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# CdS/CdSe Co-sensitized Solar Cells Based on Hierarchically Structured SnO<sub>2</sub>/TiO<sub>2</sub> Hybrid Films

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## Abstract

SnO<sub>2</sub> nanosheet-structured films were prepared on a fluorine-doped tin oxide (FTO) substrate using ZnO nanosheet as template. The as-prepared SnO<sub>2</sub> nanosheets contained plenty of nano-voids and were generally vertical to the substrate. TiO<sub>2</sub> nanoparticles were homogeneously deposited into the intervals between the SnO<sub>2</sub> nanosheets to prepare a hierarchically structured SnO<sub>2</sub>/TiO<sub>2</sub> hybrid film. The hybrid films were co-sensitized with CdS and CdSe quantum dots. The sensitized solar cells assembled with the SnO<sub>2</sub>/TiO<sub>2</sub> hybrid film showed much higher photoelectricity conversion efficiency than the cells assembled with pure TiO<sub>2</sub> films. The lifetime of photoinduced electron was also investigated through electrochemical impedance spectroscopy, which showed that the SnO<sub>2</sub>/TiO<sub>2</sub> hybrid film electrode is as long as the TiO<sub>2</sub> film electrode.

**Keywords:** SnO<sub>2</sub> nanosheet, SnO<sub>2</sub>/TiO<sub>2</sub> hybrid films, Quantum dots, CdS, CdSe

## Background

In recent years, quantum dot (QD)-sensitized solar cells have attracted remarkable attention because of the multiple exciton generation characters. The theoretical energy conversion efficiency of QD-sensitized solar cells (QDSCs) was calculated to be about 44.4 % which is much higher than that of the organic dye-sensitized solar cells [1]. Many narrow bandgap semiconductor QDs, such as PbS, CdS, and CdSe, have been extensively used to sensitize TiO<sub>2</sub> photoanode [2–5]. Compared with TiO<sub>2</sub>, SnO<sub>2</sub> has many advantages. Firstly, the energy gap of SnO<sub>2</sub> is about 3.6 eV which may reduce the effect of UV light in the sunlight on the solar cell performance and improve their long-term stability [6]. Secondly, the electron mobility of SnO<sub>2</sub> is about 150 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> which is much higher than that of TiO<sub>2</sub> (1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) [7, 8]. Thirdly, SnO<sub>2</sub> films which are suitable for sensitized solar cells could be obtained without high temperature calcination [9, 10]. Therefore, some teams began to apply nanoporous SnO<sub>2</sub> as

photoanodes in QD-sensitized solar cells. Hossain et al. found that TiCl<sub>4</sub> treatment can significantly increase the open circuit photovoltage of CdSe QD-sensitized SnO<sub>2</sub> solar cells [11]. Then, they co-sensitized SnO<sub>2</sub> films with CdS and CdSe QDs and obtained much higher short circuit current ( $J_{SC}$ , 17.40 mA cm<sup>-2</sup>) than that of TiO<sub>2</sub> film based QD-sensitized solar cells [12]. Cánovas et al. studied the electron transfer processes from PbSe quantum dots to SnO<sub>2</sub> and found that the injection time of the photoexcited electron was vitally affected by the QD size [13]. Xiao et al. found that the shape of SnO<sub>2</sub> might affect the photovoltage of SnO<sub>2</sub>-based QDSCs. They applied highly ordered SnO<sub>2</sub> inverse opal films to QDSCs and obtained high open circuit voltage ( $V_{OC}$ , 700 mV) and high short circuit current (10.13 mA cm<sup>-2</sup>). The total photoelectric transfer efficiency was about 4.37 % [14].

Specific nanostructure of nanoparticles, such as nanorod, nanosheet, and nanowire, could bring some distinctive properties. Some teams had attempted to prepare SnO<sub>2</sub> nanosheets. Li Y et al. synthesized SnO<sub>2</sub> nanosheets by hydrothermal method from SnCl<sub>2</sub> and NaOH in ethanol/water solution [15]. Fei L et al. prepared SnO<sub>2</sub> nanosheets using graphite sheets as template [16]. Dong

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CJ et al. obtained Pt-functionalized SnO<sub>2</sub> nanosheets by a facial solution combustion method [17].

