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Studies on the synthesis of $CdCO_3$ nanowires and porous CdO powder

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ABSTRACT

In the present study, we demonstrate the self transformation of aqueous cadmium acetate into $CdCO_3$ nanowires through hydrothermal reaction. The reaction temperature and the volume ratio of water to ethanol were found to be crucial for the formation of $CdCO_3$ nanowires. The nanowires are of single crystal in nature having width ~17–30 nm as observed from selected area electron diffraction (SAED) pattern and transmission electron microscopic (TEM) results. The major weight loss found in thermogravimetric analysis (TGA) corresponds to the formation of CdO and CO_2. The powder X-ray diffraction (PXRD) patterns of $CdCO_3$ and CdO are respectively indexed to pure rhombohedral and cubic phases. The photoluminescence (PL) spectrum of CdO exhibits an emission peak at 483 nm due to the transition between the valence and conduction bands.

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1. Introduction

Over the past several years, considerable attention has been paid to fabricate low dimensional (1D or 2D) nanostructures [1,2]. A wide variety of methods are reported for the synthesis of nanostructures of elements, oxides, nitrides, carbides and chalcogenides ranging from vapor-phase technique to solution-growth processes [3]. The hydro-thermal technique as one of the synthetic routes has been widely utilized to produce one dimension (1D) inorganic nanostructural materials at temperatures often below 200 °C. Its distinct advantage is to induce the formation of high-crystallized powders with narrow particle size distribution and high purity without post annealing at high temperatures. Furthermore, the properties such as particle shape and size of the products can be well controlled simply through adjusting the synthesis conditions including temperature, reaction time, pH and composition of the solution [4]. Hydrothermal synthesis is therefore considered as an attractive route for producing nano-crystalline materials with low energy waste and high efficiency.

Bulk CdO is an n-type semiconductor, with a wide direct band gap of 2.27 eV and a narrow indirect band gap of 0.55 eV [5]. Because of its large linear refractive index ($n_o = 2.49$), it is a promising candidate for optoelectronics applications and other applications, including solar cells, phototransistors, photodiodes, transparent electrodes and gas sensors [6–10]. Several techniques have been used to prepare CdO films, microwhiskers, nanoneedles, belts, cubes, nanoclusters, nano-particles, wires and rods [11–21]. But to the best of our knowledge, synthesis of porous CdO was rarely reported [22].

Generally, sodium carbonate or carbon dioxide is used for the preparation of carbonate salts such as $CaCO_3$, $PbCO_3$, $BaCO_3$ and $MnCO_3$ [23–26]. Recently, $CdCO_3$ nanoparticles, nanowires, nanobelts and nanorolls were prepared via wet chemical methods [27,28]. Even though many methods have been reported in the literature, the interest in the field of genesis of $CdCO_3$ and CdO nanostructures has not been diminished. In the present study, we demonstrate a self conversion of cadmium acetate into $CdCO_3$ in ethanol–water mixture in the absence of external carbonate source, surfactant, complexing/ capping agent and hydroxide source. The hydrothermal derived $CdCO_3$ products were heat treated at 450 °C for 0.5 h to obtain the porous CdO powder.

2. Experimental

In a typical synthesis, 1.33 g of cadmium acetate was dissolved in 25 ml distilled water. To this solution, 25 ml ethanol was added and stirred for 20 min. The obtained clear solution was subjected to hydrothermal treatment at 180 °C for one day (1d). After the hydrothermal process, the autoclaves were cooled to ambient temperature and the resultant white solid was extracted by centrifugation. Then the solid product was washed with distilled water followed by ethanol and finally dried at 60 °C for 2 h.

Powder X-ray diffraction data were recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu Kα radia-tion. The Fourier transform infrared (FTIR) spectrum of the sample was collected using Thermo Nicollet FTIR spectrometer. Thermo gravimetric analysis was carried out using Perkins Elmer 7 series thermal analysis system at a heating rate of 5 °C/min. The morphology of the product was examined by JEOL-JSM-6490 LV scanning electron microscope (SEM) and Hitachi-H-8100 transmission electron

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microscope (accelerating voltage up to 200 kV, LaB_6 filament) equipped with EDS (Kevex Sigma TM Quasar, USA). The absorption and photoluminescence studies were carried out using Shimadzu visible spectrometer (UV-3101) and Perkin-Elmer LS-55 lumines-cence spectrometer equipped with Xe lamp (excitation wavelength, 450 nm) at room temperature.
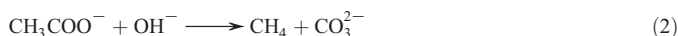
3. Results and discussion

Fig. 1a and b shows the PXRD patterns of the $CdCO_3$ nanowires and the corresponding CdO obtained by thermal decomposition at 450 °C for 0.5 h. All the diffraction peaks in the PXRD pattern (Fig. 1a) can be readily indexed to a pure rhombohedral phase of $CdCO_3$ with lattice constants $a = 4.923$ Å, $c = 16.28$ Å (JCPDS 72-1939). Thermally trea-ted $CdCO_3$ (Fig. 1b) exhibits pure cubic phase of CdO with lattice constant $a = 4.695$ Å (JCPDS 75-0594).

