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Short communication

CdSe nanofiber based photoelectrochemical cells: Influence of annealing temperatures

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Abstract

We have studied the influence of annealing temperatures on the crystal structure, surface morphology, optical and photoelectrochemical (PEC) properties of CdSe nanofiber film electrodes synthesized by electrodeposition technique. The crystal structure and surface morphology of CdSe film electrodes were examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques, respectively. The optical absorption study of as-synthesized and annealed CdSe films on tin-doped indium oxide (ITO) substrates were measured by spectrophotometer. As-synthesized amorphous/nanocrystalline CdSe film electrodes were changed to crystalline after annealing at 473 K for 1 h, where the improved photoelectrochemical performance conversion efficiency of 2.01% was obtained.

Keywords: CdSe films; XRD; SEM; Optical absorption; Photoelectrochemical cells

1. Introduction

Nanoparticles of semiconductors have attracted widespread attention because of their special structural, optical and electronic properties arising from the quantum confinement of electrons and large surface area [1]. Various nanodevices consisting of nanoscale materials, including logic circuits, nanosensors, nanolasers and nanothermometers have been assembled [2]. Certain nanocrystallites shows size dependant structural, morphological, optical and electrical properties, which make intrinsic candidates for different applications, such as light emitting diodes, solar cells, non-linear optical and luminescent devices [3]. Developments of such materials, whose structural, morphological and optoelectronic properties can be tuned, are useful in many applications. For example, optoelectronic devices particularly, solar energy conversion devices can be modified accordingly [2]. CdSe (E_g, bulk = 1.7 eV) thin films have received considerable attention because of their tunable band gap, which can vary their optical response from the infrared region to the ultraviolet led major contribution to solar cells, photo-electronics, light amplifiers, thin film transistors and single-electron transistors, light emitting diodes and lasers [4]. The nanowires [5], nanotubes [6], nanorods [7], quantum dots [8] and needles [9] are some of the well-known CdSe reported morphologies. Therefore, control over both nanocrystalline morphology and the crystal size is a new challenge to synthetic chemists and materials scientists [10]. Nanoscale particles may offer important advantages for the study of phase transformation mechanisms. The kinetics of phase transformations in very small nanoparticles (3–5 nm) is usually simpler than those in bulk materials [9b]. The temperature required to anneal out defects from nanoparticles is much lower than that in bulk material. Thus, compared with bulk materials, many small nanoparticles contain much less stable defects that could serve as nucleation sites for phase transformations. However, if defects form in the initial stage of phase transformations due to thermal fluctuations, they only need to travel small distances to reach the surface.

Synthesis of one-dimensional (1D) nanostructures is one of the major challenges. It is also accepted that the controlled synthesis of nanostructures with desired shape and size of complex structure is technologically important. In continuation to our CdSe thin films synthesis and application research [11], in this

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work, we discuss the effect of annealing temperature on structural, optical and photoelectrochemical cells (PEC) of 1D CdSe electrodes synthesized by electrodeposition technique.

2. Experimental details

A process for the synthesis of 1D CdSe film electrode composed of nanofibers is already reported [12]. All of the chemical reagents used in this experiment were of analytical grade. In a typical procedure, 0.05 M $CdSO_4$ (6 mL) solution was prepared to which 0.01 M SeO_2 in equal volume was added drop wise under constant stirring at 298 K. The resultant solution was refluxed for 20 min. The constant cathodic current density of 2 mA/cm^2 was passed for 20 min between working (ITO) and counter electrodes (Pt) using Ag/AgCl as a reference. Prior to the electrodeposition, ITO substrate was cleaned by an ultrasonic cleaner for 5 min in soap water, 10 min in distilled water, and 5 min in anhydrous ethanol. Further, as-grown CdSe film electrodes were annealed at 373, 473 and 573 K for 1 h in air and used for their characterization.

The X-ray diffraction (XRD) patterns were recorded using a Rigaku (Japan) X-ray diffractometer equipped with monochromatized Cu Kα radiation ($\lambda = 0.15478$ nm) at a scanning rate of 0.03° s^{-1} ranging from 15° to 80° (2 theta) operated at 40 kV, 100 mA for structural elucidation. The surface morphology and film thickness were observed from scanning electron microscopy (SEM) (JEOL, JSM-840A) operated at 15 kV. For the optical study, UV–vis spectrophotometer was used in the wavelength range 350–900 nm. Furthermore, CdSe film electrodes were annealed at different temperatures and used in PEC cells for photovoltaic output characteristic study under dark and in light illumination of 80 mW/cm^2 intensity. PEC of all designed CdSe cells were measured using a 1-kW xenon lamp with a photointensity of 80 mW/cm^2 calibrated by MELLES GRIOT Lux meter. The CdSe photoelectrode cells with an electrode area of 0.28 cm^2 were exposed to light. The thin sputtered Pt layer was used as the counter electrode in every case.

