Fabrication, characterization and photovoltaic study of a GaTSPc–CdS/TiO_2 particulate film

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Quantum-sized cadmium sulfide (CdS) particles have been deposited onto the surface of a microporous titanium dioxide (TiO_2) electrode by the chemical growth method, followed by modification with gallium tetrasulfophthalocyanine (GaTSPc) molecules to prepare a co-modified TiO_2 electrode. Low bandgap semiconductor CdS particles and GaTSPc have different spectral ranges in the visible range. The co-modified TiO_2 electrode effectively absorbed visible light. Experimental results showed that the sensitization of the TiO_2 electrode with CdS and GaTSPc extended the optical absorption spectrum and photocurrent action spectrum into a wider visible range; moreover, the CdS/TiO_2 coupled structure facilitated the photon-to-photocurrent conversion efficiency.

Recently there has been considerable interest in developing nanocrystalline microporous particulate films modified with organic dyes owing to the work of Grätzel and co-workers.[1–3] The nanocrystalline semiconductor films possess highly porous structures and very large surface areas. Less than even a monolayer coating could completely absorb incident light in the spectral range of the dye absorbance; the energy conversion efficiency could be improved. Subsequently, there have been some reports[4,5] of the modification of large bandgap microporous semiconductor particulate films using inorganic short bandgap quantum-sized semiconductor particles such as ultrafine CdS particles to embed into the microporous TiO_2 electrode and to use these modified layers as light-converting electrodes. Visible light was absorbed by the ultrafine particles which, consequently, transferred electrons into the TiO_2 substrate. It has been shown by others[6,7] that the photoresponse of a large bandgap semiconductor can be extended into the visible range by coupling with a short bandgap semiconductor. Since these ultrafine particles exhibit chemical and physical properties which differ markedly from those of the bulk solid as well as of the individual molecules, very high quantum yields for the electron transfer process were obtained.

In a previous paper,[8] we described the preparation and characterization of a TiO_2 microporous electrode as well as the photovoltaic properties of such an electrode sensitized with a dye. In the present work, a microporous titanium dioxide (TiO_2) electrode has been prepared on a conducting glass support. Then we included Q-CdS particles and GaTSPc dye molecules, which possess different spectral absorption regions in the visible range, to co-modify the TiO_2 electrode. Compared with electrodes using either Q-particles or organic dyes, a better spectral match to the solar spectrum was obtained for a microporous TiO_2 electrode sensitized by a combination of Q-CdS particles and phthalocyanine dye molecules.

Experimental

Preparation of TiO_2 electrode

The nanocrystalline TiO_2 films were fabricated as follows. A colloidal solution was prepared by adding commercial TiO_2 power (P25, Degussa, a mixture of *ca.* 25% rutile and 75% anatase, surface area $55\ m^2\ g^{-1}$, diameter 25 nm) to a small amount of water and surfactant (Triton x-100). The colloidal solution was then coated onto a conducting glass support. After air drying, this was heated in air in a Lindberg tube furnace in which the temperature was increased gradually to 450 °C and then held at 450 °C for 30 min. After heat treatment, the TiO_2 film was strongly attached to the glass support. Using a similar procedure to that described in ref. 1 and 8, a roughness factor of about 80 was obtained for the TiO_2 electrode.

Fabrication of Q-CdS/TiO_2 particulate film

In order to deposit CdS particles on the microporous TiO_2 electrode, we adopted the solution growth technique described in ref. 9, which is an attractive, low-cost and simple method for large area deposition onto various substrates with various materials as well as complex geometry.[9,10] We immersed the microporous TiO_2 electrode in the deposition bath composed of 5 ml of $1\ mol\ dm^{-3}$ cadmium acetate, 2.5 ml of $7\ mol\ dm^{-3}$ triethanolamine, 5 ml of $13\ mol\ dm^{-3}$ ammonia and 5 ml of $1\ mol\ dm^{-3}$ thiourea at 40 °C. After about 6 h, the TiO_2 electrode covered with an orange–yellow deposit was taken out, washed with distilled water and dried in air, to give the CdS modified electrode.

Preparation of dye-modified electrodes

The dye gallium tetrasulfophthalocyanine (GaTSPc) was synthesized in our institute and its structure is shown in Fig. 1. Dye molecules were coated on the TiO_2 electrode by immersing the electrode in a methanol solution with a dye concentration

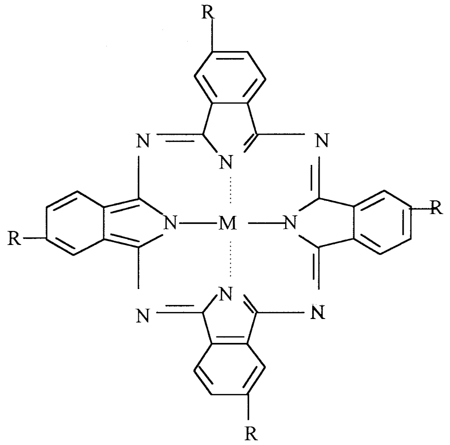

Fig. 1 The structure of GaTSPc, M = GaOH; R = SO_3^-

of about 10^{-4} mol dm^{-3}. After at least 3 h of soaking, we obtained a dye-modified CdS/TiO_2 electrode.

