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Electrospinning preparation and characterization of cadmium oxide nanofibers

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ABSTRACT

Using a facile synthesis route, cadmium oxide (CdO) nanofibers in the diameter range of 50–60 nm have been prepared employing the electrospinning technique followed by a single-step calcination from the aqueous solution of polyvinyl alcohol (PVA) and cadmium acetate dihydrate. Electron microscopy (EM) and the Brunauer–Emmett–Teller (BET) technique were employed to characterize the as-spun nanofibers as well as the calcined product. The specific surface area of the product was calculated to be 42.6711 $m^2\,g^{-1}$. Infrared (IR) absorbance spectroscopy and X-ray powder diffractometery were conducted on the samples to study their chemical composition as well as their crystallographic structure. The study on the optical properties based on the photoluminescence (PL) spectrum demonstrated that the emission peaks of CdO nanofibers are centered at 493 and 528 nm. The direct bandgap of the CdO nanofibers was determined to be 2.51 eV.

1. Introduction

Cadmium oxide (CdO) is an n-type II–VI semiconductor with a direct bandgap of 2.5 eV and an indirect bandgap of 1.98 eV [1]. Interestingly, a direct bandgap of approximately 2.32 eV and an indirect bandgap of 1.36 eV for bulk CdO have also been reported [2–4]. Bulk CdO has a cubic (NaCl type, $a = 0.469$ nm) crystal structure, with high density (8150 $kg\,m^{-3}$) and melting point (1500 °C) [5], however a phase transformation to CsCl type at very high pressures at room temperature has been also reported [6].

CdO nanostructures have low ohmic resistivity (even without doping) and high optical transmittance in the visible region of the solar spectrum along with a moderate refractive index (2.49) [7–9] which offer promising applications in optoelectric fields such as photovoltaic cells [10], photo-diodes [11], photo-transistors [12], gas sensors [13] and transparent electrodes [14]. For these applications, particle size, porosity, and specific surface area are of major importance. Up to the present time, various one-dimensional CdO nanostructures such as nanowires, nanoneedles, nanobelts and nanorods have been synthesized by solid-state transformation metal-organic framework [15], vapor phase transport [16], template-assisted [17] and solvothermal methods [18]. Guo et al. prepared porous CdO nanowires of at most 100 μm long with diameter of 120 nm by calcination of hydroxy- and carbonate-containing cadmium compound precursor nanowires. Cadmium oxide nanowires were obtained by calcinating the as-synthesized precursor nanowires at 500 °C in air for 2 h [13]. Kuo and Huang synthesized CdO nanowires having maximum length of 50 μm and diameter of 40–80 nm on gold-coated silicon substrates by a vapor transport process in an atmosphere-controlled tube furnace [16]. Lu et al. fabricated CdO nanotubes by thermal evaporation of Cd powder in a tube furnace at 500 °C under low pressure [19]. The above procedures have been complicated by the use of complex precursor materials, lengthy experimental procedures, low aspect ratio wires and atmosphere controlled heating regimes.

In this context, we present a simple and effective electrospinning technique, using sol–gel process followed by a low temperature calcination stage for the preparation of centimeter-long CdO nanofibers with diameters in the range of 50–60 nm. The prepared nanofibers were then characterized from structural and optical point of view.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA) with an average molecular weight of 145 $kg\,mol^{-1}$ and percentage of hydrolysis equal to 98–99 (Cat. No.: 814894), cadmium acetate dihydrate ($Cd(CH_3COO)_2\cdot 2H_2O$) (GR for analysis, Cat. No.: 102003) and ethanol were purchased from Merck. Distilled water ($\sigma = 6.7$ $\mu s\,cm^{-1}$) was used as the solvent.

2.2. Preparation

PVA granules was dissolved in distilled water at 80 °C with vigorous stirring for at least 30 min to prepare 20 ml of 6 wt.% PVA solution. After cooling down the resulting solution, 1.5 g cadmium

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acetate and 0.5 ml ethanol were added to the solution and stirred for additional 1 h. In this stage, the sol–gel reaction took place within the precursors and a homogeneous viscous solution was obtained which was then poured into a 50 ml syringe.

