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A three-dimensional electrode for photoelectrochemical cell: TiO_2 coated ITO mesoporous film

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ABSTRACT

In this letter, TiO_2 coated ITO mesoporous film was prepared by dipping doctor-blade ITO mesoporous film in TiO_2 sol, followed by sintering at 500 °C for 30 min. The CdS quantum dots (QDs) were deposited on TiO_2 coated ITO mesoporous film using sequential chemical bath deposition (S-CBD) method to form a three-dimensional (3D) electrode. The photo-activity of ITO mesoporous film/TiO_2/CdS electrode was investigated by forming a photoelectrochemical cell, which indicated that the ITO mesoporous film/TiO_2/CdS electrode was efficient in photoelectrochemical cell as a working electrode. The 3D electrode showed lower performance than the conventional electrode of TiO_2 mesoporous film/CdS, and more works are needed to improve the performance of 3D electrode.

1. Introduction

Since the efficiency as high as 7.1% was first reported by Grätzel and O'Regan in 1991 [1], dye-sensitized solar cell (DSSC), a typical kind of photoelectrochemical cell (PEC), has attracted significant attention because of their high efficiency and relatively inexpensive fabrication procedure compared with conventional silicon-based solar cells [2–4]. Fig. 1A shows the nanostructure and basic operation of the conventional electrode of PEC. In this electrode structure, light is absorbed by the sensitizers coated on the surface of TiO_2 nanoparticles, with photo-excited electron transfer from the sensitizers' excited states into the conduction band (CB) of TiO_2. The electrons are subsequently transferred to the conducting substrate by diffusing through the mesoporous network of TiO_2 nanoparticles. Until now, the conversion efficiencies of PEC have reached over 11% with ruthenium complex as sensitizers [5,6]. However, the highest reported efficiency of DSSC is still far lower than the maximum theoretical value efficiency (31%) [7]. One of the most important reasons for limit in efficiency is the low efficiency of electron transport in TiO_2 mesoporous film, which results in mass electron recombination losses (process 4 and 5 in Fig. 1A) [3,4,7].

In order to achieve higher efficiency of PEC, it is necessary to increase the efficiency of electron transport in TiO_2 mesoporous film to decrease electron recombination losses [3,4]. And thus, one-dimensional nanostructures have emerged as a promising electrode structure for high performance PEC, due to their fast electron transport property [7]. Recently, some researchers proposed that high electron transport rate and improved PEC performance could be achieved by reconfiguring the electrode into 3D architecture one, using conducting substrate with 3D architecture coated with thin TiO_2 active oxide layer [3,4,8], as shown in Fig. 1(B). In the 3D electrode, electrons injected into TiO_2 only need to transport a short length to a conducting substrate, and as a result, the efficiency of electron transport in the electrode is increased. Herein, we made an attempt to prepare a 3D electrode based ITO mesoporous film prepared by doctor-blade technique. Thin TiO_2 active oxide layer was deposited on the surface of ITO mesoporous film by dipping ITO mesoporous film in TiO_2 sol, followed by sintering at 500 °C. CdS QDs as sensitizers were synthesized on TiO_2 coated ITO mesoporous film by S-CBD method [9]. The photoelectrochemical property of ITO mesoporous film/TiO_2/CdS electrode was investigated by forming a photoelectrochemical cell and the performance of the 3D electrode and conventional electrode of TiO_2 mesoporous film/CdS was also compared.

2. Experimental

2.1. Preparation

ITO nanoparticles were synthesized by adding 2 M $NH_4 \cdot OH$ into the solution of 25.5 g/L $InCl_3 \cdot 4H_2O$, 3.1 g/L $SnCl_4 \cdot 5H_2O$ and 3.3 g/L $(NH_4)_2SO_4$ to adjust the pH to 7 at 60 °C while stirring vigorously. Then the indium tin hydroxide suspension was aged at 60 °C for 2 h to get the complete ITO precipitation. The resulting ITO precipitation was washed with deionized (DI) water and then ethanol and dried at 100 °C for 3 h, followed by sintering at 800 °C for 2 h in air atmosphere.