Experimental setup

The morphologies of the TiO_2 and CdS/TiO_2 electrodes were examined with an atomic force microscope (AFM) (DICO, NanoScope 3). The absorption spectra were recorded with a Shimadzu UV-2201 spectrometer. A two-electrode photoelectrochemical (PEC) cell, composed of a modified TiO_2 electrode, a counter electrode consisting of conducting glass sputter-coated with a 1 μm Pt film, and an electrolyte containing 0.1 mol dm^{-3} Na_2S and 0.01 mol dm^{-3} Na_2SO_4, was used for photovoltaic studies. The cell had an area of 0.5 cm^2. The short-circuit photocurrent was measured with a Model CMBP-1 potentiostat. Monochromatic illumination was obtained using a 500 W xenon arc lamp in combination with a grating monochromator, model WPG3D. The light intensity was calibrated using a model OM-1001C radiometer/photometer.

Results and Discussion

AFM studies

AFM pictures of the surfaces of the TiO_2 and CdS/TiO_2 electrodes are shown in Fig. 2. The TiO_2 film is microporous, composed of interconnected particles and pores. It can also be seen that the TiO_2 particles are uniform with an average diameter of about 70 nm, which is much larger than the size of the TiO_2 particles in colloidal solution. Further experimental results show that the heating process is crucial to the morphology of the TiO_2 electrode. The size of the particles in the TiO_2 film increases with increasing temperature. The AFM study of the CdS/TiO_2 surface indicates the formation of small particles on the surface of the TiO_2 electrode, a trace section analysis across the particles gives the size of these particles at about 10 nm in diameter. They are coated on the TiO_2 surface in the form of clusters. Considering the solution deposition process, this value of the particle size, however, is only the upper limit.

The chemical reaction that leads to the formation of CdS is as follows[9]

$$\mathrm{Cd(TEA)^{2+} + (NH_2)_2CS + 2OH^-}$$
$$\mathrm{\rightarrow CdS + TEA + (NH_2)_2CO + H_2O}$$

The chemical bath deposition mechanism is essentially based on the slow release of S^{2-} ions from $(NH_2)_2CS$ and Cd^{2+} from $Cd(TEA)^{2+}$ in the solution. The free Cd^{2+} and S^{2-} combine to form CdS. The CdS formed homogeneously throughout the solution grows into clusters which can diffuse to the substrate, where they aggregate to form a layer. The TiO_2 electrode used as the substrate was microporous, and when the substrate was immersed in the solution, both $(NH_2)_2CS$ and $Cd(TEA)^{2+}$ would penetrate into the TiO_2 electrode through the pores. Therefore, while some CdS particles were formed on the surface of the electrode, some CdS particles were also deposited in the pores of the TiO_2 electrode, as was demonstrated in ref. 4. Probably owing to the spatial confinement, the CdS particles inside the electrode were smaller than those on the surface of the electrode. In order to estimate the amount of CdS particles coated on the microporous TiO_2 electrode, we allowed the CdS particles to dissolve in HNO_3. After washing the electrode with water, a value of 361.8 μg cm^{-2} of Cd^{2+} ($\rho = 4.82$ g cm^{-3}) was found by atomic absorption spectroscopy. Considering the diameter of CdS particles as well as the roughness factor of the bare TiO_2 electrode, approximately one or two layers of CdS particles were estimated to coat the TiO_2 electrode. The interconnected ultrafine particles and pores on the TiO_2 electrode form a three-dimensional network structure. These pores not only increase the surface area and allow the electrode to adsorb more monolayer dye molecules, but also enable the adsorbed dye molecules to come into direct contact with the electrolyte. When dye molecules absorb incident light, the photogenerated electrons can transfer directly into the conduction band of semiconductor particles; at the same time, the holes remaining in the dye can be rapidly removed by electron transfer from the redox system in the electrolyte, thus decreasing the probability of recombination and increasing the photoresponse.

