

CdSe-TiO₂ heterojunction photoelectrochemical cells

Xian-Kui Lv¹, Liu-ying Zhao¹, Song-jie Han¹, Ping Wang², Hong-gang Nian², Xiang Wang¹, Yong-Chun Yang¹, Fu-fang Zhou^{1,*}

¹ College of Physics and Electronic Information, Yunnan Normal University, Kunming 650500, P. R. China

² College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650500, P. R. China

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CdSe nano films were electrodeposited on TiO₂ nano architectures to form heterojunction. CdSe-TiO₂ heterojunction in the hybrid layers largely enhanced photoelectrochemical cells efficiency under illumination of visible lights. Systematic characterizations of 113s-1125s periods deposition of CdSe were performed on the structure and components by scanning electron microscopy and X-ray diffraction, cyclic voltammetry, and electrochemical impedance spectra, I-V curves. The results indicated that the open circuit voltage always increases with time of electrodeposition of CdSe, but the conversion efficiency increases within short time of electrodeposition and decreases with more continued electrodeposition. As the electrochemical impedance spectra demonstrated the impedance drops with deposition time, so the limit of conversion efficiency may be dominated by the changed composition from stoichiometric to nonstoichiometric.

Keywords: TiO₂; CdSe; Photoelectrochemical cell; Electrochemical impedance spectrum

1. Introduction

TiO₂ is famous for dye sensitized solar cells and quantum dots sensitized solar cells which attract condense interest of workers. Mesoporous TiO₂ afford high area ratio for dye to adsorb on it, but the path for transportation of electrons is always in interception. A continuous network is most important for enhancement of photovoltaic conversion efficiency [1,2]. CdSe is a well known narrow gap semiconductor of II-VI compound sensible to a range of light from visible to infrared (IR), easily controllable by particle size and shape [3-4]. Narrow-gap CdSe were widely studied, as biosensors or applied in nonlinear optical devices, etc. [4-9]. When incorporated into a well constructed TiO₂ network, with a fine heterojunction style to improve photoelectric conversion efficiency, since they have well aligned electron energy levels they can make up excellent photovoltaic cells [4]. So far a lot of synthesis techniques were applied to obtain ideal CdSe on a variety of TiO₂ [10-19].

The aim of this work is to study the law of CdSe growth on a type of novel TiO₂ to learn its electrochemical nature of synthesis further its photovoltaic properties in aqueous solvent [10-19].

2. Materials and method

The titanium plate (99.99% purity) with a size of 3.0 cm×2.0cm×0.1mm was washed by distilled water, and dried in the oven. The sample was put into 30 mL solution of 0.5 M Tetramethyl-ammonium hydroxide (TMAOH) in a 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C for 6 hours in the oven. After the hydrothermal treatment, the specimen was completely washed with distilled water for several times. Finally, the sample was dried in the oven at 70 °C.

All CdSe thin films were electrochemically grown on titanium oxide substrates using a CHI660D instrument (CH Instruments, Inc.). The substrates approximately 9

mm². The electrolyte solution was prepared, a fresh solution was made for each set of depositions. Electrodepositions were carried out potentiostatically at various potentials in a three compartment cell with Ti/TiO₂ substrate as working electrode on a Polyfulon set and a saturated calomel reference electrode, Pt counter electrode.

5 mM Na₂ SeSO₃ solution was prepared by mixing 0.1 M Na₂SO₃ and weighed powdered 5 mM Se in 1M NH₃/NH₄⁺buffer in a 70 ° C bath until Se was completely dissolved. All solutions were prepared with triply distilled water and reagent grade of Na₂SO₃, NH₄OH, NH₄Cl, CdSO₄ and ethylene diaminetetraacetic acid (EDTA) Na₂ with a concentration of 0.1, 1, 1,0,2 and 0.2 M, respectively. The pH value was measured to be about 10 [7].

The morphologies of the samples were observed through field emission scanning electron microscopy (FESEM) (LEO-1530VP). The X-ray diffraction (XRD) measurement was performed with a Bruker D8 diffractometer with Cu K α radiation operated at 40 kV, 36 mA ($\lambda = 0.154056$ nm).