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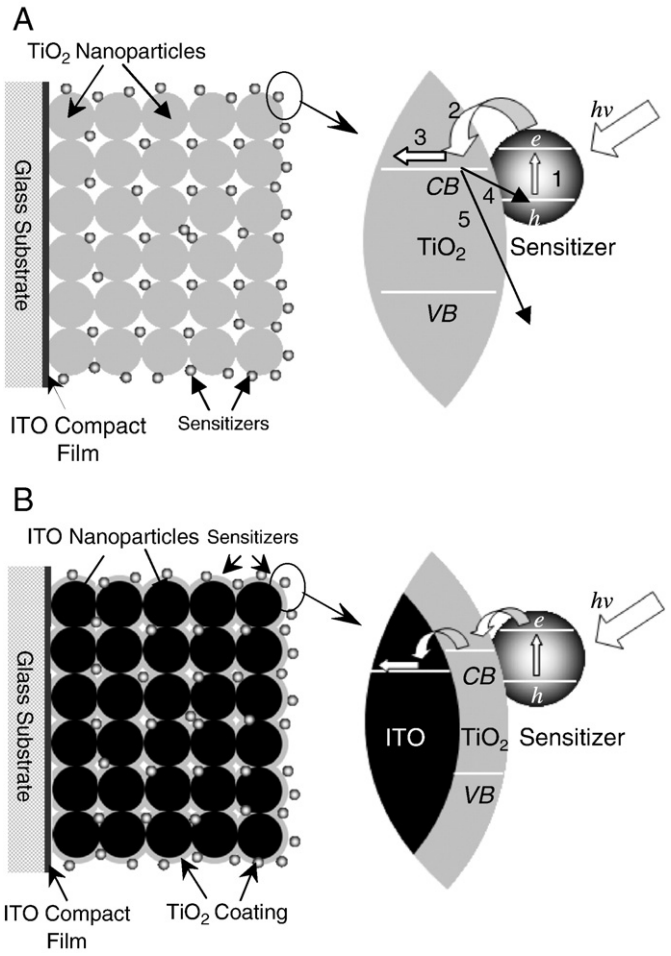

Fig. 1. Schematic of the nanostructure and basic operation of (A) conventional and (B) 3D electrode.

For the preparation of ITO mesoporous film, ITO nanoparticles were mixed with some surfactants such as acetylactone (AcAc), octylphenol ether (OP-10) and polyethylene glycol (PEG) by grinding until slurry was formed and doctor-blade technique was used to prepare ITO mesoporous film on cleaned indium tin oxide (ITO) glass substrates, followed by sintering at 500 °C for 30 min in air atmosphere. The same procedure was applied to prepare TiO_2 mesoporous film used for conventional electrode, which TiO_2 (Dugess P25) nanoparticles were purchased from Solaronix.

The composition of the TiO_2 sol used for coating was butyl titanate: $EtOH:H_2O:HNO_3$:AcAc = 1:30:2:0.2:0.5. For preparing the electrode of ITO mesoporous film/TiO_2/CdS, the as-prepared ITO mesoporous film was dipped in TiO_2 sol and kept for some time, and then drove out at the speed of 3 cm/min. After being dried at 100 °C for 15 min, the TiO_2 sol coated ITO mesoporous film was sintered at 500 °C for 30 min.

Finally, sequential chemical bath deposition (S-CBD) method was used to deposit CdS QDs on TiO_2 coated ITO mesoporous film and TiO_2 mesoporous film [9].