Absorption characteristics and photovoltaic study

The absorption spectra of the electrode at various stages of modification are shown in Fig. 3. A conducting glass support is used as reference in the measurement. The TiO_2 contains 25% rutile and 75% anatase and the bandgap of rutile is 3 eV, as compared to 3.2 eV for anatase, corresponding to fundamental absorption edges of 413 nm and 388 nm, respectively; therefore the bare TiO_2 film exhibits the fundamental absorption edge of rutile. Curve (*b*) is the absorption spectrum of the Q-CdS/TiO_2 electrode. It shows that the CdS/TiO_2 electrode displaces the characteristic absorption of CdS well in to the visible region with an apparent absorption shoulder around 500 nm and an weak absorption tail. The low-energy tail arises from the large particles, while the high-energy absorption shoulder arises predominantly from the small particles. The

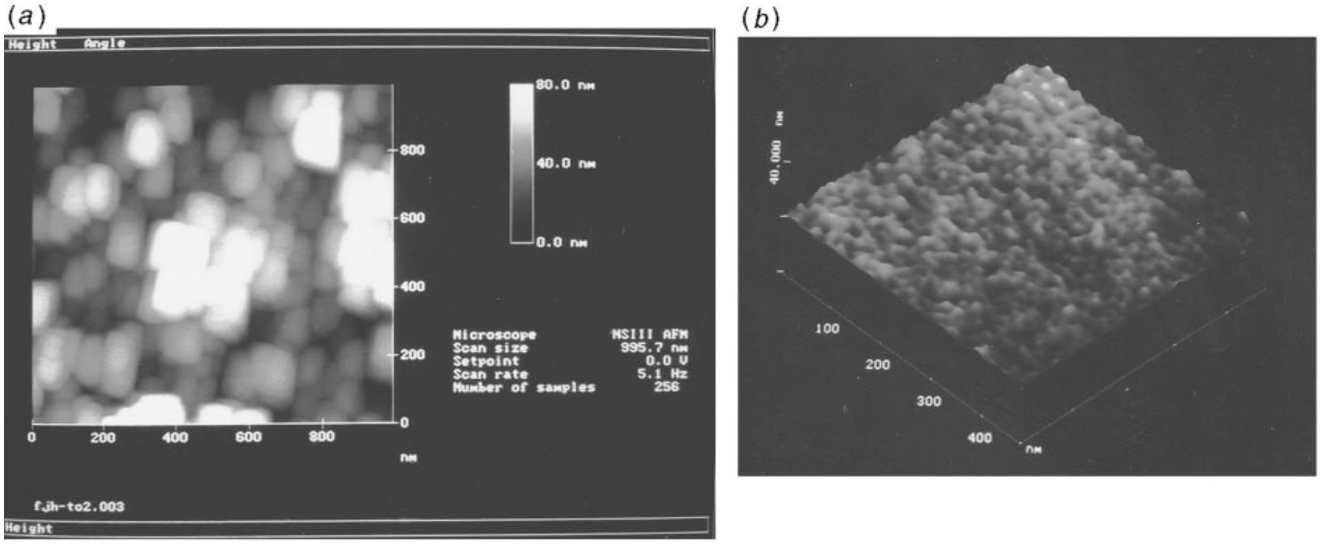

Fig. 2 AFM pictures of the TiO_2 (*a*) and CdS/TiO_2 (*b*) electrodes

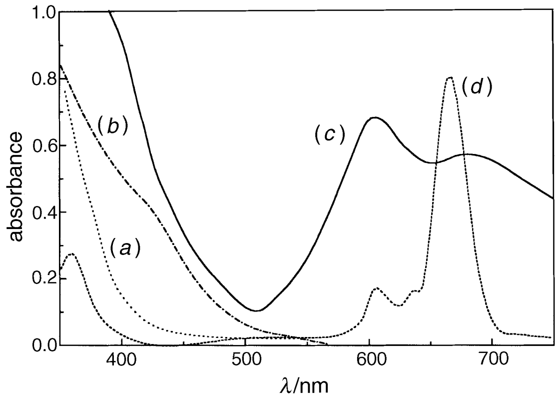

Fig. 3 Absorption spectra of bare TiO_2 (*a*), CdS/TiO_2 (*b*), GaTSPc–CdS/TiO_2 electrodes and GaTSPc in methanol solution (*d*); all except (*d*) used a conducting glass support

absorption of the GaTSPc–CdS/TiO_2 electrode further extends the absorption range of the electrode into the red and displaces the characteristic absorption of GaTSPc with a maximum in the visible region around 610 nm. The shoulder around 690 nm in curve (*c*) of Fig. 3 is assigned as the monomeric GaTSPc Q-band.[11] The broad band around 610 nm is enhanced compared with the spectrum of GaTSPc in dilute methanol solution (*d*), indicating the occurrence of aggregation[11] of GaTSPc molecules on the electrode. Compared with the CdS/TiO_2 electrode, GaTSPc–CdS/TiO_2 displays efficient absorption over a wider spectral range. Higher solar energy conversion efficiency may be expected, since more incident light was absorbed by the GaTSPc–CdS/TiO_2 electrode. We can conclude from the above that modification of TiO_2 with Q-CdS particles extends the optical absorption spectrum into the visible region, and that the absorption spectrum of the CdS/TiO_2 electrode can be further extended into the red region by sensitization with GaTSPc dye molecules.