The electrospinning setup used in this study consisted of a syringe with a flat-end stainless steel needle (with inner diameter of 0.495 mm and length of 13 mm), a syringe pump (Top 5300, Japan) for controlled feed rates, an electrically grounded aluminum plate, and a high voltage DC power supply (Glassman High Voltage Inc., USA). During electrospinning, a high voltage was applied to the PVA/cadmium acetate solution contained in the syringe via an alligator clip attached to the syringe stainless steel needle that were positioned horizontally on the syringe pump. The solution was electrospun with a constant feed rate of 0.5 $cm^3\ h^{-1}$ at positive voltage of 16.5 kV at collection distance of 20 cm. The fibers were collected on the electrically grounded aluminum plate (the most common collector in the electrospinning). The electrospinning process was carried out at 22 °C and relative humidity of 36–38% (measured by humidity and temperature meter Mastech, MS6505). The PVA/cadmium acetate fibers were calcined at 450 and 400 °C for 30 min on aluminum substrates in a tube furnace in air. The precursor fibers were also calcined at 450 °C for 30 min on silicon substrate.

2.3. Characterization

Scanning electron microscopy (SEM) images of the precursor and calcined nanofibers were recorded on a Cambridge-S360 scanning electron microscope, while working at 20 kV acceleration voltage. The average fiber diameter of the electrospun fibers was determined by taking 100 random fibers from the SEM images in the original magnification of 10k, using Image J software [20]. Energy dispersive X-ray spectroscopy (EDS) was performed on a VEGAII TESCAN. X-ray powder diffractometeries (XRD) of the precursor and calcined nanofibers were conducted on a Philips X-ray diffractometer (PW3710) with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 30 mA. Transmission electron microscopy (TEM) images were collected on a Zeiss (CEM902A) electron microscope with an acceleration voltage of 80 kV. FT-IR spectra of nanofibers before and after calcination were recorded on a Bruker (Vector33) spectrometer in KBr matrix in the range of 400–4000 cm^{-1}. To study the thermal behavior of composite fibers, simultaneous thermal analysis (TG–DTA) was carried out with a STA 1640 (Polymer Laboratories-England) in air at a temperature range of 25–600 °C. Specific surface area of the nanofibrous mat before and after calcination was determined employing the BET technique with Micromeritics (Gemini 2375) in the range of relative pressures from 0.05 to 1.00. Degassing of the samples was done at 75 °C for 1 h. The room-temperature PL spectrum was performed on a Perkin Elmer (LS-5) spectrometer with a pulsed Xenon discharge lamp as the exciting source at 430 nm.

3. Results and discussion

In this study, electrospinning was used to prepare CdO nanofibers with ultra-high aspect ratio. Fig. 1 illustrates SEM image of nonwoven electrospun PVA/cadmium acetate composite fibers with an average diameter of 210 ± 21 nm. Actually, the resulting fibers are smooth and no bead was observed, indicating that the electrospinning process has been done properly.

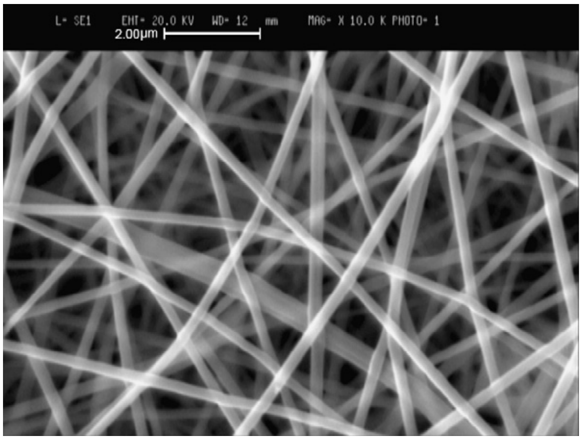

Fig. 1. SEM image of the electrospun PVA/cadmium acetate fibers.