2.2. Characterization

A field-emission gun scanning electron microscope (SEM, 6700F) was used to characterize the morphology of the samples. Transmission electron microscope (TEM, JEM-2100F) with an energy dispersive X-ray (EDX) spectroscopy system was used to evaluate transmission electron microscopy images and composition of the samples. The photo-activity of electrode was studied by forming a two-electrode PEC with platinum foil as a counter electrode and the electrolyte used was 1 M Na_2S. A xenon lamp (500 W) with an illumination intensity of 100 mW/cm^2 and wavelength range from 380 nm to 700 nm was used as a light source and a CHI 600A electrochemical analyzer was employed to measure the current and voltage obtained from an illuminated area of 0.5 cm × 0.5 cm.

3. Results and discussion

The surface morphology of electrode was examined using the SEM. The SEM images shown in Fig. 2 reveal the ITO mesoporous film/TiO_2/CdS electrode at different stages of preparation. Fig. 2A is the morphology of the ITO mesoporous film prepared by doctor-blade technique, showing a highly porous structure because of the use of the polymer templates which decomposed, evaporated away and left large cavities during heat treatment process. The morphology of TiO_2 coated ITO mesoporous film is presented in Fig. 2B. It can be readily observed that the morphology of TiO_2 coated ITO mesoporous film

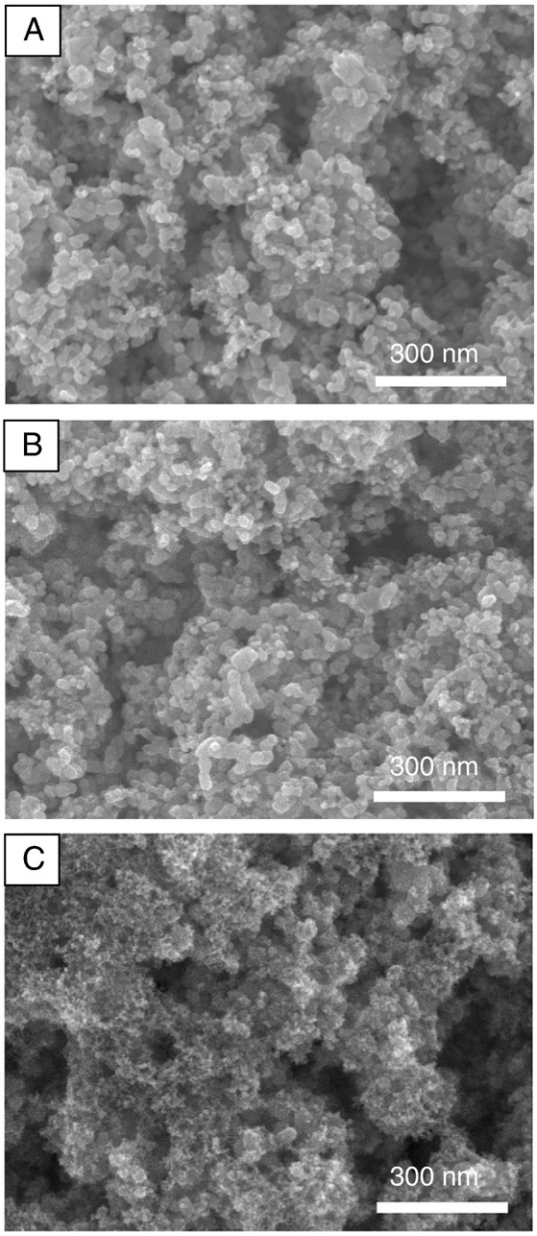

Fig. 2. SEM images of (A) ITO mesoporous film, (B) TiO_2 coated ITO mesoporous film and (C) ITO mesoporous film/TiO_2/CdS electrode.

shows almost nothing different from the ITO mesoporous film, which indicates that the TiO_2 coating on the ITO mesoporous film is ultrathin. S-CBD method was used to deposit CdS QDs on TiO_2 coated ITO mesoporous film to function as an electrode, and the surface morphology is shown in Fig. 2C. Compared with Fig. 2B, it can be seen that the TiO_2 coated ITO mesoporous film is obviously coated with CdS QDs and the pore size of porous network decreases.