The formation of $CdCO_3$ products was further confirmed by FTIR and TGA studies. The peaks (Fig. 1c) around 1400 cm^{-1}, 850 cm^{-1} and 718 cm^{-1} are the characteristic vibration bands of CO_3^{2-} [29]. The initial weight loss ~5% observed in TGA curve up to 160 °C (Fig. 1d) is due to the evaporation of physically adsorbed water. The subsequent major weight loss ~26% found between 160 °C and 500 °C is related to the decomposition of $CdCO_3$ into CdO and CO_2. The TGA result is well within the theoretical weight loss of ~25.6% that can be depicted by the following reaction [30].

$$CdCO_3 \longrightarrow CdO + CO_2$$

The probable reaction mechanism for the formation of $CdCO_3$ can be explained as follows. Conversion of acetate ion into carbonate ion takes place in presence of OH^- ions [27], which results by the intrinsic weak basicity of acetate ion as shown in Eq. (1) [31].

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \tag{1}$$

$$CH_3COO^- + OH^- \longrightarrow CH_4 + CO_3^{2-} \tag{2}$$

$$Cd^{2+} + CO_3^{2-} \longrightarrow CdCO_3 \tag{3}$$

It is found that the formation of the $CdCO_3$ nanowires has been influenced significantly by the temperature. Generally, temperature is believed to have a great impact on the crystal forms of the final products. We have carried out analogous experiments at 140 °C, 160 °C and 180 °C for comparative studies. The $CdCO_3$ product obtained at 140 °C (Fig. 2a) exhibits round rose-lets nanostructures made of platelets. Whereas, the products obtained at 160 °C and 180 °C were mainly nanowires as observed in Fig. 2b and c. Obtained $CdCO_3$ nanowires having the smooth surface with an average diameter of about 60 nm and the length of several tens of micrometers. TEM images (Fig. 3a and b) reveal that the $CdCO_3$ products consist of ultralong nanowires of a few micrometers in length and several tens of nanometers in width (17–30 nm). The SAED pattern (Fig. 3c) shows that the $CdCO_3$ nanowires are single crystal in nature. The EDX spectrum (Fig. 3d) reveals the existence of Cd, C and O only.

Generally, the solution with a lower supersaturation was favorable for the anisotropic or 1D growth of the crystals, which can be achieved using dilute reactants or chelating agents [9]. Formation of carbonate ion takes place in presence of OH^- ions. Since no base being added in the present case, hydroxide ion is formed due to the equilibrium reaction between acetate ion and water under hydrothermal process [31]. This equilibrium reaction is responsible to achieve lower supersaturation of reactants. Because of in situ formation of carbonate ion by the reaction between acetate ion and hydroxide ion, the $CdCO_3$ nanowires formed when the reactants achieved supersaturation. This preparation method is different from the previous reports made for the preparation of other 1D material such as, TiO_2 nanofibres, VO_2 nanobelts and $CdCO_3$ nanobelts [10,32,33].

The influence of water quantity in water–alcohol mixture on the growth of $CdCO_3$ nanowires is another important parameter. $CdCO_3$ nanowires are obtained when water to ethanol ratio is 1 ($V/V = 1$) (Fig. 2c) whereas, irregular morphology is observed when water to ethanol ratio is 2:1 ($V/V = 2$).
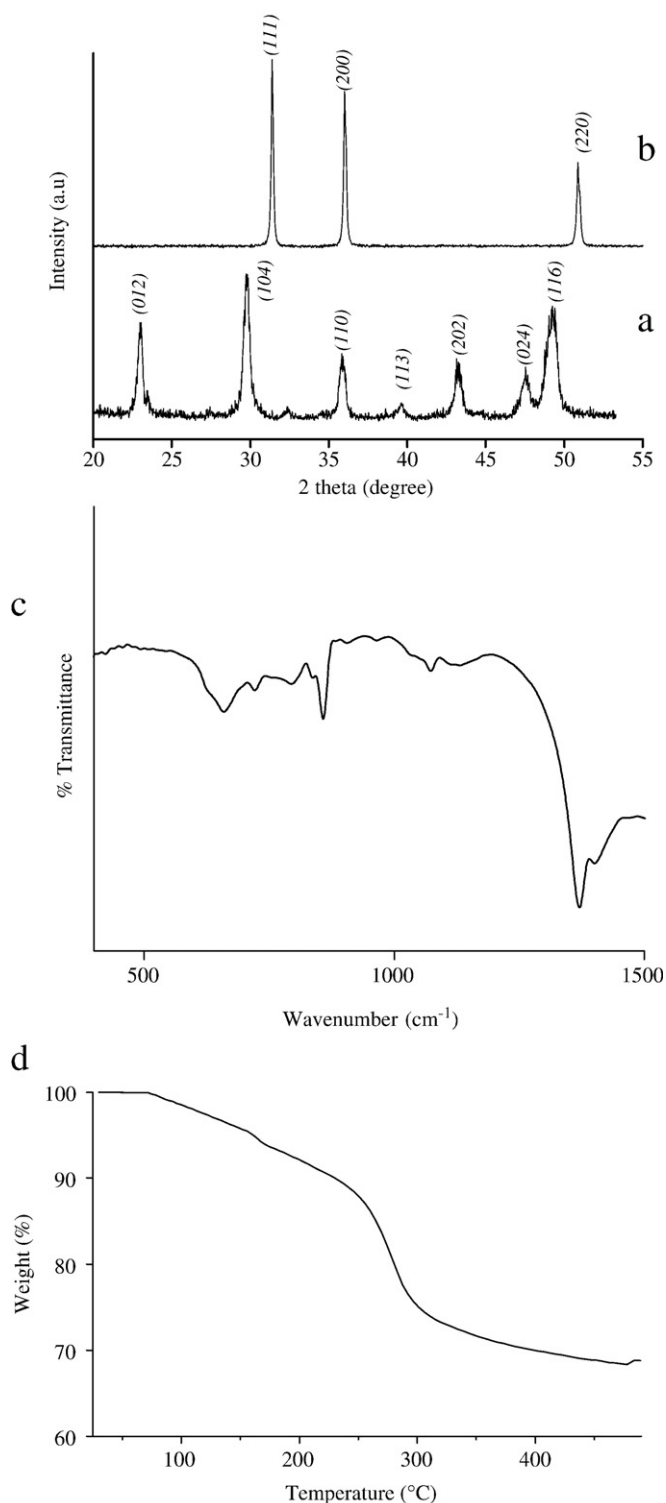