3. Results and discussion

The CdSe film electrodes composed of 1D nanofibers have been annealed at 373, 473 and 573 K in air for 1 h and used for various characterizations. Fig. 1 shows the XRD patterns of CdSe films deposited on ITO substrate and annealed at different temperatures. Fig. 1(a) indicates that as-deposited CdSe film is amorphous and/or nanocrystalline as small and weak intense peaks are observed. Fig. 1(b) is the XRD pattern of CdSe film annealed at 375 K, for 1 h where some weak intense diffraction peaks can be seen which appear in the positions of wurtzite-type CdSe structure, in agreement with the reported standard values (JCPDF data file card no. 08-0459). Fig. 1(c and d) show the XRD patterns of CdSe film annealed at 473 and 573 K, respectively. It is interesting to note that CdSe film electrode annealed at 473 K shows intense and sharp diffraction peaks corresponding to wurtzite-type CdSe indicating that at 473 K temperature CdSe nanofibers are changed to crystalline. However, at 573 K temperature (Fig. 1(d)), the crystallinity was decreased. This could arise from the fact that to some extent surface oxidation of CdSe might have occurred. This observation lead to make conclusion that the annealing temperature 473 K for 1 h is critical one for the improvement in crystallinity of CdSe, which was also reflected from the performance of PEC cells (see later).

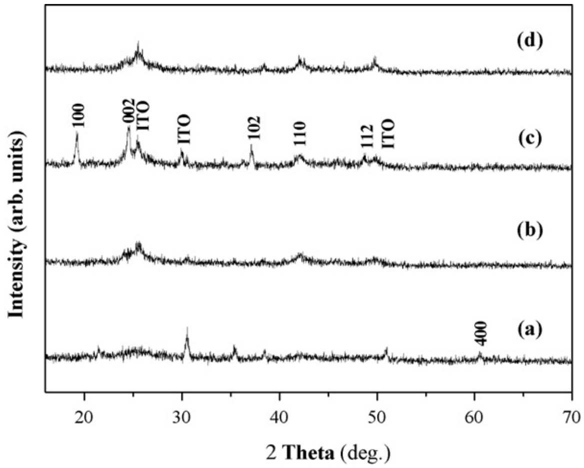

Fig. 1. X-ray diffraction patterns of CdSe nanofiber films annealed at different temperatures: (a) as-deposited, (b) 373 K, (c) 473 K and (d) 573 K for 1 h.

The influence of annealing on surface morphology of CdSe film electrodes was observed by SEM. The surface morphology images of CdSe are shown in Fig. 2. The surface morphology of as-deposited CdSe film possesses narrow nanometer scale sized fibers. The diameters of all these observed fibers were different. Fig. 2(a) is the cross sectional image of as-deposited CdSe film. The average thickness of about 500 nm was estimated, as exact thickness measurement was not possible due to uneven fibers. In Fig. 2(b–e) images, no significant change in fiber morphology is observed. The synthesized CdSe nanofibers are long, with length of about 5 μm (here end terminals are not seen) with an external diameter of about 30–40 nm. In reality, these nanofibers are tubular with their ends as capped [12]. In a nutshell, SEM images do not present any information about surface morphological change due to the annealing.

Fig. 3 shows the visible absorbance spectra of CdSe nanofiber film electrodes annealed at different temperatures. It can be seen that the absorbance of as-deposited CdSe film is high in spite of about 50 nm thickness. In the visible region, it is well know that CdSe is perfect absorbent with absorption edge at 700 nm [11]. For annealed film electrodes, absorbance was increased slightly which is common in semiconducting thin films, as reported by other [3a,13]. This may be due to the scattering, depending on the different surface homogeneiety of the films at different temperatures.

Among the various applications, CdSe has been studied intensively as a photoanode in PEC cells [14]. The conversion efficiency of these cells as well as the physicochemical stability of the anode in an electrolyte system depends critically on the structure and the composition of CdSe [15]. Fig. 4 (a and b) shows current density–voltage (J–V) curves under dark and in light illumination of as-deposited and annealed at 473 K for 1 h CdSe film photoelectrodes. Electronic parameters, such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor

