Modification of TiO_2 Microporous Electrode with Quantum-Sized FeS_2 Particles

Jing Huai Fang,* Jing Wen Wu, Lian Yong Su, Xiang Yang Zhang, and Zu Hong Lu
National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing, 210096, P.R.China

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Ultrafine FeS_2 particles were coated on a TiO_2 electrode by low temperature chemical reaction of iron pentacarbonyl with sulfur in xylene. The coating extends both the optical absorption spectrum and the photocurrent action spectrum of TiO_2 into visible region by sensitization mechanism. A blue shift observed in both the absorption and photocurrent action spectrum of the FeS_2/TiO_2 electrode is explained in terms of quantum size effect.

The photosensitization of large bandgap semiconductors by absorbed dyes has become attractive for solar cell application mainly due to the work[1] of Gratzel and collaborators. The main feature of this work was the preparation of microporous TiO_2 electrodes. The effective surface area of this kind of electrodes was so large that less than a monolayer of adsorbed dye molecules was sufficient for total the light absorption in the respective spectral range of the dye absorbance. So the energy conversion efficiency was improved by use of a large surface area electrode. Another hopeful method is to sensitize microporous large bandgap semiconductors with inorganic short bandgap semiconductor materials such as CdS. One way to attain this is to embed the ultrafine CdS particles into the porous TiO_2 film and to use this modified layer as light-converting electrode. Since these ultrafine particles exhibit fascinating physical and chemical properties which are quite different from the conventional semiconductor thin films, a very high quantum yield for electron transfer process was observed.[2,3]

Semiconductor FeS_2 is a favorable photosensitization material. The main advantages such as its environmental compatibility, high stability toward photocorrosion as well as very good absorption in the visible region of the solar spectrum make it to be another hopeful candidate for sensitization via inorganic semiconductor materials.

Recently, there was the report[4] of modification of large bandgap TiO_2 semiconductor with FeS_2 thin film by CVD method, and the interesting photoresponse of modified TiO_2 electrode was attained.

In a previous paper,[5] we described the preparation and characterization of TiO_2 microporous electrodes as well as the photovoltaic properties of the electrodes coated with dye. In the present work, a microporous TiO_2 electrode was prepared on a conducting glass support by spreading the colloidal solution of TiO_2 (Degussa P25, a mixture of ca 25% rutile and 75% anatase, surface area 55 m^2/g, diameter 25 nm), followed by annealing about 30 min at 450 ℃ in air after air drying. Then the quantum-sized FeS_2 particles were coated on the TiO_2 electrode by a similar procedure to the synthesis of FeS_2 described by Chatzitheodorou.[6] 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 ℃. The whole experiment was carried out under an argon atmosphere. This procedure was repeated several times. The morphology of electrodes were examined with an atomic force microscope (DICO., NanoScopeIII). The absorption spectra were recorded with a shimadzu UV-2201 spectrometer. A two-electrode photoelectrochemical (PEC) cell was used for photovoltaic study, which is composed of a FeS_2/TiO_2 electrode, a platinum electrode, and an electrolyte containing 0.1M Na_2S and 0.01M Na_2SO_4. The short-circuit photocurrent was measured by a Model CMBP-1 potentiostat. Monochromatic illumination was obtained using a 500 W Xenon arc lamp in combination with a grating monochrometor, Model WPG3D. The light intensity was calibrated using a model OM-1001C radiometer /photometer.

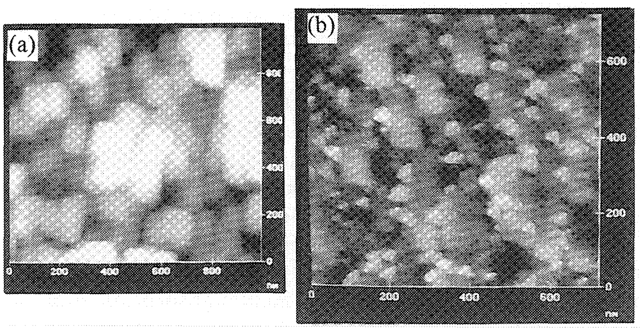

Figure 1. The AFM pictures of TiO_2 (a) and FeS_2 /TiO_2 electrode (b).