Cyclic voltammetry (CV) were measured using the same CHI660D instrument (CH Instruments, Inc.). The working electrode in all cases was a Ti/TiO₂ plate with CdSe deposited on top of TiO₂ surface. A Pt counter electrode and a saturate calomel electrode (SCE) reference electrode were also used in the measurements of open circuit potential and alternating current impedance in the similar way as that in the previous CdSe growth step. Electrochemical impedance spectra were determined immediately after the films had been deposited.

The supporting solution was prepared with 1M NaOH, 1M Na₂S, 1M S in twice distilled water. The photoelectrochemical cells properties of the as-prepared specimens of Ti/TiO₂/CdSe were further investigated in two-electrode system on electrochemical workstation CHI660D, using Ti/TiO₂/CdSe as the counter electrode, working electrode, respectively.

*Corresponding author. Email: ffz144@126.com

3. Results and discussions

3.1 Crystal structure of TiO₂

Hydrothermally grown TiO₂ architectures were investigated with XRD. The XRD pattern is represented in Fig. 1. The peaks of Ti are denoted as T, according to JCPDS No.44-1294, and similarly those attributed to anatase TiO₂ marked as A are consistent with JCPDS No.21-1272. Inset shows FESEM images of TiO₂ nano-pillars layers top view. The average pillar diameter is within 200 nm and exhibit bipyramidal profiles, in accord with references [10-12]. In Fig. 1 anatase (112) and (200) crystal planes appear much weak compared with those coming from substrate Ti. But the strongest diffraction planes (101) corresponding 2θ=25.6 in JCPDS No.21-1272 are missing. Orientation preference can be inferred from this data evidence, therein consistent with the appearance the crystal pillars take.

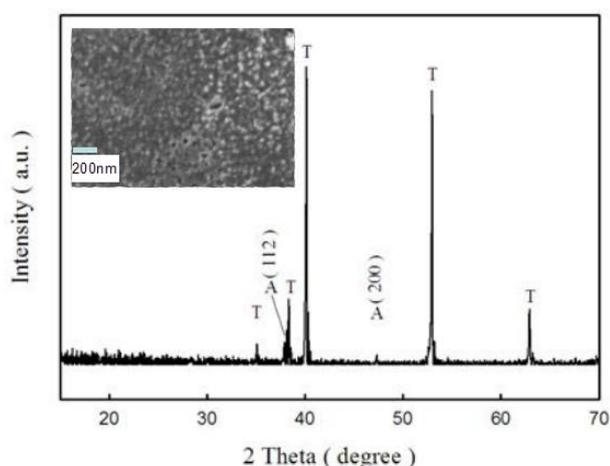


Fig. 1 XRD patterns of nano TiO₂ architectures synthesized in 0.5 M TMAOH, at a hydrothermal temperature 200 °C for 6 h with the TMAOH concentration of 0.5 M. Inset shows FESEM images of TiO₂ nano-pillars layers.

3.2 CV curve of deposition of CdSe on Ti/TiO₂ electrode

The CV trace presented in Fig. 3 was obtained at a Ti/TiO₂ electrode. The major two waves start at -1.35V and -1.50V should be assigned to Equations 1 and 2 respectively [2].

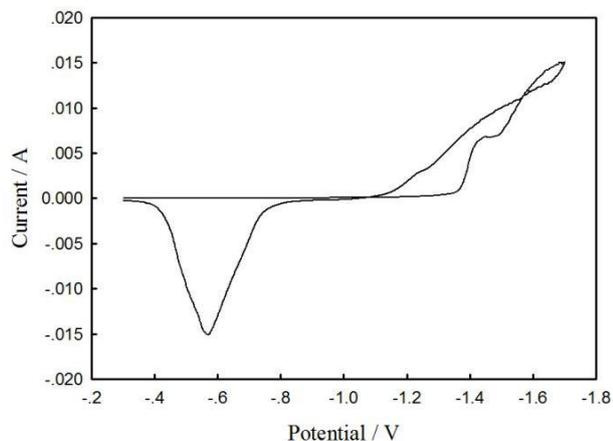


Fig. 2 Cyclic voltammograms on a Ti/TiO₂ nano architecture thick CdSe film. Sweep rate is 10 mV/s.