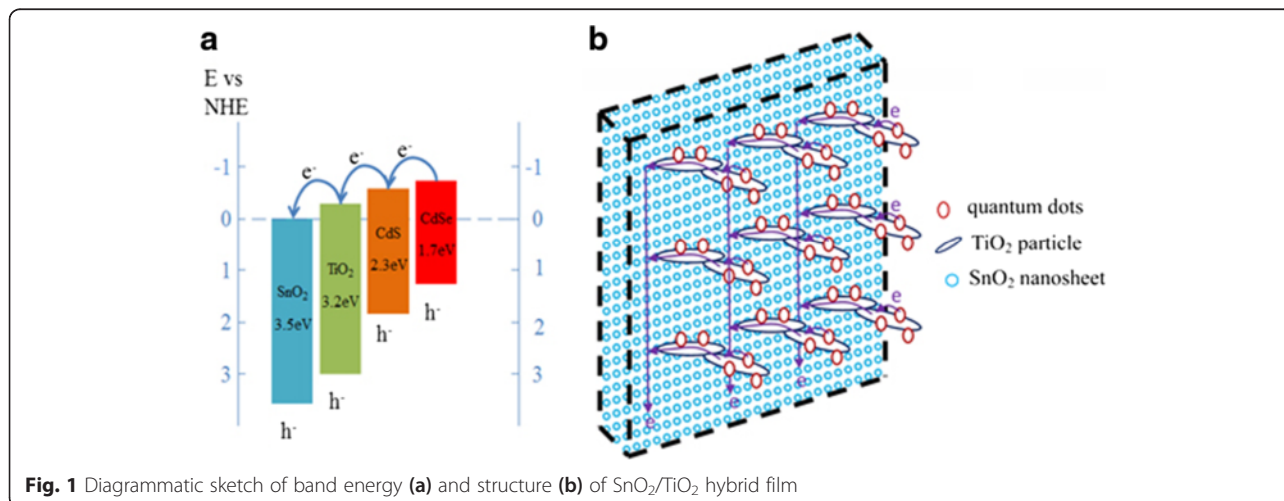
In this experiment, we prepared SnO<sub>2</sub> nanosheet-structured films using ZnO nanosheet as template. The as-prepared SnO<sub>2</sub> nanosheets contain plenty of nanovoids and are generally vertical to the substrate, which should provide an efficient collection path for the photo-induced electron. To obtain SnO<sub>2</sub>/TiO<sub>2</sub> composite films, TiO<sub>2</sub> nanoparticles were deposited on SnO<sub>2</sub> nanosheet through electrophoresis method. And these films were introduced into QDSCs. From the band energy structure of SnO<sub>2</sub> and TiO<sub>2</sub>, we can see that the electron can transfer from the conduction band of TiO<sub>2</sub> to that of SnO<sub>2</sub> shown in Fig. 1a. So the SnO<sub>2</sub>/TiO<sub>2</sub> composite films could combine the advantages of both SnO<sub>2</sub> nanosheet and TiO<sub>2</sub> particle. The photoexcited charges were separated efficiently on the surface of TiO<sub>2</sub> nanoparticles. Thereafter, photoinduced electron will be collected by SnO<sub>2</sub> nanosheets and transported to the fluorine-doped tin oxide (FTO) substrate fluently. The schematic diagram of these processes is shown in Fig. 1b.

## Methods

### Materials

Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), zinc acetate (Zn(CH<sub>2</sub>COO)<sub>2</sub>), ammonium hexafluorostannate ((NH<sub>4</sub>)<sub>2</sub>SnF<sub>6</sub>), boric acid (H<sub>3</sub>BO<sub>3</sub>), cadmium acetate (Cd(CH<sub>2</sub>COO)<sub>2</sub>), selenium powder (Se), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O), nitrilotriacetic acid trisodium salt (C<sub>6</sub>H<sub>8</sub>NNa<sub>3</sub>O<sub>7</sub>), copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), and sodium sulfide (Na<sub>2</sub>S) were all purchased from Sinopharm Chemical Reagent Co. (SCRC, China). Ethanol and methanol were purchased from Aladdin Reagent Co. (China) with a purity >99.9%. All of these materials were used as received without any further purification.

The electrodeposition of ZnO nanosheets was carried out in a simple three-electrode glass cell. The precursor solution (for ZnO deposition) consisted of 0.05 M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.1 M KCl. The working electrode was FTO glass substrates (10 × 10 mm). The reference electrode was Ag/AgCl electrode with saturation potassium chloride aqueous solution, and the counter electrode was Pt metal sheet. The distance between the working electrode and the counter electrode was about 3.5 cm. The deposition temperature was fixed at 70 °C by an oil bath. The deposition potential was controlled to be -1.1 V. The deposition time was controlled to be 30 min unless specially instructed. The deposited samples were cleaned with deionized water, dried at room temperature, and annealed at 450 °C for 30 min in the air atmosphere. The deposition time was controlled to be 30 min. For the formation of SnO<sub>2</sub> layer, the ZnO nanosheets were then immersed in a mixture of 3 mL 0.15 mol L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>SnF<sub>6</sub>, 1 mL 0.5 mol L<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>, and 1 mL deionized water [18]. The immersion time was 4 h to convert all ZnO nanosheets to SnO<sub>2</sub> nanosheets. The SnO<sub>2</sub> nanosheets were cleaned with deionized water, dried at room temperature, and sintered at 500 °C for 30 min under air atmosphere. Then, the SnO<sub>2</sub> nanosheet-structured films were immersed into 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C. The immersion time was controlled to be 40 min. The TiCl<sub>4</sub>-treated SnO<sub>2</sub> films were annealed at 500 °C for 30 min under air atmosphere. Then, commercial TiO<sub>2</sub> nanoparticles (P25) were deposited on the SnO<sub>2</sub> nanosheet through electrophoresis method in a colloid solution (0.5 g P25 dispersed in a mixture of 8 mL butanol, 4 mL isopropanol, and 2 mL ethanol). In the electrophoresis processes, an FTO glass (1 × 2 cm<sup>2</sup>, 15 Ω sq<sup>-1</sup>; OPV Tech) was used as the cathode and another FTO glass was used as the anode. The distance between the two electrodes was maintained at 1 cm, and the DC power supply was set at 48 V. The electrophoresis