In order to assess the appropriate calcination temperature, the thermal behavior of PVA/cadmium acetate composite fibers was investigated by thermal and differential gravimetric analyses (TG and DTA, respectively). As it is evident from Fig. 2, there are three exothermic peaks at 248, 365 and 446 °C which correspond to cadmium acetate decomposition and PVA side and main chains dissociation, respectively. The calcination temperature should be greater than 450 °C because all the reactions have been carried out and there is no change in sample's weight, representing the formation of pure inorganic oxide. In general, the two following reactions (1) and (2) can take place during calcination process and lead to the formation of cadmium oxide:

$$Cd(CH_3COO)_2{\cdot}2H_2O \rightarrow Cd(CH_3COO)_2 + 2H_2O\uparrow \tag{1}$$

$$Cd(CH_3COO)_2 + 2R\text{–}OH \rightarrow CdO + 2CH_3\text{–}CO\text{–}R + H_2O \tag{2}$$

Eq. (1) describes the dehydration of cadmium acetate dihydrate at about 248 °C. The second equation describes the condensation reaction in the sol–gel process. After 48 h at ambient temperature, some precipitates were observed at the bottom of the syringe which indicated that the second reaction had progressed during the solution preparation stage to some extent, causing an increase in the viscosity of the solution.

The SEM image of calcined sample at 450 °C for 30 min on Al substrate is presented in Fig. 3(a). Unexpectedly, a rock candy-like structure was obtained by individual growth of crystalline CdO octahedrals that was observed all over the sample. Fig. 3(b) shows SEM micrograph of calcined product at 400 °C on Al substrate. Reducing the calcination temperature down to 400 °C did not prevent the growth of crystalline CdO octahedrals from the fibers and the same structure but with less packing density of octahedrals was obtained. The occurrence of this phenomenon might be ascribed to the reduction in activation energy required for the

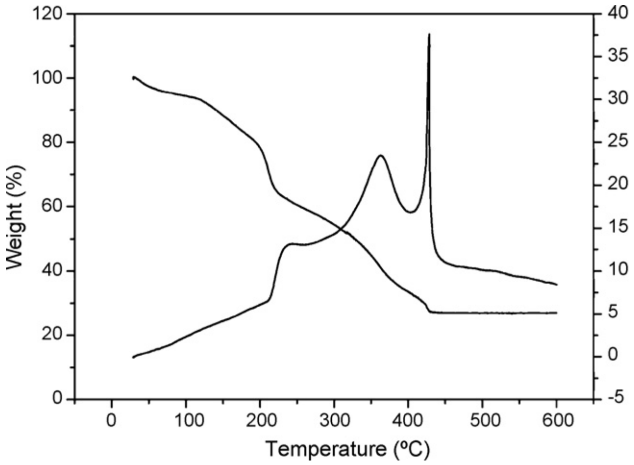

Fig. 2. Simultaneous thermal analysis of PVA/cadmium acetate fibers.