The mechanism was suggested as follows [3]:



Fig. 2 shows the growth curve by cyclic voltammogram technique. In the oxidization run, there appears oxidization current peak at -0.56V, where Cd²⁺ ions transferring from (EDTA)Cd to CdSe. The curve takes perfectly reproducible cycles. Referred to [2], the oxidation potential peak occurs at -0.65V in non-aqueous solvent ethylene glycol, the difference depends on the polarization of different solvents [13-19]. And the CdSe synthesis potential lies between deposition potentials of Cd and Se [2].

Fig. 3 shows the curves of photocurrent density against potential for seven Ti/TiO₂/CdSe electrodes after different deposition periods in photoelectrochemical cells under illumination (60 mW/cm² with visible filter permitting wavelength more than 400nm, the distance between anode and cathode is 2 cm). It can be observed that as a result of different deposition periods, from 113 s to 675 s, the open circuit potential continuously increases, as if at the cost of the short circuit current simultaneously, for the short circuit current continuously decreases. The details are listed in Table 1.

Usually there is a optimization time for the films formed at the same synthesis potential, for example there was a optimized time of 40 min for the best J_{sc} and V_{oc}, at that case, at the same time achieved.[2] As for our case, they do not maintain a balanced step. The nature of this needs further studies.

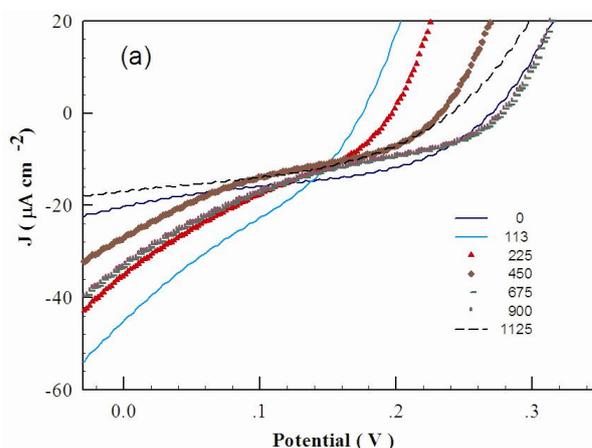


Fig. 3 Photocurrent density of Ti/TiO₂/CdSe nanoarchitectures based photoelectrochemical cells under illumination (60 mW/cm², the distance between anode and cathode is 2 cm).

3.3 Impedance (Nyquist) plots for CdSe/TiO₂/Ti films

To characterize the impedance behaviour of TiO₂/CdSe electrodes and for subsequent extraction of useful information from this, we took the EIS spectra for the Ti/TiO₂/CdSe nanoarchitectures, which are shown in Fig. 4. In Fig. 4 some impedance (Nyquist) plots for CdSe/TiO₂/Ti films in the same 1 M NaOH/Na₂S/S electrolyte solutions at the open circuit potential values, which is measured previously and listed in Table 1. Z' is the real part and Z''

is the imaginary part of the complex impedance Z . electrical parameters in figures correspond to the films deposited on 0.12 cm^2 TiO_2/Ti plate. All the spectra are semi-closed circles of different diameters. The parameters obtained via fitting on the software Zview from behaviors in Fig. 4 are presented in Table 1, which includes the photovoltaic parameters in Fig. 3., the model selected for fitting is inset in Fig. 4 too, wherein symbols have their usual meanings [19-22]. R_{ct} and C_{dl} are the resistance and capacitance between the electrode and electrolyte, and R_s series resistance, respectively.

