

## Fabrication and Photoelectric Properties of CdTe/TiO<sub>2</sub> Nanocrystals Multilayer

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**Abstract.** In this paper, we report the fabrication and photoelectric properties of CdTe/TiO<sub>2</sub> nanocrystal multilayer. Negatively charged CdTe nanocrystal hydrosols were synthesized in the aqueous phase with 3-mercaptopropionic acid as a surface modifier. The characterization of transmission electron microscopy (TEM) and UV-visible absorption spectrum indicates the resultant CdTe nanocrystal hydrosols are monodisperse and have a very narrow size distribution with a mean diameter of about 5 nm. Clear TiO<sub>2</sub> aqueous colloidal nanocrystals with positive surface charges were prepared by using tetrabutyl titanate as precursor. Through the electrostatic interaction between the positive surface charges on TiO<sub>2</sub> nanocrystals and those on CdTe nanocrystal hydrosols, multilayer of CdTe/TiO<sub>2</sub> nanocrystals were fabricated on the pretreated quartz substrate by layer-by-layer electrostatic self-assembly method. UV-Vis absorption spectrum and atomic force microscopy (AFM) were used to characterize the as-prepared CdTe/TiO<sub>2</sub> multilayer. The results show that the surface of the CdTe/TiO<sub>2</sub> multilayer are flat and the adsorption intensity in UV-Vis spectrum increases with the layer numbers of the CdTe/TiO<sub>2</sub> complex, indicating that CdTe/TiO<sub>2</sub> multilayer could be fabricated successfully on the surface of quartz glass and the resultant multilayer have good quality. In the same way, CdTe/TiO<sub>2</sub> multilayer were fabricated on the surface of Indium Tin Oxides (ITO) substrate disposed by the poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). The CdTe/TiO<sub>2</sub> complex is measured under AM1.5G simulated solar illumination with 100mWcm<sup>-2</sup> in air. The results show the maximum open circuit current density (Voc) and short circuit current density (Isc) of CdTe/TiO<sub>2</sub> complex on ITO substrate is 0.45V and 0.050mA, which were better than TiO<sub>2</sub> or CdTe nanocrystal hydrosols individual due to the interfacial hole-electron converter between the adjacent layers of CdTe and TiO<sub>2</sub> nanocrystals.

### Introduction

Energy shortage has become a serious problem in 21 century. Exploiting high efficient, low-cost, non-polluted and reproducible energy is important for human to settle this problem. In this process, inorganic semiconductor photoelectric materials used in solar cells have attracted more and more attention due to its low cost and simple preparation method. The electrostatic layer-by-layer self-assembly technology, based on alternate adsorption of opposite charged components, has been developed to coat nanoscaled films on any surface<sup>[1-3]</sup>. It provides an effective way for controlling the molecular orientations and packing at the molecular level<sup>[4]</sup>. In addition, the morphology and thickness of film can be controlled. Multilayer complex films like polymer/polymer, polymer/metal colloid particles, polymer/inorganic nano particles and inorganic nano particles/inorganic nano particles have been fabricated by using this self-assembly method<sup>[5]</sup>. Due to the as-prepared multilayer possessing many unique properties different from those of the bulk materials such as optical, electric, magnetic, acoustic, and thermal properties, electrostatic self-assembly techniques offers substantial advantages over traditional manufacturing approaches in the fabrication of functional nanoscaled films or complex films<sup>[6-8]</sup>.

CdTe semiconductor nanocrystals have a narrow forbidden band (1.47eV) and high photoelectric transformation efficiency and TiO<sub>2</sub> semiconductor nanocrystals are easily prepared, non-toxicity