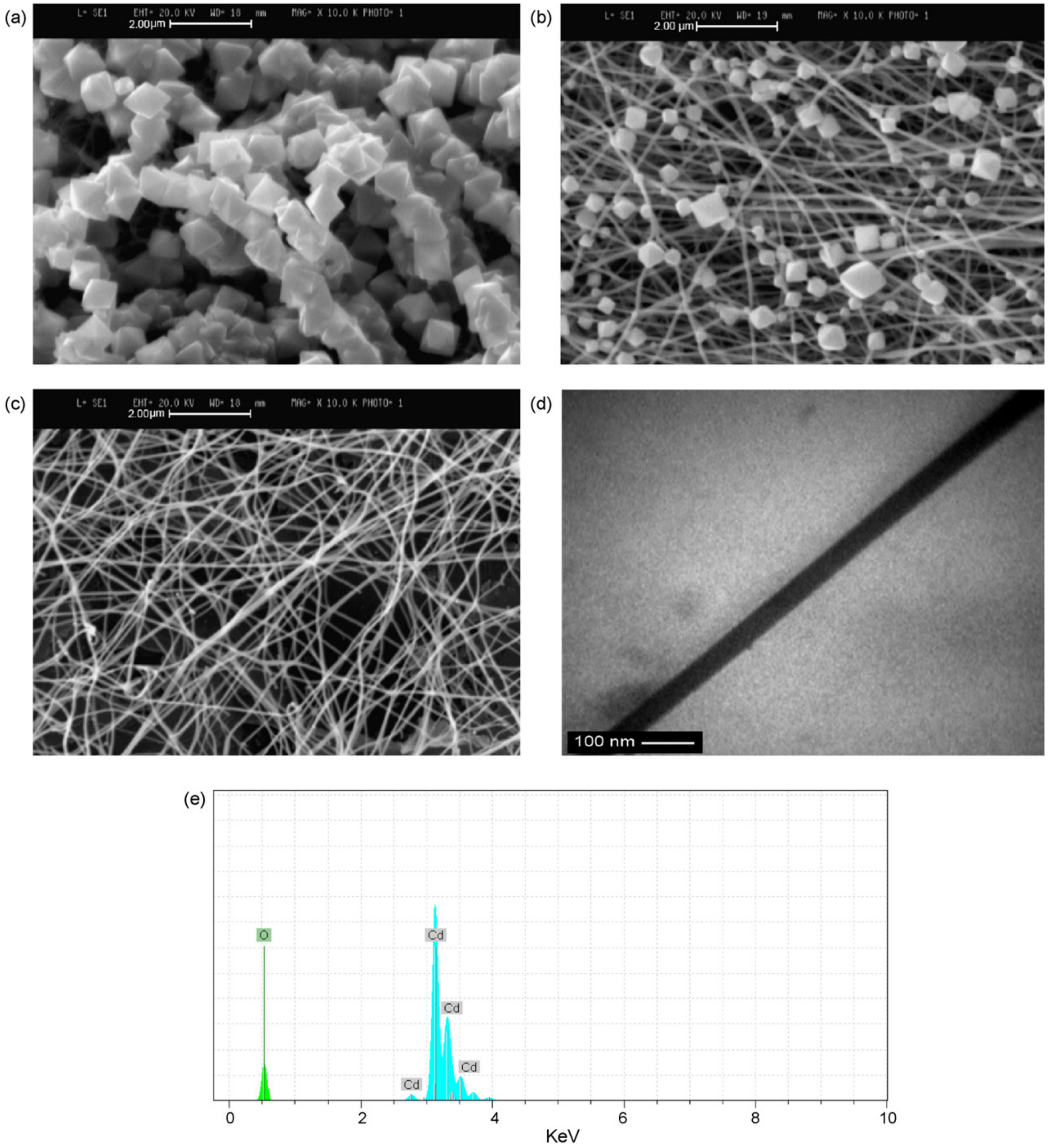

Fig. 3. SEM images of calcined nanofibers at (a) 450 °C for 30 min and (b) 400 °C for 30 min on Al substrates, (c) SEM image of calcined nanofibers at 450 °C for 30 min on Si substrate, (d) TEM image of a single CdO nanofiber and (e) EDS spectrum of CdO nanofibers.

nucleation and growth of CdO crystals due to the presence of Al as substrate. Based on the results obtained, a decision was made to change the substrate and use Si instead. The solution was electrospun on Si wafer and calcined at 450 °C for 30 min. The SEM image of the product is presented in Fig. 3(c). As it can be seen, besides the smooth morphology, the CdO nanofibers have uniform diameter in the range of 50–60 nm. However during the calcination process the precursor fibers have lost about 72% of their weight, their fiber-like shape has fundamentally retained. The size and morphology of calcined CdO nanofibers were also investigated by TEM. Fig. 3(d) shows the TEM image of a single CdO nanofiber. No undesired morphology is found and the nanofibers diameter is in good agreement with SEM observations.

The composition of obtained nanofibers was then analyzed by means of EDS. As shown in Fig. 3(e), only Cd (in the range of 2.7–4 eV) and O peaks are present in the spectrum. The results show that prepared CdO nanofibers are elementally pure.

The FT-IR spectra of nanofibers before and after calcination are shown in Fig. 4. The FT-IR spectrum of PVA/Cadmium acetate (Fig. 4(a)) shows that there are absorption peaks of O–H from the intermolecular and intramolecular hydrogen bonds in the wavenumber range of 3200–3550 cm^{-1} [21,22], C–O–C in between 1085 to 1150 cm^{-1} [21–23], C–H from alkyl groups between 2840 to 3000 cm^{-1} [24], C=O from 1737 to 1750 cm^{-1} [24], and C–O (crystallinity) at about 1141 cm^{-1} [25]. In Fig. 4(b), a peak observed around 470 cm^{-1} is assigned to Cd–O of CdO which confirms the