**Fig. 1** Diagrammatic sketch of band energy (a) and structure (b) of SnO<sub>2</sub>/TiO<sub>2</sub> hybrid film

time is 10 s. The SnO<sub>2</sub>/TiO<sub>2</sub> hybrid films were sintered at 500 °C for 30 min.

### CdS/CdSe Co-sensitized Photoanodes and Solar Cell Device Fabrication

CdS and CdSe quantum dots were deposited on these nanoporous films (pure SnO<sub>2</sub> film, TiCl<sub>4</sub>-treated SnO<sub>2</sub> film, SnO<sub>2</sub>/TiO<sub>2</sub> hybrid film, or pure TiO<sub>2</sub> film) in sequence. The deposition process was summarized as follows. Firstly, the nanoporous films were sensitized with CdS quantum dots by successive ionic layer adsorption and reaction (SILAR) method. The deposition process was summarized as follows: (i) The pure ZnO and ZnO/TiO<sub>2</sub> composite samples were firstly dipped in the 0.1 M Cd(NO<sub>3</sub>)<sub>2</sub> ethanol solution for 1 min, then rinsed with ethanol for 1 min, followed by dipping in the 0.1 M methanol solution for 1 min and then rinsing with methanol for 1 min. (ii) The former processes were repeated 14 times in order to grow sufficient amount of CdS QDs on the films. Secondly, the CdS-sensitized films were immersed in a mixture of aqueous solution, 0.2 mol L<sup>-1</sup> Na<sub>2</sub>SeSO<sub>3</sub>, 0.16 mol L<sup>-1</sup> C<sub>6</sub>H<sub>8</sub>NNa<sub>3</sub>O<sub>7</sub>(NTA-3Na), and 0.08 mol L<sup>-1</sup> Cd(CH<sub>2</sub>COO)<sub>2</sub> (V:V:V = 1:1:1), for 4 h. Thirdly, the CdS/CdSe co-sensitized films were passivated with ZnS by immersion into 0.1 mol L<sup>-1</sup> Zn(CH<sub>2</sub>COO)<sub>2</sub> and 0.1 mol L<sup>-1</sup> Na<sub>2</sub>S aqueous solution in sequence. For QDSCs fabrication, CuS counter electrodes were prepared according to the reported literature [19]. The polysulfide aqueous solution of 1 mol L<sup>-1</sup> Na<sub>2</sub>S, 1 mol L<sup>-1</sup> S, and 0.1 mol L<sup>-1</sup> NaOH was used as the QDSCs electrolyte.

### Measurement and Characterization

The crystalline phase of the samples was characterized by DX-2700 X-ray diffractometer (XRD) with a monochromatized CuK irradiation ( $k = 0.154145$  nm). The morphology was studied using JSM-7001F field emission scanning electron microscope (FE-SEM). Energy dispersive spectroscopy analysis (EDS) was obtained from Bruker-ASX (Model Quan-Tax 200).

The assembled QDSCs were tested under simulated sunlight (AM 1.5G illumination) from a Newport Oriel Solar Simulator (model 94043A, Oriel) using Keithley 2440 Source Meter. The light intensity was calibrated with a standard Si solar cell provided by Newport Oriel. The active cell area of the testing QDSCs was 0.25 cm<sup>2</sup>. The monochromatic incident photon-to-electron conversion efficiency (IPCE) was measured using an IPCE system (QS 500ADX, Crowntech, Inc.). The testing ranged from 300 to 800 nm. A 150-W tungsten halogen lamp was used as the light source to generate a monochromatic beam. A silicon solar cell was used as the reference during the IPCE measurement. An electrochemistry workstation (IM6) was used to investigate the electrochemical

impedance spectra (EIS) of QDSCs. This measurement was also carried out with the same structured QDSCs as that used in the former experiments. The impedance measurement of QDSCs was recorded under dark condition at the bias potential of -0.6 V over a frequency range of 0.1–1 MHz with an AC amplitude of 10 mV.