To further determine whether TiO_2 and CdS have been deposited on ITO nanoparticles through the mesoporous network of ITO mesoporous film, transmission electron microscope (TEM) with an energy dispersive X-ray (EDX) spectroscopy system was used to evaluate the ITO mesoporous film/TiO_2/CdS electrode. Following the electrode fabrication, the film was removed from the ITO glass substrate, powdered and then deposited on TEM copper grid. The resulting HRTEM image and EDX pattern are shown in Fig. 3. Fig. 3A is the HRTEM image of ITO mesoporous film/TiO_2/CdS electrode. The observed lattice spacing of 0.292 nm and 0.179 nm corresponds to the (222) and (440) planes, respectively, of the cubic phase of In_2O_3 (JPCDS 88-2160), while the 0.352 nm and 0.336 nm correspond to the planes of anatase TiO_2 (JPCDS 84-1285) and cubic CdS (JPCDS 80-0019) respectively. Fig. 3B is the EDX pattern, which shows the peaks of O, In, Sn, Ti, Cd and S. Both the HRTEM image and EDX pattern confirm that the electrode is composed of ITO, TiO_2 and CdS.

In order to demonstrate the potential use of the electrode based on TiO_2 coated ITO mesoporous film, the photo-activity of ITO mesoporous film/TiO_2/CdS electrode was studied by forming a two-electrode photoelectrochemical cell. Fig. 4A is the experimental current–voltage (I–V) characteristics measured from ITO mesoporous film/TiO_2/CdS electrode. For I–V measurement, the 0.25 cm^2 area of ITO mesoporous film/TiO_2/CdS electrode was exposed to light illumination. Without light illumination, almost no short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) are observed, while the J_{sc} of 0.26 mA/cm^2 and V_{oc} of 0.225 V are achieved under light illumination with intensity of 100 mW/cm^2 and wavelength range from 380 nm to 700 nm. Here, we believe that excited electrons in CdS can inject into TiO_2 and hence ITO mesoporous film. And it can be explained by the energy levels of components of the ITO mesoporous film/TiO_2/CdS electrode, as shown in Fig. 4B. Because the conduction band (CB) level of CdS (−3.98 eV) lies above the CB level of TiO_2 (−4.21 eV) and the CB level of TiO_2 is higher than the work function level of ITO (−4.70 eV) [7,10–12], the electron injection from the CB of CdS to the CB of TiO_2 and finally to ITO mesoporous film was thermodynamically permitted. The I–V curve of the conventional electrode of TiO_2 mesoporous film/CdS under light illumination is also presented in Fig. 4A and its performance is higher than the 3D electrode of ITO mesoporous film/TiO_2/CdS. It can be explained that the high resistance of 3D electrode induced by more than one heat treatment will decrease the electron transport rate; the not completed cover of TiO_2 sol–gel film on ITO mesoporous film by dip coating method will lead to much recombination losses of the electrons injected into ITO mesoporous film; and too small quantity of TiO_2 on ITO mesoporous film will decrease the driving force of photo-excited electrons from CdS to TiO_2 and finally the ITO mesoporous film. Thus, a suitable preparation procedure of ITO mesoporous film, exploring a novel TiO_2 coating method and optimizing the quantity of TiO_2 on ITO mesoporous film are needed to improve the performance of 3D electrode. More works are being undertaken to achieve this.

