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Preparation and Performance of CdSe sensitized TiO_2-based Solar Cell Photoelectrode

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With the explosion of energy demand in human society, the efficient use of solar energy has become an inevitable part for human to develop and make progress today. Solar cell has gotten widespread concern of the scientific researchers due to its low production costs and high theoretical conversion efficiency. CdSe/TiO_2 heterojunction films are prepared by cyclic voltammetry and the CdSe is deposited on the TiO_2 nanorod array film. And the materials are cadmium chloride ($CdCl_2 \cdot 5H_2O$) and selenous dioxide in this paper. The crystal structure, optical absorption capacity and photoelectric properties of the samples are studied by XRD, UV-VIS and electrochemical workstation at different annealing temperatures. The experimental results show that the CdSe/TiO_2 heterojunction thin films have the best photoelectric properties when the annealing temperature is 450 °C. And the photoelectric conversion efficiency can reach 8.75%, which indicates that the CdSe/TiO_2 nanorod array film has potential applications in the field of solar cells.

1. Introduction

The energy is the most essential fundamental material for economic development and improvement of people's livelihood. At present, because the traditional fossil energy is limited and brings great environmental pollutions in the use of the process, such as greenhouse effect, haze, etc., which has seriously hampered the sustainable development of mankind. It has received the world's attention to develop the energy that is environmentally friendly and renewable and full of energy-rich and low cost. Solar energy just meets the above characteristics. Therefore, it has imperative significances to develop the solar cell with low cost, simple process, rich material resources, large area production and excellent photoelectric performance. (Cummings et al., 2012; Kim et al., 2016; Semache et al., 2015; Cirillo et al., 2016; Zhang et al., 2016).

TiO_2 nanocrystalline semiconductor materials have excellent photoelectrochemical properties and photocatalytic properties and are widely used in solar cell, photocatalytic degradation of pollutants and so on (Iraj et al., 2016). However, the band gap of rutile TiO_2 is 3.0 eV, the electrons are excited from the valence band to the conduction band, and the wavelength of the incident light is not more than 413 nm, which leads to the only use of ultraviolet light in the sunlight, and the utilization rate is less than 5%. At the same time, the photo-generated electrons and holes of TiO_2 are easily recombined, which results in a very low quantum efficiency of absorbed light (Zhao et al., 2016; Tahir et al., 2017; Mulewa et al., 2017).

In order to suppress the recombination of the TiO_2 photo-generated electron-hole and to improve the utilization of TiO_2 on sunlight, the nanocrystalline sensitized TiO_2 can be used to improve the absorption properties of visible light and the photo-generated electron-hole recombination problem. However, during all the semiconductor nanocrystals, CdSe is a narrow bandgap semiconductor, which has a more negative conduction band position than TiO_2. It can be used to sensitize the TiO_2 nanorods, and there are so many preparation methods, including vacuum evaporation, chemical bath deposition, chemical vapor deposition, spray pyrolysis, molecular beam epitaxy (MBE), laser deposition, sol gel, electrodeposition, etc. (Mahato et al., 2015).

Among the many methods of preparing CdSe nanocrystals, electrochemical deposition has the advantage of being easy to operate (Gubur et al., 2015). The TiO_2 nanorod array has a regular structure and a larger specific surface area. Based on the preparation of ordered arrays of TiO_2 nanorods by hydrothermal synthesis,

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CdSe nanoparticles are deposited on the TiO_2 nanorod arrays by electrochemical deposition, and the recombination of TiO_2 and CdSe are realized (Xue, et al., 2013). The CdSe/TiO_2 thin films have a wider optical absorption spectrum to improve the utilization of visible light (Yan, et al., 2014).

2. The experiment

2.1 Experimental reagents

The chemical reagents in the experiment were acetone, anhydrous ethanol, concentrated hydrochloric acid, butyl titanate, cadmium chloride, selenium dioxide, sodium tartrate and so on (all of these were chemically pure). All the experimental water was deionized water.