### Results and Discussion

ZnO nanosheet-structured film was firstly electrodeposited on FTO substrate. Then, the ZnO nanosheet-structured film was immersed in (NH<sub>4</sub>)<sub>2</sub>SnF<sub>6</sub> aqueous solution. The SnF<sub>6</sub><sup>2-</sup> ions in the solution will hydrolyze and form SnO<sub>2</sub> nanoparticles on the surface of ZnO nanosheets following Eq. 1. The generated F<sup>-</sup> ion in Eq. 1 could be trapped by boric acid as described in Eq. 2. The H<sup>+</sup> in HBF<sub>4</sub> would dissolve ZnO into the solution. If the immersion time was long enough, all the ZnO nanosheets on the FTO substrate might be totally dissolved into the solution. As a result, pure SnO<sub>2</sub> nanoporous nanosheet film was prepared. The chemical reactions in the treatment process might proceed with the following mechanisms [18]:

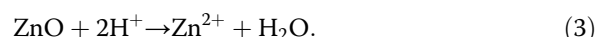
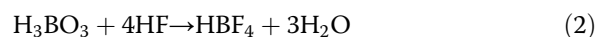
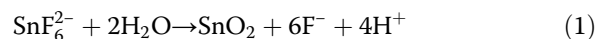
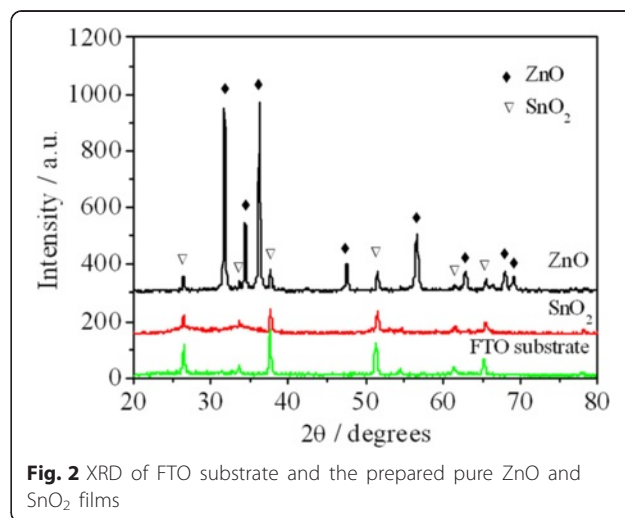


Figure 2 shows the XRD patterns for the pure ZnO films before and after 4 h immersion in the (NH<sub>4</sub>)<sub>2</sub>SnF<sub>6</sub> aqueous solution. Before the treatment of (NH<sub>4</sub>)<sub>2</sub>SnF<sub>6</sub> aqueous solution, there is a series of narrow peaks at 31.76°, 34.4°, 36.24°, 47.56°, and 56.6° in the X-ray diffraction spectra. These peaks indicate the growth of wurtzite-structured ZnO (hexagonal phase, space group



**Fig. 2** XRD of FTO substrate and the prepared pure ZnO and SnO<sub>2</sub> films

P63mc) (JCPDS database card no. 36-1451). Other peaks are all in accordance with the diffraction peaks of the FTO substrate. After 4 h of immersion in the  $(\text{NH}_4)_2\text{SnF}_6$  aqueous solution, no diffraction peaks of ZnO can be found in the spectrum which indicates that all ZnO nanosheets have been dissolved into the solution. The ultimate sample consists of pure  $\text{SnO}_2$ .

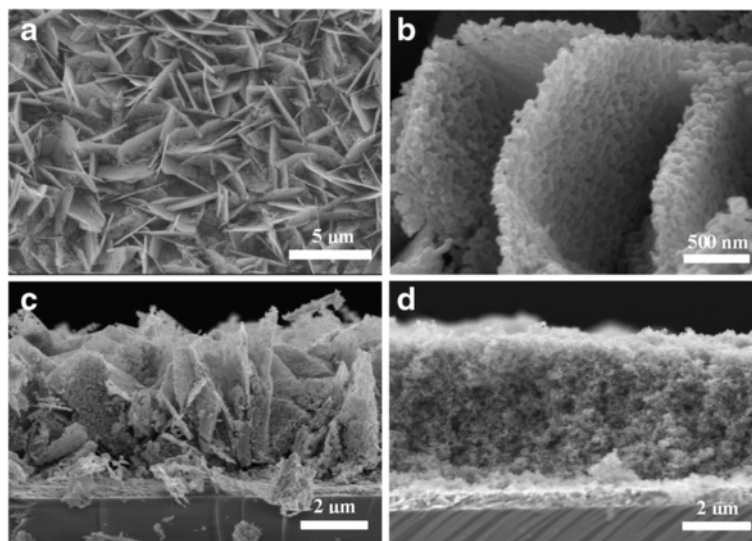
Figure 3a–c shows the top view and cross section of the prepared pure  $\text{SnO}_2$  nanosheet film. The as-prepared  $\text{SnO}_2$  films are not as regular as ZnO films, but it maintains the nanosheet structure. And the  $\text{SnO}_2$  sheets are also generally vertical to the substrate. The microstructure of the  $\text{SnO}_2$  nanosheet is much different from that of ZnO. There are plenty of homogeneous nano-voids distributed between  $\text{SnO}_2$  nanoparticles. These nano-voids are suitable for the deposition of  $\text{TiO}_2$  nanoparticles and quantum dots. The thickness of the film is about 6  $\mu\text{m}$ .