Figure 1 (a) is the atomic force microscope (AFM) picture of surface morphology of TiO_2 electrode on a conducting glass support. 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 width of particles about 60 nm and a length of particles about 130 nm, which is larger than the size of TiO_2 particles in colloidal solution. Probably, the annealing increases the connectivity of the particles and makes them coalesce to much larger crystallites. The AFM picture of figure 1 (b) shows the surface morphology of modified TiO_2 electrode. Compared with the surface morphology of the bare TiO_2 electrode of the figure 1 (a), we can find that there are many little particles consisted of aggregated clusters on the surface of TiO_2 electrode. Because of our synthesis method is similar to the method of FeS_2 synthesis,[6] these particles are made of FeS_2. The size of the particles distribution extends from about 20 nm to 50 nm. Considering the solution reaction procedure, when the substrate was immersed in the solution, the reaction solution would penetrate into the TiO_2 electrode through the pores. Therefore FeS_2 particles could be formed in the pores of the TiO_2 electrode during the formation of FeS_2

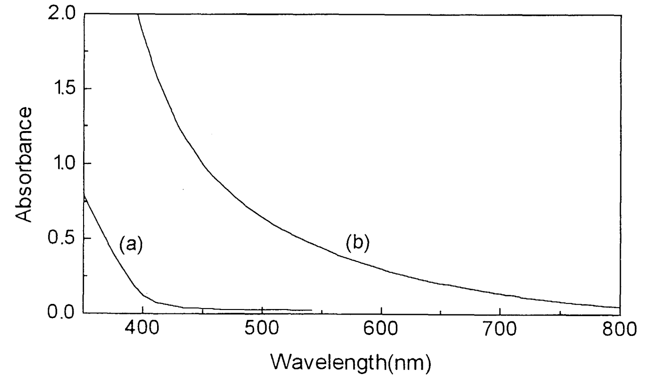

Figure 2. The absorption of bare TiO_2 electrode (a) and FeS_2/TiO_2 (b) electrode. both of them use a conducting glass as reference.

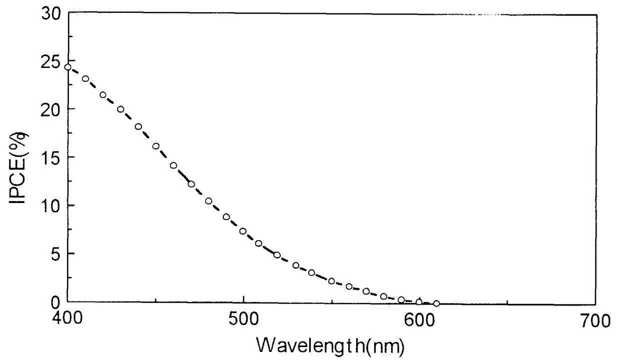

Figure 3. The photocurrent action spectrum of FeS_2/TiO_2 electrode.

on the surface of the electrode. Since microporous electrode possesses larger inner surface than outer surface, it is reasonable that most of the FeS_2 particles are maintained in the pores. Moreover, it can also be estimated in the picture that the size of little FeS_2 clusters that consist of larger particles is about 8 nm. This value, however, is only the upper limit as, due to the limited spatial resolution of the microscope, smaller clusters cannot be seen in the picture.

The absorption spectra of the electrodes with and without modification of semiconductor FeS_2 particles are shown in Figure 2. 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, whereas that of anatase is 3.2 ev, corresponding to a fundamental absorption edge of 413 and 388 nm, respectively. So the bare TiO_2 film exhibits the fundamental absorption edge of rutile. The FeS_2/TiO_2 electrode displays the characteristic absorption of FeS_2 in the visible range with an apparent absorption shoulder around 580 nm and a weak absorption tail. The low-energy tail comes from large particles. while the high-energy absorption shoulder comes predominantly from small particles. A significant blue shift of the absorption spectrum of ultrafine FeS_2 particles compared with that of bulk crystalline FeS_2 semiconductor[7] is observed, which is quite similar to that reported for absorption shift in colloidal FeS_2 particles in solution.[8]

Figure 3 depicts the photocurrent action spectrum of a FeS_2/TiO_2 electrode. The photoresponse of the TiO_2 electrode has been extended into the visible range. In addition, we can see the spectral shift to the shorter wavelength compared with that of the bulk FeS_2 material. This spectrum shift is very similar to the shift of the absorption spectrum and also understood in terms of the quantum size affect.

Although the FeS_2/TiO_2 electrode shows a visible absorption in wavelengths longer than 580 nm, no photorespone was detected at these wavelengths. This suggests that only small quantum-sized FeS_2 particles play a dominant role in the spectral sensitization on TiO_2 particles, while the larger FeS_2 particles on the TiO_2 surface have less or even no contribution to the photocurrent.

In summary, quantum-sized FeS_2 ultrafine particles can be prepared on the microporous TiO_2 electrode by low temperature solution chemical reaction, which is an attractive, low cost and simple method for large area fabrication onto various substrate with various materials as well as complex geometry. The sensitization of the TiO_2 electrode with quantum-sized FeS_2 particles extends both the absorption spectrum and photocurrent action spectrum into the visible region. Quantum size effects are clearly seen in the absorption and photocurrent action spectrum. Quantum-sized FeS_2 particles play a dominant role in the photoresponse of the electrode. Further work to improve efficiency is currently investigated.

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