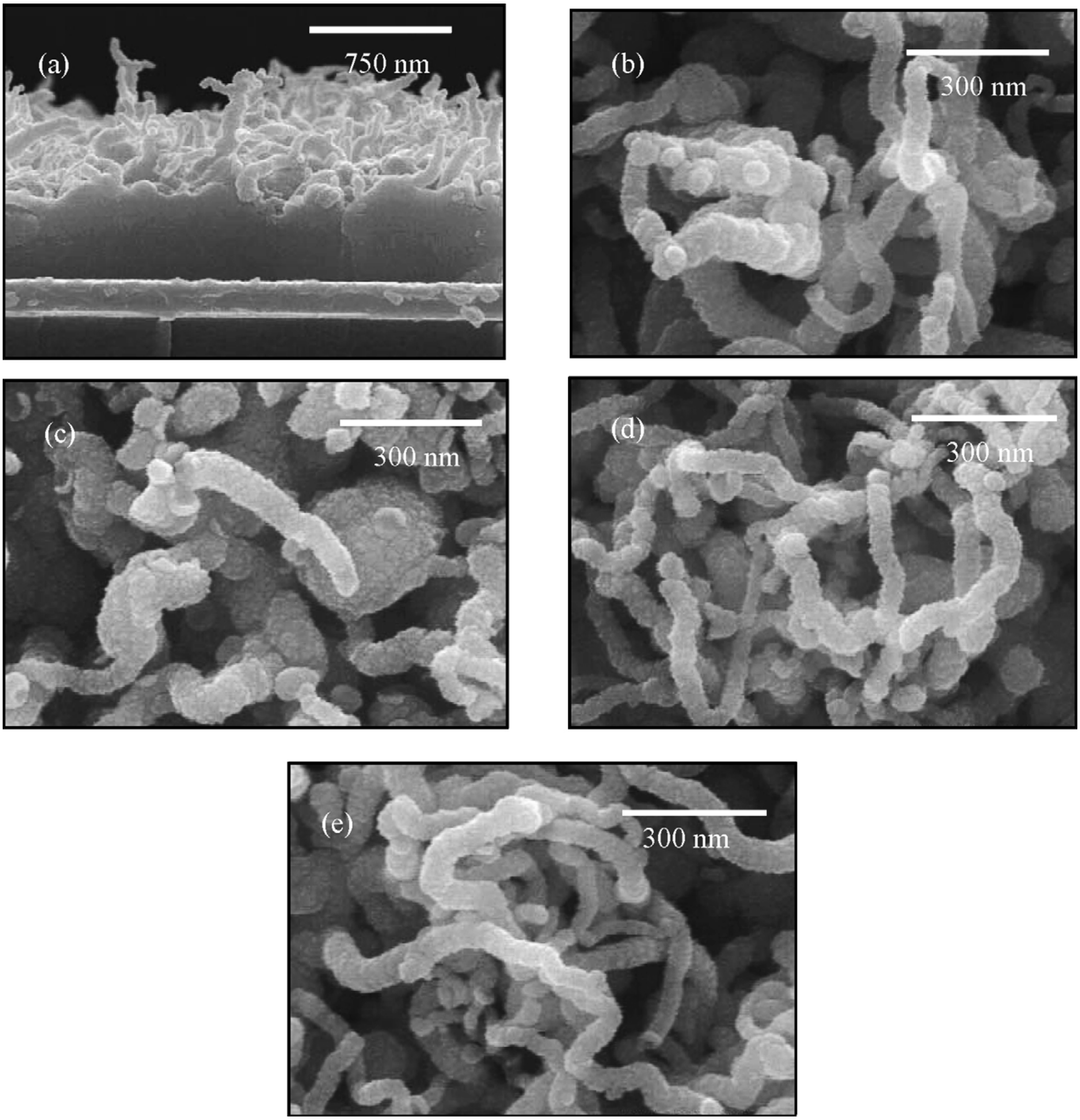

Fig. 2. SEM images of CdSe film electrodes annealed at different temperatures: (a) cross sectional view, (b) as-deposited, (c) 373 K, (d) 473 K and (e) 573 K.

(FF) and photoconversion efficiency (η) were measured by using standard relations reported elsewhere [16] for as-deposited and to that of annealed CdSe film electrodes and are presented in Table 1. The power conversion efficiency was calculated from the relationship, $\eta = I_m V_m / p_r \times 100\%$, where $I_m V_m$ is the maximum multiplied value in the J–V sweep, and p_r is the illumination power input, which was controlled to 80 mW/cm^2. The open circuit voltage (V_{oc}) was set at $I = 0$, and the short circuit current density was defined at $V = 0$. As observed from J–V plots and Table 1, as-deposited CdSe film electrode do not show good PEC

Table 1
Annealing temperatures influence on various PEC parameters of CdSe film electrodes composed of nanofibers

Annealing temperature (K)	Short circuit current density, J_{sc} (mA/cm^2)	Open circuit voltage, V_{oc} (V)	Fill factor (FF%)	Photoconversion efficiency (η%)
As-deposited	0.15	0.23	0.29	0.01
373	1.54	0.25	0.31	0.12
473	10.11	0.40	0.40	2.01
573	4.20	0.28	0.28	0.33