The conduction band edge of  $\text{SnO}_2$  is 0.4 V (versus the standard hydrogen electrode (SHE)) which is more positive than that of  $\text{TiO}_2$ . Photoexcited electrons in the conduction band of  $\text{SnO}_2$  undergo serious back reactions [20]. Coating  $\text{SnO}_2$  with thin layers of  $\text{TiO}_2$  is an efficient way to inhibit these back reactions. So the as-prepared  $\text{SnO}_2$  sheet films were treated in 40 mM  $\text{TiCl}_4$  aqueous solution at 70 °C for 40 min for the covering of a passivation layer of  $\text{TiO}_2$ . Then, commercial  $\text{TiO}_2$  nanoparticles (P25) were deposited on the  $\text{SnO}_2$  sheets through electrophoretic method. Figure 3d shows the cross section of the  $\text{TiO}_2$  nanoparticle-covered  $\text{SnO}_2$  film. It can be seen that  $\text{TiO}_2$  nanoparticles were homogeneously filled in the intervals between  $\text{SnO}_2$  nanosheets. From the cross section of  $\text{SnO}_2/\text{TiO}_2$  hybrid film, the  $\text{SnO}_2$  nanosheets become so distinct that we can almost not find them. This change of  $\text{SnO}_2$  might

be caused by the mild dissolution of  $\text{SnO}_2$  in  $\text{TiCl}_4$  treatment. And the  $\text{TiO}_2$  nanoparticles were efficiently coated on  $\text{SnO}_2$  skeleton.

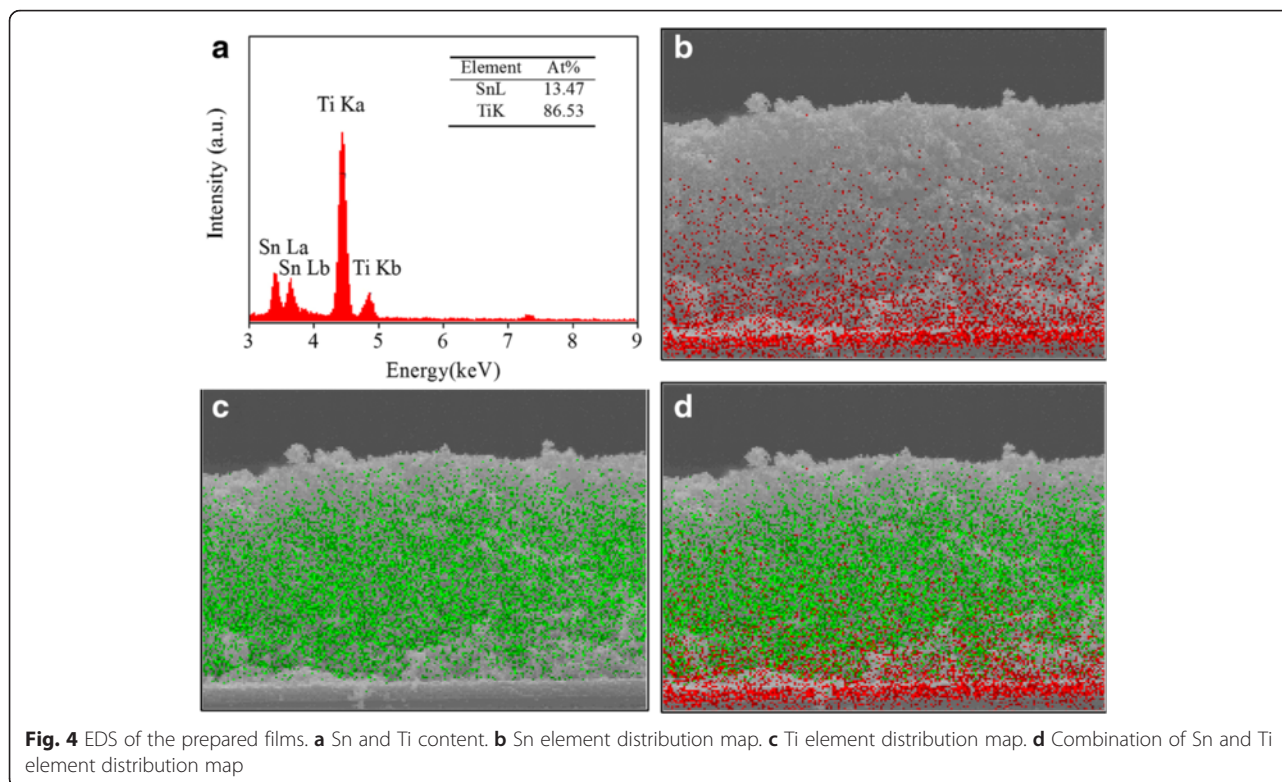
X-ray EDS was carried out to confirm the final composition of the  $\text{SnO}_2/\text{TiO}_2$  hybrid film. The EDS spectra are shown in Fig. 4. The peaks at about 3.4, 3.6, 4.44, and 4.82 KeV should correspond to Sn(La), Sn(Lb), Ti(Ka), and Ti(Kb), respectively. The composition analysis revealed that the ratio between Sn and Ti was about 13.5:86.5. The element distribution diagrams are also given in Fig. 4b–d. It can be seen that Sn element exists throughout the whole films. At the bottom of the film, there is a gathering of Sn element which should be attributed to the F-coated  $\text{SnO}_2$  layer on the glass substrate. The Ti element was homogeneously filled in the  $\text{SnO}_2$  frameworks.