As showed in Figure 4, the impedance arch radii of 0s, 113s and 1125s are large enough so that seem to be like lines in the region displayed. Further, that they almost parallel, implies they have similar a.c. impedance performance except the deviation of R_s , after all the semiconductor properties of CdSe layer discriminate from naked TiO_2 surface by large. The impedance decreases slowly during 0s, 113s, 225s-deposition, however from 225s to 450s, it drops sharply until 900s, unexpectedly approaching data of 113s, with only insignificant difference. Referred to Table 1, the most obvious difference between 225s to 450s lies in their R_{ct} and C_{dl} . Even so they are in line with a law: a trend of R_{ct} decreasing and C_{dl} increasing, with only 1125s as an exception. Regardless of what aspect taken, from photovoltaic or impedance, too long period does not facilitate photoelectronic properties, for supposed nonstoichiometric composition for Cd:Se occurs with thickness.[2]

We stress that the C_{dl} attains the largest at 900s might be a reason for its optimization, for C_{dl} is directly related to photon induced charge generation capability.[19-22]

In Table 1 off all the deposition periods, 900s is the outstanding one, so 900s is the best length of time to electrochemically deposit excellent CdSe layer on TiO_2/Ti substrate.

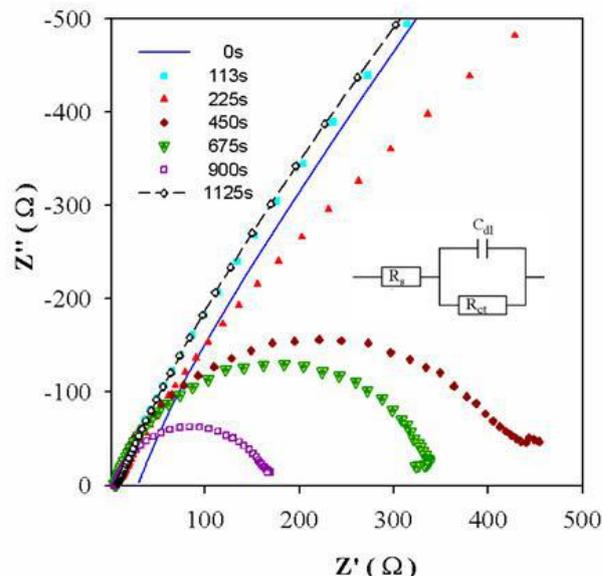


Fig. 4 Complex plane plots for the CdSe films of different electrodeposition time noted in figure in the same 1M NaOH/Na₂S/S electrolyte solutions.

Compared with results of other groups, the photovoltaic properties might seem relatively low in the key parameters, this can be presently attributed to: (1) poorly sealed edges of all samples which guaranteeing the contact limit within the CdSe/ TiO_2 electrode surface only; (2) the as-prepared TiO_2 un-annealed perhaps have left anatase phase in poor crystallization. Nevertheless this does not detriment the quality of a systematic analysis.

Table 1 Open current potential, photoelectrochemical alternating current impedance spectra and photovoltaic results

Time (s)	V _{oc} (V)	R _{ct} (Ω)	C _{dl} (mF)	V _{oc} (V)	J _{sc} (μA/cm ²)	FF (%)	η (%)×10 ³
0	-0.67	19982	1.4	0.140	7.25	7.4	6.2
113	-0.70	11900	17.4	0.267	19.8	47.1	7.4
225	-0.86	1650	68.4	0.160	41.0	62.5	6.2
450	-0.90	223.3	991	0.200	37.1	56.5	5.4
675	-0.95	180	711	0.236	27.9	39.8	7.0
900	-0.98	87	1257	0.280	34.2	45.1	7.0
1125	-0.82	12450	12.2	0.240	17.5	62.0	4.8

4. Conclusions

CdSe nano films were electrodeposited on TiO_2 nano architectures to form heterojunction. CdSe- TiO_2 heterojunction in the hybrid layers largely enhanced photoelectrochemical cells efficiency under illumination of visible lights. Systematic characterizations were performed on the structure and components by SEM, XRD, cyclic voltammetry, and electrochemical impedance spectra, I-V curves. The results indicated that the open circuit voltage always increases with time of electrodeposition of CdSe, but the conversion efficiency increases within short time of electrodeposition and decreases with more time of electrodeposition. As the electrochemical impedance spectra demonstrated the impedance drops with time, so

the limit of conversion efficiency may be dominated by the changed composition from stoichiometric to nonstoichiometric.

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