Fig. 4 shows the photocurrent action spectra of the CdS/TiO_2 electrode (*a*), GaTSPc–CdS/TiO_2 (*b*) and GaTSPc/TiO_2 electrodes (*c*). The photocurrent action spectrum of the Q-CdS/TiO_2 electrode correlates well with its absorption spectrum, indicating that Q-CdS contributes significantly to the photocurrent of the electrode. It is obvious that the photocurrent action spectra of the GaTSPc-CdS/TiO_2 and GaTSPc/TiO_2 electrodes are very different from the absorption spectra in that the maximum of the curve changes from about 610 nm to 690 nm. We infer from the above that the monomeric GaTSPc molecules have contributed to the photocurrent of the electrode, while the GaTSPc molecules in the aggregated form contribute little or nothing to the photocurrent. It should be noted that both GaTSPc–CdS/TiO_2 and GaTSPc/TiO_2 electrodes show significant photocurrent responses corresponding to the monomeric absorption of GaTSPc. The photocurrent of the GaTSPc–CdS/TiO_2 electrode is about three times that of GaTSPc/TiO_2 at the excitation wavelength in the red region. The improvement of the sensitization efficiency can be explained as follows. First, owing to the absence of an effective space charge layer at the particle/electrolyte interface,[12] by utilizing nanocrystalline semiconductor particulate films in photoelectrochemical cells, the photogenerated charge carrier can move in both directions under this circumstance. Thus, the photogenerated electrons either recombine readily with holes or leak out at the electrolyte interface, instead of flowing through the external circuit. However, Q-CdS particles were coated onto the surface of the TiO_2 particles to form a CdS/TiO_2 coupled structure. In this coupled system, the injected charge from the excited state of the dye molecules quickly migrates from CdS into the lower lying conduction band of TiO_2; meanwhile, the junction between the TiO_2 and CdS particles creates an energy barrier against the flow of electrons towards the electrolyte, thus reducing the possibility of reverse electron flow, *i.e.* the CdS/TiO_2 coupled structure exhibits a beneficial rectification effect, so an effective charge carrier separation and transport throughout the particulate film becomes feasible. The recombination and electron leakage losses are relatively low. In addition, a TiO_2 electrode coated with smaller Q-CdS particles possesses a larger surface area than the bare TiO_2 electrode. As a result, a relatively high photocurrent response is generated in this system.

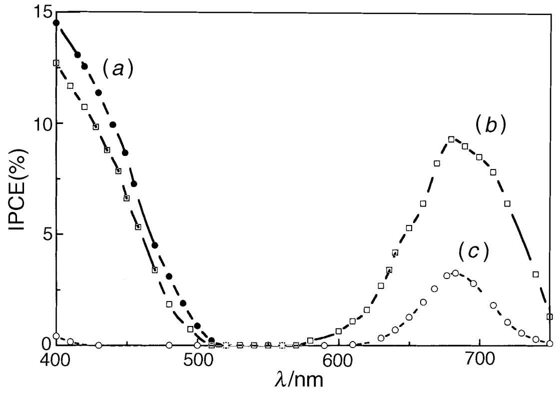

Fig. 4 Photocurrent action spectra of incident photon conversion efficiency (IPCE) of CdS/TiO_2 (*a*), GaTSPc–CdS/TiO_2 (*b*) and GaTSPc/TiO_2 (*c*) electrodes. Electrolyte 0.1 mol dm^{-3} Na_2S and 0.01 mol dm^{-3} Na_2SO_4

Conclusion

Based on the present results and the above considerations, this paper can be summarized as follows. (1) A microporous TiO_2 electrode can be modified with Q-CdS particles by the chemical deposition method, and a CdS/TiO_2 electrode can be further sensitized with GaTSPc molecules. (2) Compared with conventional electrodes using either CdS particles or phthalocyanine, modification of the TiO_2 electrode with both CdS particles and GaTSPc not only results in a better spectral match to the solar spectrum, but also extends the photoresponse of the electrode to cover most of the visible range. (3) The monomeric molecules contribute to the spectral sensitization effect on the CdS/TiO_2 electrode, while the contribution of the GaTSPc molecules in aggregated form is negligible. (4) The rectification of the coupled CdS/TiO_2 system can effectively increase the response of the electrode. (5) Among the phthalocyanines (such as GaTSPc, ZnTSPc, InTSPc, VoTSPc, *etc.*) studied in our experiments, GaTSPc shows the best sensitization effect on the electrode.

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