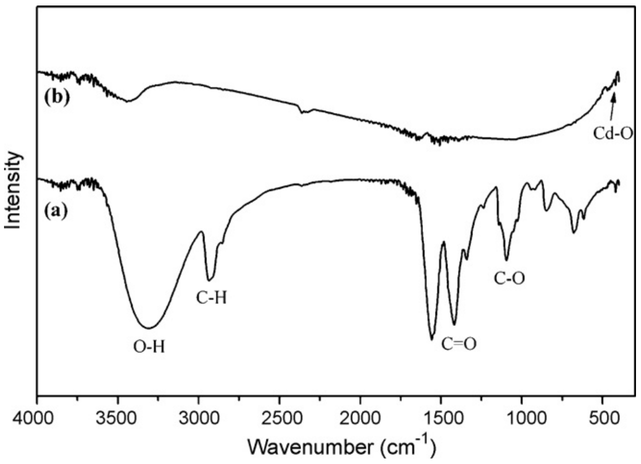

Fig. 4. FT-IR spectra of nanofibers (a) before calcination and (b) after calcination on Si substrate at 450 °C for 30 min.

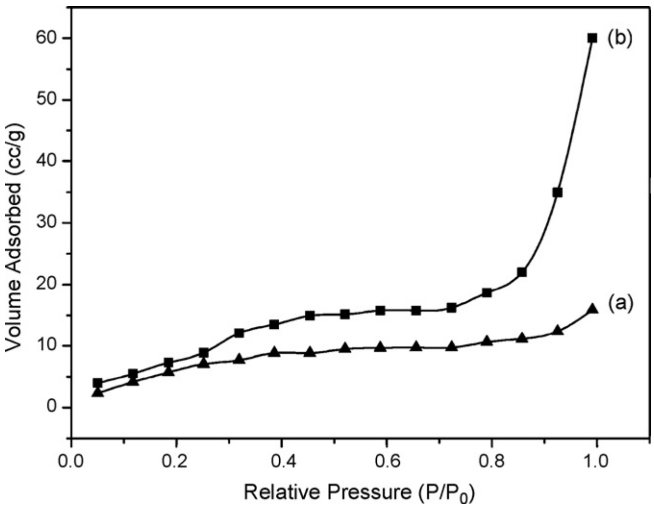

Fig. 6. N_2 adsorption curves of nanofibrous mat (a) before and (b) after calcination.

formation of pure CdO nanofibers. The other peak at 3400 cm^{-1} corresponds to the absorbed water vapor after bringing the specimen out of the furnace.

Fig. 5 depicts the XRD patterns for the electrospun fibers before and after calcination at 450 °C on Si substrate. As shown in Fig. 5(a), in the PVA/cadmium acetate composite fibers, no sharp diffraction peak was observed which indicates presence of no crystalline CdO. Instead, a broad peak with very low intensity around $2\theta = 20°$ corresponds to the (1 0 1) plane of PVA [26,27]. These results signify that the crystallinity of PVA is affected by the presence of cadmium acetate in the PVA fibers, saying that there might be some interaction between PVA and cadmium acetate molecules. After the PVA/cadmium acetate composite fibers were calcined at 450 °C (Fig. 5(b)), crystalline peak of PVA disappeared, and five diffraction peaks appeared at $2\theta = 33.05$, 38.34, 55.33, 65.96 and 69.28 which are associated with (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2). The planes have d-spacing values of 2.71, 2.35, 1.66, 1.42 and 1.36 Å respectively, corresponding to pure CdO crystalline phase. The crystal lattice parameter was calculated from the crystallographical relations to be $a = 4.698$ Å which is consistent with the CdO ASTM value (card 05-0640), 4.695 Å.

Certainly, decomposition of organic materials during the calcination process leads to the reduction in the diameter of precursor fibers and also to the formation of some pores in the structure which increases the specific surface area of the nanofibers. The specific surface area of the nanofibrous mat before and after calcination was evaluated by taking advantage of BET equation and using the data of the lower part of N_2 adsorption isotherm ($0.05 < p/p_0 < 0.35$), shown in Fig. 6. Calculated surface areas, which are 30.1235 and 42.6711 m^2 g^{-1} respectively, confirm the idea of increase in surface area after calcination due to decrease in fibers diameter and organic materials decomposition. Such a high surface area makes the resultant CdO nanofibers an excellent candidate for application in dye sensitized solar cells and gas sensors [28].