To investigate the effects of  $\text{TiCl}_4$  treatment and coverage of  $\text{TiO}_2$  nanoparticles on the photovoltaic characteristics of the  $\text{SnO}_2$  films, these nanoporous films (pure  $\text{SnO}_2$  film,  $\text{TiCl}_4$ -treated  $\text{SnO}_2$  film,  $\text{SnO}_2/\text{TiO}_2$  hybrid film, or pure  $\text{TiO}_2$  nanoparticle film) were all co-sensitized with CdS and CdSe quantum dots. They were assembled with CuS counter electrodes, separately, to form a complete QDSC. The  $J$ - $V$  curves of the former assembled QDSCs are shown in Fig. 5. The pure  $\text{SnO}_2$  nanosheets film shows poor photovoltaic characteristics. After  $\text{TiCl}_4$  treatment, the  $J_{\text{SC}}$  and  $V_{\text{OC}}$  increased from 2.9  $\text{mA cm}^{-2}$  and 25 mV to 7.7  $\text{mA cm}^{-2}$  and 161 mV, respectively. These characteristic parameters are significantly improved because the recombination reaction at the surface of  $\text{SnO}_2$  nanosheet was restricted by the treatment of  $\text{TiCl}_4$ . However, the  $\text{TiO}_2$  layer might not be enough to get rid of the back reaction on  $\text{SnO}_2$  nanosheet film. The reason for the low photocurrent might



**Fig. 3** SEM of the prepared films. **a, b** Top view of pure  $\text{SnO}_2$  film. **c** Cross section of pure  $\text{SnO}_2$  film. **d** Cross section of  $\text{SnO}_2/\text{TiO}_2$  hybrid film

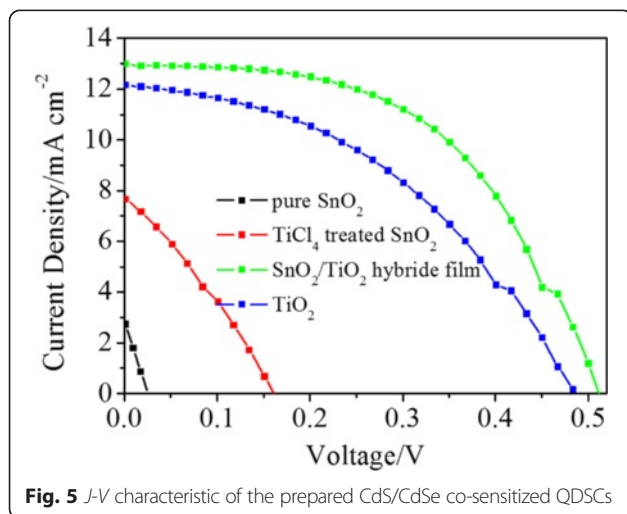




be attributed to the low quantity of QDs on the photoelectrode. The specific surface area is a major factor affecting the loading of QDs. Those are also the reasons why the characteristic parameters are lower than that of the former reports [11–13]. To solve this problem, commercial  $\text{TiO}_2$  nanoparticles (P25) were deposited on the  $\text{SnO}_2$  nanosheet films. From Fig. 4, it can be seen that the photoelectric conversion properties of the photoanode are significantly improved. The  $J_{SC}$ ,  $V_{OC}$ , and fill factor ( $FF$ ) are about  $13.0 \text{ mA cm}^{-2}$ ,  $514 \text{ mV}$ , and  $52.2 \%$ , respectively. The total photoelectric conversion