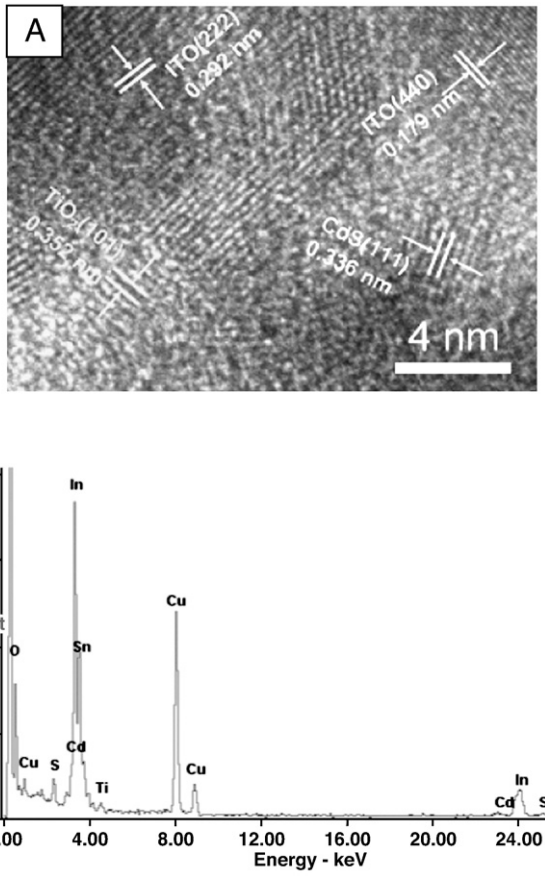

Fig. 3. Characterization of the ITO mesoporous film/TiO_2/CdS electrode: (A) HRTEM image and (B) EDX spectra. Cu signals were generated from the copper grid used in the EDX/HRTEM measurement.

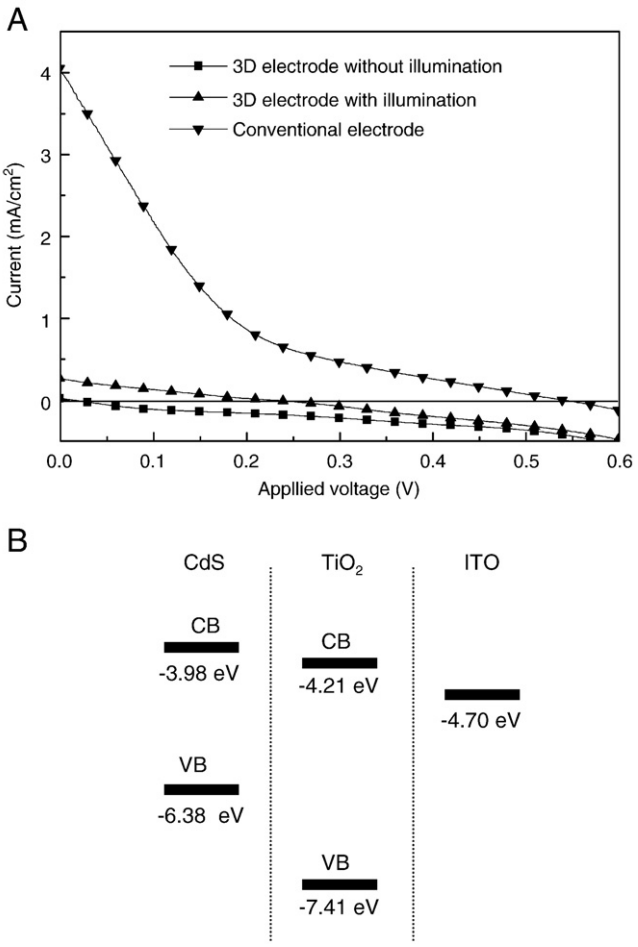

Fig. 4. (A) Current–voltage (I–V) curves of 3D and conventional electrode. (B) Energy levels of components of the ITO mesoporous film/TiO_2/CdS electrode.

4. Conclusions

A 3D electrode based on TiO_2 coated ITO mesoporous film has been successfully developed with CdS QDs as sensitizers. The photo-activity of ITO mesoporous film/TiO_2/CdS electrode was investigated by forming a photoelectrochemical cell and the ITO mesoporous film/TiO_2/CdS electrode as a working electrode was efficient under light illumination. The 3D electrode showed lower performance than the conventional electrode, and more works are needed and being undertaken to improve the performance of the 3D electrode.

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