2.2 Preparation of materials

2.2.1 Preparation of TiO_2 nanorod array film

To begin with, FTO conductive glass was cut into 1 cm × 3 cm sample. The acetone was used to clean the glass in the ultrasonic cleaner for 1 hour before using, in order to remove the grease and dust on the surface of the glass and to prevent the film from generating defects as the deposition of water heat. And then the anhydrous ethanol was used to clean for 1 hour with ultrasonic cleaning, in order to remove the residual acetone and impurities on the surface of the glass. Finally, the deionized water was used to clean with ultrasonic cleaning for 1 hour in order to remove the residual ethanol and impurity ions. And then the nitrogen was used to dry for spare application.

In addition, the measuring cylinder was used to measure the amount of ionized water, concentrated hydrochloric acid, respectively, and they were put into the same beaker. The mixture was stirred on a magnetic stirrer for 10 minutes to get the mixture A.

But beyond that, the butyl titanate was slowly added dropwise (15 drops/min) to the mixed solution A, and the process was completed in the process of stirring the magnetic stirrer until the solution was clear to obtain the solution B.

What’s more, the digital multimeter was used to measure the conductive surface of the FTO glass. The cleaned FTO glass with the conductive side facing down was leaned in the 25mL reactor liner. 20 mL of the clear solution B was added to the reactor liner by using a graduated cylinder, and the reaction vessel was placed in a vacuum oven. And it was taken out and cooled at room temperature after heating at 150 °C to 180 °C for 18 hours.

At the end, the samples that were cooled at room temperature were washed with deionized water for 5 minutes and dried with nitrogen to obtain an experimental sample.

2.2.2 Preparation of CdSe sensitized TiO_2 nanorod array composite films

CdSe quantum dot sensitized TiO_2 nanosheet array films were fabricated by electrochemical deposition. The preparation process was as follows.

First of all, the TiO_2 nanorod array films were prepared (hydrothermal method).

Secondly, the 0.1 mol. L^{-1} $CdC1_2$. $5H_2O$ + 0.01 mol. L^{-1} $C_4O_6H_4Na_2$ + 4 mmolSeO_2 of 100 mL deionized aqueous solution were configured to make the PH of the hydrochloric acid that the amount-of-substance concentration was 1 mol. L^{-1} was 3.

Next, at room temperature, the electrode system was used on the electrochemical workstation to prepare. And the TiO_2 nanorod array was used as the working electrode. The platinum electrode was used as the counter electrode, and the Ag/AgCl was used as the reference electrode. And the cyclic voltammetry was used to proceed the electrodeposition, and the deposition voltage was -0.9 ~ -0.3 V.

Finally, after the deposition, the deionized water was used to wash off the residual electrolyte that was in the prepared samples, which was dried to room temperature. In the tubular annealing furnace, the argon was as the protective gas. Respectively, the sample was annealed for 5 hours at different temperatures. After cooling, the sample could be gotten.

2.3 Test and analysis

The crystal structure of the film was analyzed by DX-2700 X-ray diffractometer in Dandong Hao Yuan, Liaoning Province. The scanning range was 20º ~ 80º. The chemical composition of the film was characterized by Amicus Budget X-ray photoelectron spectroscopy. The optical properties of CdSe/TiO_2 heterojunction films were measured by U-3900 ultraviolet and visible spectrophotometer. The photoelectric properties of CdSe/TiO_2 heterojunction thin films were tested by CHI660D electrochemical workstation of

Shanghai Chenhua Instrument Co., Ltd., and the CHF-XM-SOOW short arc xenon lamp was used as analog light source. The aqueous solution of 0.1mol. L^{-1} Na_2S was electrolytic solution.

3. Results and discussion

3.1 Crystal structure of CdSe sensitized TiO_2 composite films

In order to study the crystal structure of CdSe/TiO_2 heterojunction thin films prepared by the best process, XRD analysis of the films were carried out. It can be seen from the analysis that there were obvious diffraction peaks at 2θ of 26.57º, 37.77º, 51.76º, 65.74º, which were consistent with (110), (200), (211), (301) of SnO_2 in FTO conductive glass, (JCPDS 46-1088). The two diffraction peaks at 36.09º and 62.74º corresponded to the diffraction peaks of the (101) and (002) planes of the TiO_2 rutile. Respectively, it corresponded to the tetragonal TiO_2 standard diffractive card (JCPDS 21-1276). About (111), (220) diffraction peaks (JCPDS 19-2179) of tetragonal CdSe at 2θ of 25.35° and 42.00°, the diffraction peaks of each of the diffraction peaks were narrow and relatively sharp. And there were no diffraction peaks of Se and Cd, which confirmed that the prepared CdSe/TiO_2 heterojunction films were relatively pure.