and stable. However, the chemical property of pure CdTe nanocrystal hydrosol is instable<sup>[9]</sup> and the forbidden band of TiO<sub>2</sub> is wide (3.2eV). What's more, TiO<sub>2</sub> only absorbs ultraviolet light and its quantum efficiency is lower (about 10%). Therefore, CdTe and TiO<sub>2</sub> nanocrystals both suffer disadvantage when they were used in photoelectric devices. It was reported that CdTe nanocrystals can enhance the charge separation ratio, extend spectrum response of TiO<sub>2</sub> and improve quantum efficiency<sup>[10]</sup>. In this paper, we report a novel nanoscaled CdTe/TiO<sub>2</sub> complex film which could be applied in photoelectric system by layer-by-layer electrostatic self-assembly technology. The short circuit current density (I<sub>sc</sub>) and the open circuit current density (V<sub>oc</sub>) values of CdTe/TiO<sub>2</sub> complex on ITO substrate are better than TiO<sub>2</sub> or CdTe nanocrystals individual. The results demonstrate here are meaningful because they provide the promising prospect for self-assembly of CdTe and TiO<sub>2</sub> nanocrystals toward nanoarchitecture with well photoelectric properties.

### Experimental Method

**Materials.** NaBH<sub>4</sub> (China Medicine (Group) Shanghai Chemical Reagent Corporation), Te powder (Aldrich), 3-mercaptopropionic acid (MPA, Aldrich), TiO<sub>2</sub> sol (prepared according the method described in ref.11), poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, 1.3wt%, Aldrich).

**The preparation of CdTe nanocrystal hydrosols.** NaBH<sub>4</sub> and Te powder with the mol ratio (NaBH<sub>4</sub>:Te=2:1) were added into a hermetic centrifuge tube. Then deionized water was added into ice-bath. NaHTe generated in tube after 4 hours. Next, fresh NaHTe was added into CdCl<sub>2</sub> and MPA mixed solution with the ratio (Cd:Te:MPA=2:1:4.8), and the pH value was controlled between 8~8.2. Finally, the mixture was cohabated for 6 hours at 90 °C ~ 95 °C to generate CdTe nanocrystal hydrosols.

**Fabrication of CdTe/TiO<sub>2</sub> multilayer.** Quartz substrates were oxidized thoroughly in fresh piranha solution (98%H<sub>2</sub>SO<sub>4</sub> and 30%H<sub>2</sub>O<sub>2</sub> with a volume ratio of 7:3) for 20 minutes and washed with deionized water. ITO (2cm×2cm, 10Ω·cm<sup>-2</sup> per square) substrates were ultrasonicated in deionized water, acetone and isopropanol for 15 minutes, respectively. Then, PEDOT:PSS was spin-coated on the surface of ITO substrates and dried in N<sub>2</sub> flow. The surfaces of quartz and ITO substrates treated took negative charges. The quartz and ITO substrates were put into fresh TiO<sub>2</sub> sol and CdTe nanocrystal hydrosols respectively for 15 minutes and dried in N<sub>2</sub> flow. Repeat above "dipping-drying" procedure from one to five times. Put these substrates into 450°C muffle for 2 hours after pretreatment.

**Measurement.** Transmission electron microscopy (TEM, JEM-1230, JEOL) was used to characterize the morphology of CdTe nanocrystal hydrosols. UV-visible absorption spectra were measured with a Uv-vis absorption spectrophotometer (Agilent 8453). AFM (Benyuan Co. Ltd., CSPM-4000) was used to characterize the morphology of film. Electrochemical workstation (Chenghua Co. Ltd., CHI660) was used to measure photoelectric properties. The light source was Xe lamp (HAYASHI LA-410UV) under AM 1.5G simulated solar irradiation at 100mWcm<sup>-2</sup>.

### Results and discussions

Fig.1 shows TEM image of CdTe nanocrystal hydrosols. The average diameter of CdTe nanocrystal is 5 nm with a spherical shape and CdTe nanocrystal individual disperses equably in the hydrosols. MPA which acts as a surface modifier plays an important role in the preparation of CdTe nanocrystals. It prevents CdTe particles to aggregate and improved their stability. Coated by MPA, CdTe nanocrystals take negative surface charges<sup>[12]</sup>. As-prepared TiO<sub>2</sub> nanocrystals take positive charges and the mean diameters which are about 8 nm in definitely spherical form<sup>[11]</sup>. Therefore, TiO<sub>2</sub> and CdTe nanocrystals can be layer by layer electrostatic self-assembled to shape multilayer complex films<sup>[13]</sup>. Fig.2 shows typical AFM image of CdTe/TiO<sub>2</sub> complex films on ITO substrate. The CdTe/TiO<sub>2</sub> multilayer is flat and well shaped after heat treatment, which is good for electrons-holes transfer.