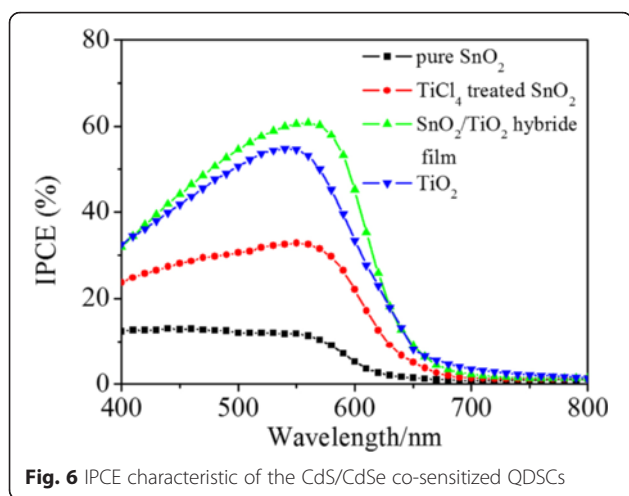
efficiency ( $\eta$ ) is about  $3.49 \%$ . There might be two reasons for the improvement of the photoelectric properties after the deposition of commercial  $\text{TiO}_2$  nanoparticles (P25). One is the significant improvement of the specific surface area, the film electrode. The other reason is that the deposition of commercial  $\text{TiO}_2$  nanoparticles (P25) further isolated  $\text{SnO}_2$  from QDs and electrolyte, which further restricted the recombination of the photoexcited electron in the  $\text{SnO}_2$  conductive band. As a reference, pure  $\text{TiO}_2$  nanoparticles were also directly deposited on the FTO substrate under the same electrophoretic time as that used in the former experiments. The photoelectric conversion efficiency is about  $2.51 \%$  which is much lower than that of QDSCs assembled with  $\text{SnO}_2/\text{TiO}_2$  hybrid films. All the characteristic parameters are shown in Table 1.

Figure 6 shows the IPCE spectra of QDSCs assembled with these different photoanodes. IPCE spectra reflect the light response of photovoltaic devices at different

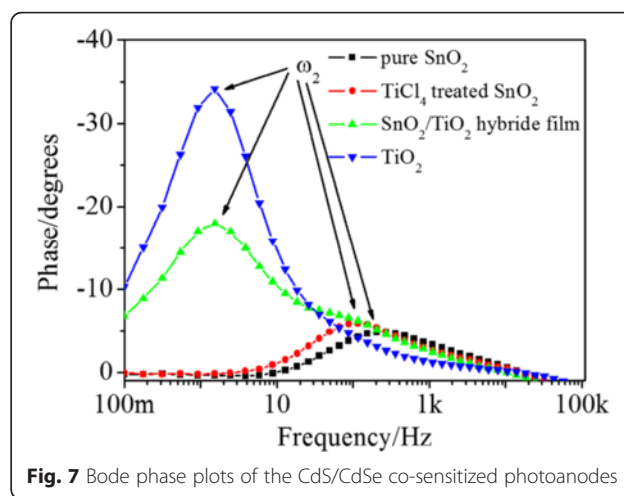


**Table 1** Detailed photovoltaic parameters of the QDSCs obtained from Fig. 5

Photoanodes	$V_{OC}$ (mV)	$J_{SC}$ ( $\text{mA cm}^{-2}$ )	FFP (%)	Efficiency (%)
$\text{SnO}_2$	25	2.9	23.8	0.02
$\text{SnO}_2 + \text{TiCl}_4$	161	7.7	29.7	0.37
$\text{SnO}_2 + \text{TiCl}_4 + \text{P25}$	514	13.0	52.2	3.49
P25	488	12.2	42.0	2.51



**Fig. 6** IPCE characteristic of the CdS/CdSe co-sensitized QDSCs



**Fig. 7** Bode phase plots of the CdS/CdSe co-sensitized photoanodes

light wavelengths, which is directly related to photocurrent density and can be calculated from Eq. 4.

$$\text{IPCE (\%)} = 1240J_{\text{SC}}/(\lambda P_{\text{in}}), \quad (4)$$

where  $J_{\text{SC}}$  is the short circuit photocurrent density at a single wavelength,  $\lambda$  is the wavelength of the incident light, and  $P_{\text{in}}$  is the power of the incident light. The light absorbed by the photoanodes ranged from 400 nm to about 700 nm which is in accordance with the absorption range of CdS and CdSe. Comparing the curves obtained by different photoanodes, it can be seen that  $\text{TiCl}_4$  treatment and  $\text{TiO}_2$  nanoparticle coverage dramatically enhanced the IPCE values during the 400–700 nm, which is in accordance with the results of  $J$ - $V$  curves.