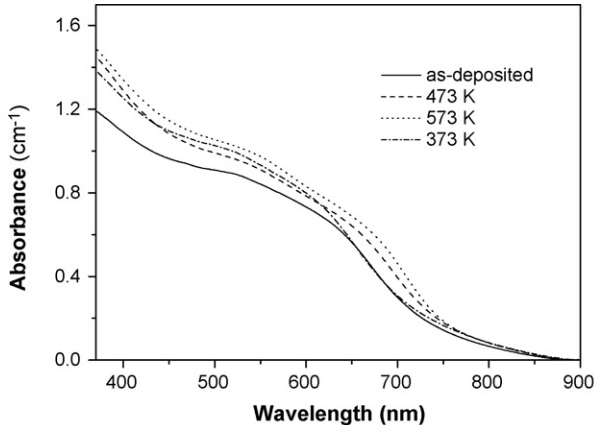

Fig. 3. Optical absorbance of 500 nm thick CdSe film electrodes annealed at different temperatures.

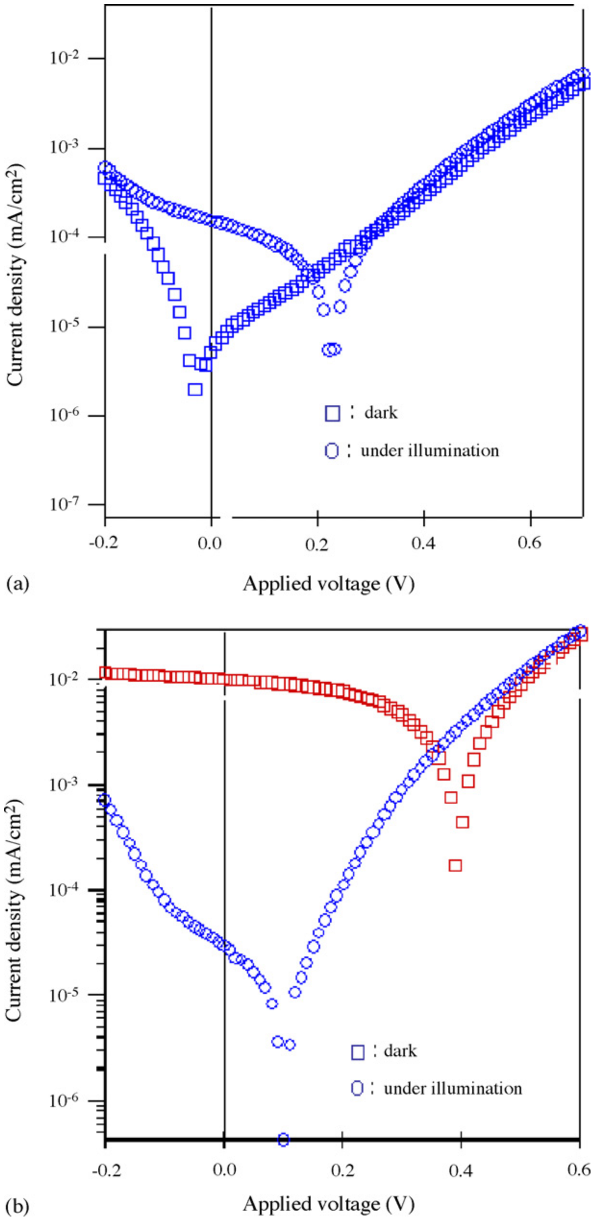

Fig. 4. *J–V* characteristics of CdSe film electrodes under dark and in light illumination: (a) as-deposited and (b) annealed at 473 K for 1 h.

performance due to its amorphous nature. However, PEC performance drastically improved for film electrode annealed at 373 and 473 K for 1 h and then again decreased for further annealing temperatures. This behavior is closely in consistent to the XRD observation providing the qualitative evidence that at 573 K annealing temperature, surface oxidation of CdSe nanofibers is responsible for large hole–electron recombination, resulting into poor PEC performance. We believe that CdSe film electrode annealed at 473 K for 1 h provides better crystallinity with easy electron transport path than percolation through the random spherical nanoparticles (grain boundary acts as recombination barrier) [17], which increases electron diffusion length with enhanced photochemistry; as reported by Law et al. [18]. Garuthara and Tomkiewicz have reported 5.8% photoconversion efficiency for crystalline CdSe/polysulfide liquid-junction solar cells without study of micro-structural aspects [19].

4. Conclusions

In summary, the electrodeposition technique was successfully applied for the synthesis of CdSe nanofiber film electrodes composed of micrometer range long and nanometer range in diameter. After annealing at 473 K for 1 h, improvement in the crystallinity and optical absorbance were observed, however, no change in surface morphology and nanofiber geometry was seen. The annealed CdSe nanofiber electrode at 473 K showed the best PEC performance.

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