3.2 The mechanism of CdSe sensitized TiO2

The principle of semiconductor recombination was to use the difference of energy level between the semiconductor to improve the charge separation efficiency of the composite system and extend the life of the charge carrier to enlarge the spectral response range. TiO_2 and CdSe were n-type semiconductors, and the band gap characteristics both the two were generally same. CdSe was relatively narrow to 1.73 eV, which was combined with TiO_2 (3.00 eV) with wide band gap. Since CdSe conduction band (CB) was relatively correct than the conduction band (CB) of TiO_2. Under the irradiation of ultraviolet light, CdSe valence band (VB) electrons were excited by light. The relative energy barrier between the two conduction bands was different, resulting in the internal driving force. So that the excitation to the CdSe conduction band of electrons transferred to the TiO_2 conduction band (CB). The electrons converge on the conduction band (CB) of TiO_2 gathered. However, the holes accumulated on the valence band (VB) of CdSe. This phenomenon was beneficial to the separation of charge, which improved the photoelectric response effect and photoelectric conversion efficiency. CdSe played a major role in visible light irradiation (Meng, et al., 2013). And only the valence band (VB) of CdSe transited to its conduction band (CB) and was further transferred to the conduction band (CB) of TiO_2 to allow the photogenerated carriers to be effectively separated. It can be seen that the combination of CdSe and TiO_2 not only reduced the recombination of photo-generated electron-hole pairs, but also broadened the response range to the spectrum. The electrons accumulating on the TiO_2 conduction band (CB) entered the circuit through the FTO conductive glass, and the holes accumulating on the CdSe valence band (VB) entered the electrolyte solution.

3.3 Effect of annealing temperature on crystal structure of CdSe/TiO2 thin film

Figure 1 showed the XRD patterns of CdSe/TiO_2 heterojunction films after annealing and annealing at 250 °C and 450 °C. It can be seen from the figure that 2θ exhibited obvious diffraction peaks at 25.35° and 42°, corresponding to the (111) and (220) plane diffraction peaks (JCPDS 19-2179) of the cubic CdSe, respectively, CdSe was successfully deposited on the TiO_2 nanorod film. The diffraction peaks appeared at 2θ of 26.57°, 37.77°, 51.76°, and 65.74°, which corresponded to the crystal diffraction peaks of (110), (200), (211) and (301) of SnO_2 in the conductive layer of the FTO conductive glass (JCPDS 46-1088). The two diffraction peaks at 2θ of 36.09° and 62.74° corresponded to the diffraction peaks of (101) and (002) planes of the TiO_2 rutile phase, respectively. Corresponding to the rutile TiO_2 standard diffraction card (JCPDS 21-1276), the (002) crystal diffraction peak was intense. Under the condition of unannealing, the peak width of CdSe (111) diffraction was wide and the degree of crystallization of CdSe nanoparticles was not high. After annealing at 250 °C, the peak width reduced to some extent, which indicated that after annealing at 250 °C, some CdSe nanoparticles can obtain enough surface driving force to promote the growth of CdSe. So that the degree of crystallization had a certain degree of improvement. Under the condition of 450 °C, the (111) and (220) diffraction peak sharpened and peak width of CdSe obviously reduced, indicating that the crystallization degree of CdSe obviously improved after this temperature annealing. In addition, the figure did not appear Se, CdO, SeO_2 characteristic diffraction peak. There were three possibilities. First, Se, CdO, SeO_2 existed one or more types in the film, and existed as the form of amorphous. Second, the content was very low. Third, there was nothing.