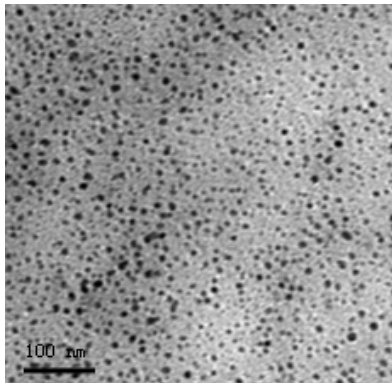


Fig. 1 TEM image of CdTe nanocrystal hydrosols.

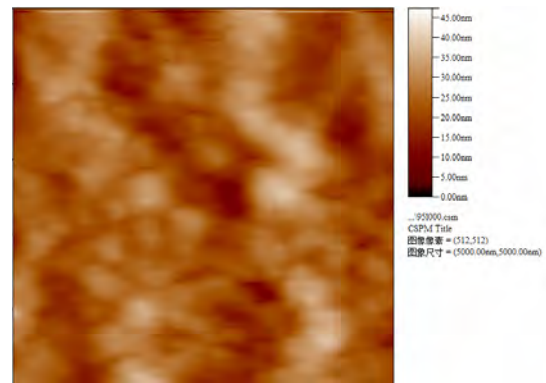


Fig.2. AFM image of three layers CdTe/TiO<sub>2</sub> photoelectric films on ITO substrate (0.5 $\mu$ m $\times$ 0.5 $\mu$ m).

Fig.3 shows UV-visible absorption spectrum of multilayer films on quartz substrates from 1 to 5 layers. With the increase of film layers, the UV-visible absorption intensity increase. Inset of Fig.3 shows basically linear relationship between layers and absorption intensity which indicates each layer of CdTe and TiO<sub>2</sub> nanocrystals deposited on the quartz substrate are well-proportioned and the complex multilayer is flat and even.

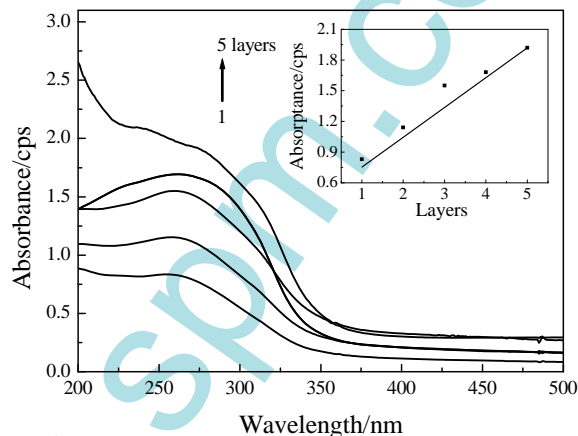


Fig.3. UV-visible absorbance of different layers of CdTe/TiO<sub>2</sub> photoelectric films.

In order to investigate the photoelectric property of the resultant CdTe/TiO<sub>2</sub> complex nanofilms, electrochemical photoelectric characterization was measured in three-electrode system in phosphate buffer. Short circuit current density (I<sub>sc</sub>) and open circuit current density (V<sub>oc</sub>) values of different layers of CdTe/TiO<sub>2</sub> photoelectric films are shown in Table 1.

Table 1 I<sub>sc</sub> and V<sub>oc</sub> value of different layers of CdTe/TiO<sub>2</sub> complex nanofilms

Layers	I <sub>sc</sub> /mA	V <sub>oc</sub> /V
1	0.025	0.25
2	0.040	0.40
3	0.050	0.45
4	0.045	0.40
5	0.025	0.35