Electrochemical impedance spectroscopy (EIS) is an efficient method to investigate the recombination process of the photoexcited electrons. EIS was carried out on  $\text{SnO}_2$ ,  $\text{TiCl}_4$ -treated  $\text{SnO}_2$ ,  $\text{SnO}_2/\text{TiO}_2$  hybrid film, and  $\text{TiO}_2$  film photo-electrodes under dark condition. A bias potential,  $-0.6$  V, was applied in the testing process. Figure 7 shows the Bode phase plots of the QDSCs assembled with  $\text{SnO}_2$ ,  $\text{TiCl}_4$ -treated  $\text{SnO}_2$ ,  $\text{SnO}_2/\text{TiO}_2$  hybrid film, and  $\text{TiO}_2$  film. According to the previous work, there should be an electrochemical process ( $\omega_1$ ) at high frequency ( $10^3$ – $10^5$  Hz) to correspond to the charge-transfer processes occurring at the counter electrode/electrolyte interface [21]. But it is not obvious in this experiment. However, there is an obvious electrochemical reaction process at the frequency range from about 1 to  $10^3$  Hz which was marked as  $\omega_2$ . This process corresponds to the charge-transfer processes occurring at the  $\text{SnO}_2$  ( $\text{TiCl}_4$ -treated  $\text{SnO}_2$  film,  $\text{SnO}_2/\text{TiO}_2$  hybrid film, or P25 film)/electrolyte (or QD) interface [21]. The characteristic frequency of  $\omega_2$  may reflect the electron lifetimes ( $\tau_e$ ) of the injected electrons [22]. The lifetimes ( $\tau_e$ ) of the photoexcited

electron in the photoanodes were determined using the following equation (Eq. 5):

$$\tau_e = \frac{1}{2\pi f_{\text{max}}}. \quad (5)$$

The characteristic frequency of these photoanodes,  $\text{SnO}_2$ ,  $\text{TiCl}_4$ -treated  $\text{SnO}_2$ ,  $\text{SnO}_2/\text{TiO}_2$  hybrid film, and pure  $\text{TiO}_2$  film, were 202.7, 115.4, 1.5, and 1.5 Hz, respectively. According to Eq. 5, the electron lifetimes ( $\tau_e$ ) were calculated to be about 0.8, 1.4, and 106.2 ms for the  $\text{SnO}_2$ ,  $\text{TiCl}_4$ -treated  $\text{SnO}_2$ ,  $\text{SnO}_2/\text{TiO}_2$  hybrid film, and  $\text{TiO}_2$  electrodes, respectively. It can be seen that  $\text{TiCl}_4$  treatment exactly inhibited the recombination reaction of  $\text{SnO}_2$  nanosheet electrode. But the effects of  $\text{TiCl}_4$  treatment are very finite. After the coverage of  $\text{TiO}_2$ , the electron lifetime was lengthened by two orders to the same value as that of the pure  $\text{TiO}_2$  photoanode. It can be seen that the  $\text{SnO}_2/\text{TiO}_2$  hybrid electrode might combine the advantages of both  $\text{SnO}_2$  nanosheet and  $\text{TiO}_2$  nanoparticle. This result is in accordance with the  $J$ - $V$  curves.

## Conclusions

$\text{SnO}_2$  nanosheet-structured films were prepared using ZnO nanosheet as template. The as-prepared  $\text{SnO}_2$  nanosheets contained plenty of nano-voids and were generally vertical to the substrate.  $\text{TiO}_2$  nanoparticles were homogeneously deposited into the intervals between  $\text{SnO}_2$  nanosheets to prepare hierarchically structured  $\text{SnO}_2/\text{TiO}_2$  hybrid film. The hybrid films were co-sensitized with CdS and CdSe quantum dots. The photoinduced electron showed the same lifetimes in this  $\text{SnO}_2/\text{TiO}_2$  hybrid film as that in the pure  $\text{TiO}_2$  particles films. But the  $\text{SnO}_2/\text{TiO}_2$  hybrid film photoanode had higher IPCE than pure  $\text{TiO}_2$  nanoparticle photoanode. The total photoelectric conversion efficiency was about 3.49 %.

**Competing Interests**

The authors declare that they have no competing interests.

**Authors' contributions**

ZC and CCW carried out the experiment. WL, WPK, CLD, and ZLZ analyzed the data and finished the figures of the manuscript. SJL and WFZ modified the manuscript. All authors read and approved the final manuscript.

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