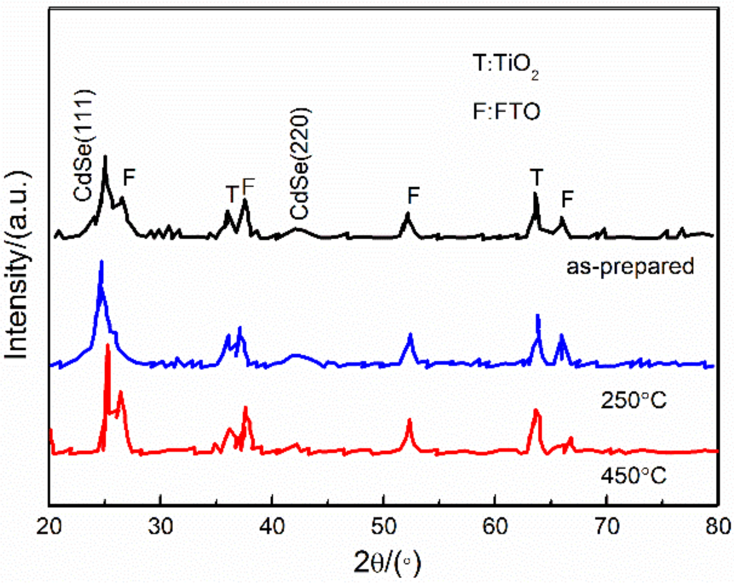

Figure 1: XRD patterns of CdSe/TiO_2 thin film prepared by different temperature annealing

3.4 Effect of annealing temperature on photoelectric properties of CdSe/TiO2 thin film

3.4.1 UV-Vis analysis

In order to accurately measure the response range and intensity of CdSe/TiO2 heterojunction films under different temperature annealing, the reflectance of the CdSe/TiO2 heterojunction film was measured by integrating sphere. And the results were converted into absorption intensity to obtain the UV-Vis absorption spectra. As the Figure 2 showed, it can be seen that CdSe/TiO2 heterojunction films were in the wavelength range of 300 nm ~ 700 nm and annealed at 450 °C, not only at 300 nm ~ 400 nm, but also at 680 nm absorption peak. It can be seen that the absorption intensity of visible light was significantly enhanced after annealing at 450 °C. After the annealing, the degree of crystallization of CdSe crystal was further improved, and its absorption ability to visible light was improved. CdSe was further grown by transfer and Oswald aging, and its response to visible light was redshift. The CdSe/TiO2 heterojunction film that annealed at 450 °C had the best response to ultraviolet - visible light in terms of absorptive capacity and band gap.

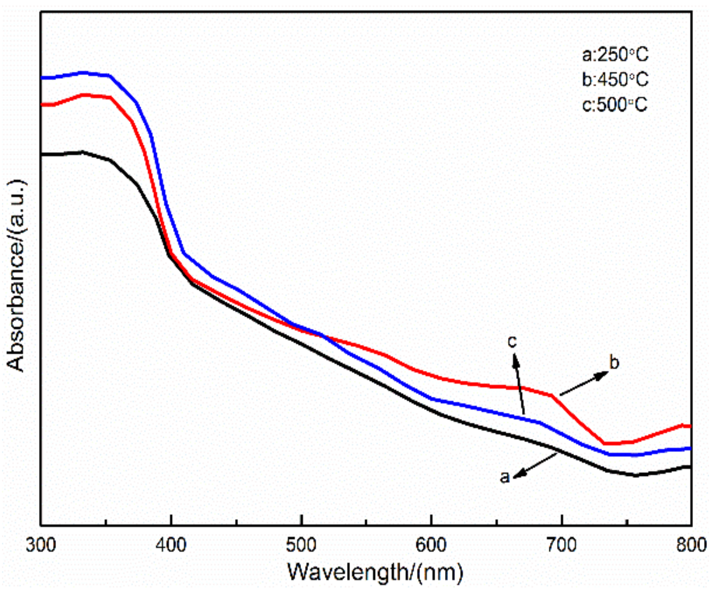

Figure 2: UV-Vis absorption spectra of CdSe/TiO_2 thin film prepared at different annealing temperatures