Fig.4 and Fig.5 show the photocurrent and photovoltage versus time profiles of CdTe/TiO<sub>2</sub> complex and that of pure TiO<sub>2</sub> and CdTe films on ITO substrate. The I<sub>sc</sub> and V<sub>oc</sub> values of CdTe/TiO<sub>2</sub> complex films are about 0.050mA and 0.45V, which are better than pure TiO<sub>2</sub> and CdTe films. Since TiO<sub>2</sub> is a large bandgap semiconductor, it can only be excited with the UV light (less than 400 nm). CdTe can extend its photoresponse into the visible light (from 400 to 700 nm). Under

visible light irradiation, the electrons of CdTe nanocrystals in the prepared multilayer are excited to the conduction band of TiO<sub>2</sub>. CdTe itself also generates a great amount of holes. With the transfer of electrons and holes between CdTe and TiO<sub>2</sub> nanocrystals, CdTe/TiO<sub>2</sub> multilayer has higher photoelectric transformation efficiency than pure TiO<sub>2</sub> and CdTe nanofilms. In addition, the photocurrent of CdTe/TiO<sub>2</sub> complex is very stable, which means the inside hole-electron pairs transfer of film is steady and ordered. Therefore, CdTe/TiO<sub>2</sub> complex nanofilms provide the prospect in solar cell device.

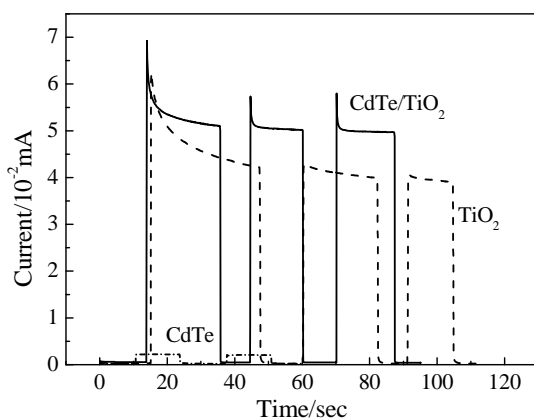


Fig.4 The photocurrent versus time profiles of three layers of CdTe/TiO<sub>2</sub> complex films and pure TiO<sub>2</sub> and CdTe films on ITO substrate.

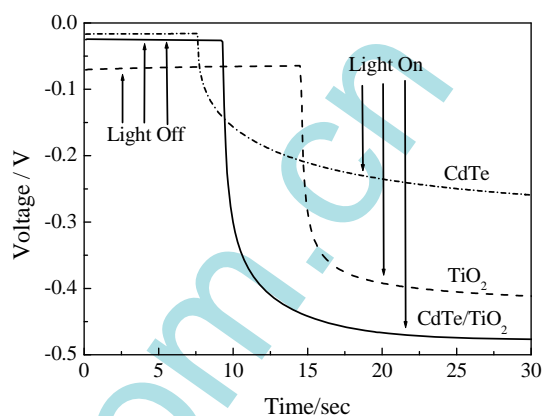


Fig.5 The photovoltage versus time profiles of three layers of CdTe/TiO<sub>2</sub> complex films and pure TiO<sub>2</sub> and CdTe films on ITO substrate.

## Summary

In this paper, we report the fabrication and photoelectric properties of CdTe/TiO<sub>2</sub> nanocrystal multilayer. Negatively charged CdTe nanocrystal hydrosols and positively charged clear TiO<sub>2</sub> aqueous colloidal nanocrystals were prepared. CdTe/TiO<sub>2</sub> complex was electrostatic self-assembled on the surface of pretreated ITO substrates disposed by PEDOT:PSS. Each layer of CdTe and TiO<sub>2</sub> nanocrystals deposited on the substrate are well-proportioned and the complex multilayer is flat and even. The maximum open circuit current density (V<sub>oc</sub>) and short circuit current density (I<sub>sc</sub>) values of CdTe/TiO<sub>2</sub> complex on ITO substrate are 0.45V and 0.050mA, which are better than that of TiO<sub>2</sub> or CdTe nanocrystal hydrosols individual due to the interfacial hole-electron converter between the adjacent layers of CdTe and TiO<sub>2</sub> nanocrystals. The photocurrent of CdTe/TiO<sub>2</sub> complex is very stable. The results demonstrate here provide the prospect for self-assembly of CdTe and TiO<sub>2</sub> nanocrystals toward functional films with well photoelectric properties.

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## Multi-Functional Materials and Structures II

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### Fabrication and Photoelectric Properties of CdTe/TiO<sub>2</sub> Nanocrystals Multilayer

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