In order to study the optical properties of the product, the related PL spectrum was recorded. Fig. 7 shows room temperature PL spectrum of CdO nanofibers under excitation wavelength of 430 nm. Clearly, it could be seen that there are two emission peaks at 493 and 528 nm. The first one is attributed to the excitonic transitions which is size-dependent and excitation wavelength-independent in certain wavelength range and the second one can be ascribed to the deep trap emission and surface-state emission that is less size dependent [3]. Thus bandgap of nanofibers that is related to the first wavelength would be estimated to be about 2.51 eV. Compared to the previously reported data on the photoluminescence of CdO nanowires [13,16], our PL results show an emission peak at shorter wavelengths with a narrow fwhm (about 47 nm), indicating a narrow distribution of nanofibers diameters.

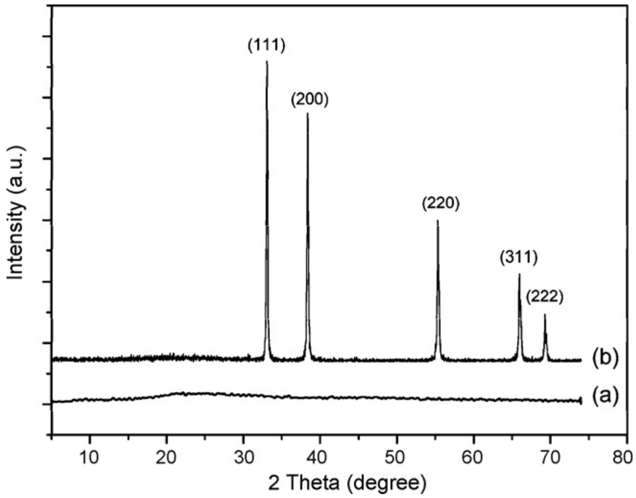

Fig. 5. XRD patterns of (a) PVA/cadmium acetate precursor fibers and (b) CdO nanofibers.

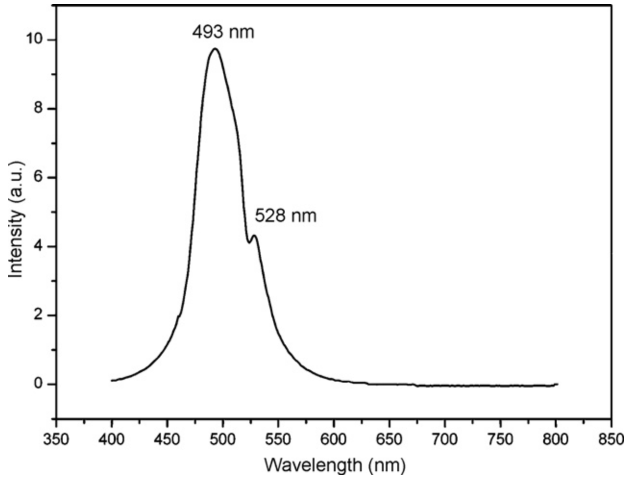

Fig. 7. Room temperature photoluminescence spectrum of CdO nanofibers excited at 430 nm.

The low intensity of peak at 528 nm indicates a low concentration of surface defects.

4. Conclusion

In this paper we have reported the successful implementation of the electrospinning technique followed by a single-step calcination to produce centimeter-long CdO nanofibers from the aqueous solution of PVA and cadmium acetate dihydrate, for the first time. The results of the EDS, FT-IR and XRD analyses proved that the obtained nanofibers were pure phases of CdO on Si collectors.

Furthermore SEM and TEM micrographs illustrated that the resulting nanofibers were smooth and exhibited uniform diameter in the range of 50–60 nm along their entire length.

The BET surface area determination verified that the decomposition of organic materials during the calcination process results in an increase in the specific surface area of the nanofibers which makes them suitable for different applications in various fields from gas sensors to dye synthesized solar cells. The specific surface area of the product was calculated to be 42.6711 $m^2\,g^{-1}$.

The study on the optical properties based on the PL spectrum demonstrated that the emission peaks of CdO nanofibers are centered at 493 and 528 nm. The low intensity of the green emission properly indicates that the number of deficiencies is low.

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