3.4.2 Analysis of photoelectric conversion efficiency

Figure 3 showed the current-voltage characteristic curves of the heterojunction film after annealing and annealing at different temperatures by using an electrochemical workstation, and 0.1 mol·L^{-1} Na_2S aqueous solution was electrolyte. According to its current - voltage characteristic curve, the photoelectric conversion efficiency was determined. And the parameters were shown in Table 1. It can be seen from the Table 1 that the photoelectric conversion efficiency after annealing at 250 °C, 450 °C, 500 °C were 1.20%, 8.75% and 4.45% respectively, and decreased firstly and then increased. When the annealing temperature was 450 °C, the photoelectric conversion efficiency was (8.75%), which was significantly higher than that of the untreated CdSe/TiO2 heterojunction thin film (5.03%). The short circuit current was basically consistent with the photoelectric response effect. The open potential decreased firstly and then increased, and reached the maximum at the heat treatment temperature of 450 °C, which indicated that the separation efficiency of the carrier decreased first and then increased at 450 °C. This may be caused by the increase of the annealing temperature, and the coverage of CdO and SeO2 increased first and then decreased.

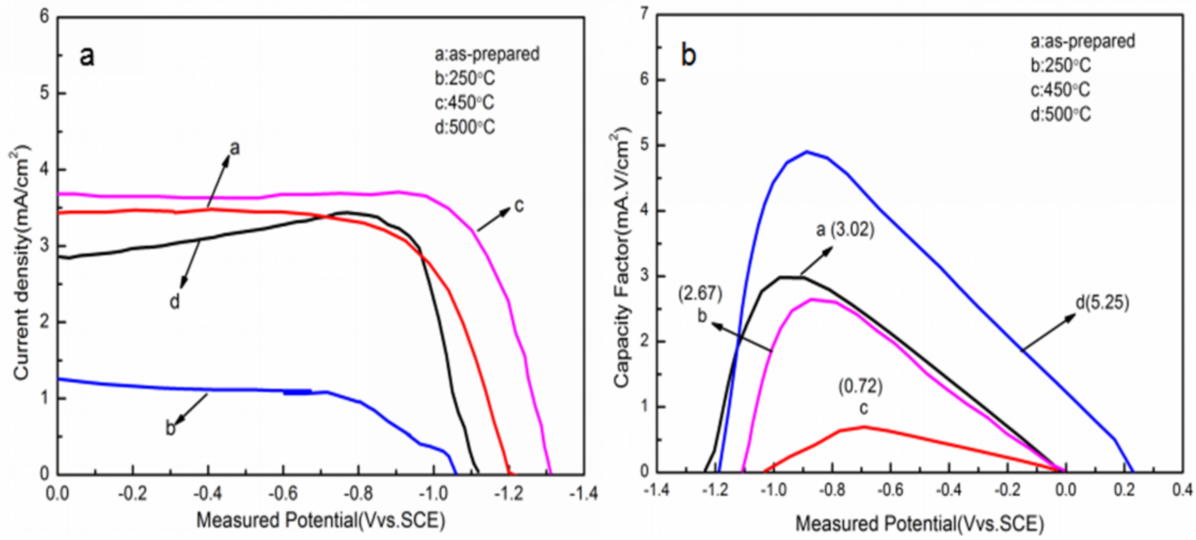

Figure 3: Preparation of CdSe/TiO_2 thin film at different annealing temperatures (a) Current-voltage characteristic curve, (b) Power-voltage relationship curve

Table 1: The current-voltage characteristic curve of CdSe/TiO_2 thin film prepared at different annealing temperatures

Sample number	V_{oc}(V)	J_{sc}(mA.cm^{-2})	P_{max}(mW.cm-2)	Conversion efficiency (%)	FF (%)
As-prepared	1.21	3.52	3.02	5.03	70.9
250 °C	1.07	1.24	0.72	1.20	54.3
450 °C	1.31	5.28	5.25	8.75	75.9
500 °C	1.11	2.81	2.67	4.45	85.6

4. Conclusions

In this paper, cadmium chloride (CdCl2·5H2O) and selenium dioxide (SeO2) are used as raw materials, and CdSe/TiO2 heterojunction films are prepared by cyclic voltammetry and CdSe is deposited on TiO2 nanorod array. The results show that the annealing temperature has a great influence on the structure and photo electrochemistry of the product. After annealing at 450 °C, the CdSe/TiO2 heterojunction film has the best crystallinity. The photoelectric conversion efficiency can reach to 8.75%, and the photoelectric properties of CdSe/TiO2 thin film are also improved.

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