution to the photo-current. (3) The TiO$_2$ electrode has been co-modified with phthalocyanine dye molecules and quantum-sized semiconductor particles. Co-sensitization of the TiO$_2$ electrode with CdSe particles and ZnTcPc dye molecules not only extends the photorespose of CdSe/TiO$_2$ electrode further into red region, but also improve the quantum efficiency of photoelectric conversion. More experimental studies using electrochemical STM are currently underway to get a further insight into the electron transfer process between dye molecules and semiconductor quantum-sized particles.

Acknowledgements

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