Fig. 1. PXRD patterns of (a) $CdCO_3$ nanowires, (b) porous CdO, (c) FTIR and (d) TGA curve of $CdCO_3$ nanowires prepared at 180 °C for 1d.
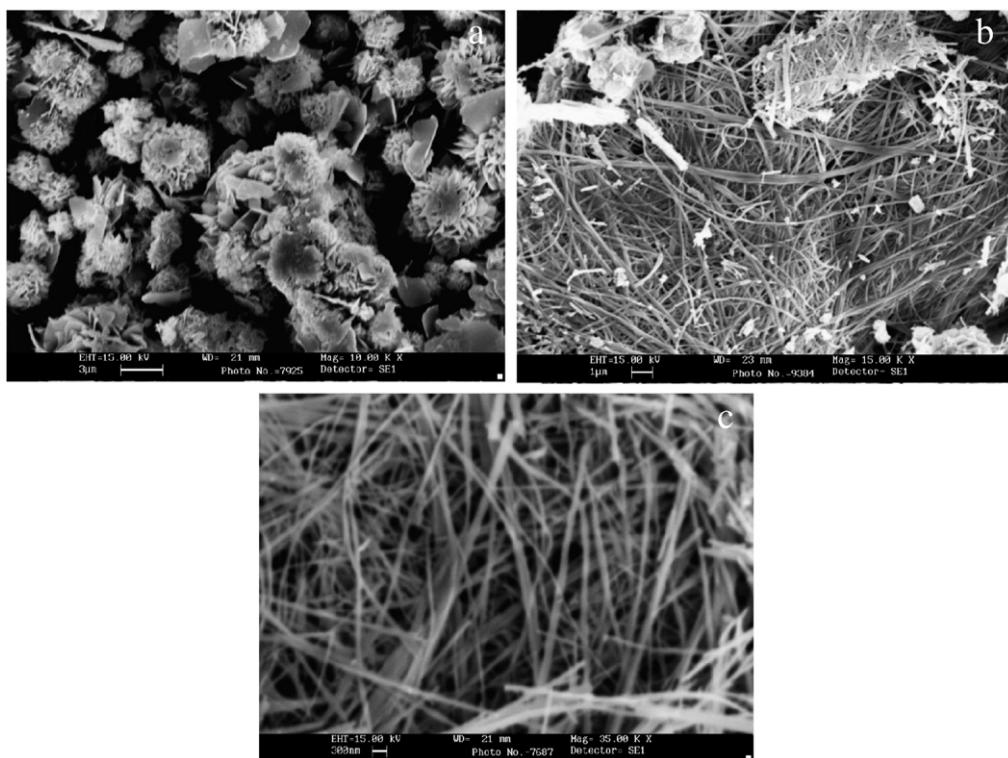
Fig. 2. SEM images of CdCO$_3$ products prepared at a) 140 °C, b) 160 °C and c) 180 °C for 1 d.

Fig. 4 shows the SEM image of the CdO products obtained from thermal decomposition of CdCO$_3$ nanowires does not retain the parent morphology of nanowires as observed in Fig. 2c. Instead, the SEM image exhibits an agglomerated porous CdO due to the liberation of CO$_2$ during thermal treatment [28].

The UV–Vis spectrum of CdO product (Fig. 5a) dispersed in ethanol showed a maximum absorbance at 490 nm, attributed to exciton absorption [34]. Room temperature PL spectrum of CdO excited at 450 nm (Fig. 5b), exhibit a band at 483 nm. The band at 483 nm arises from the transition between the conduction and valence bands [19].
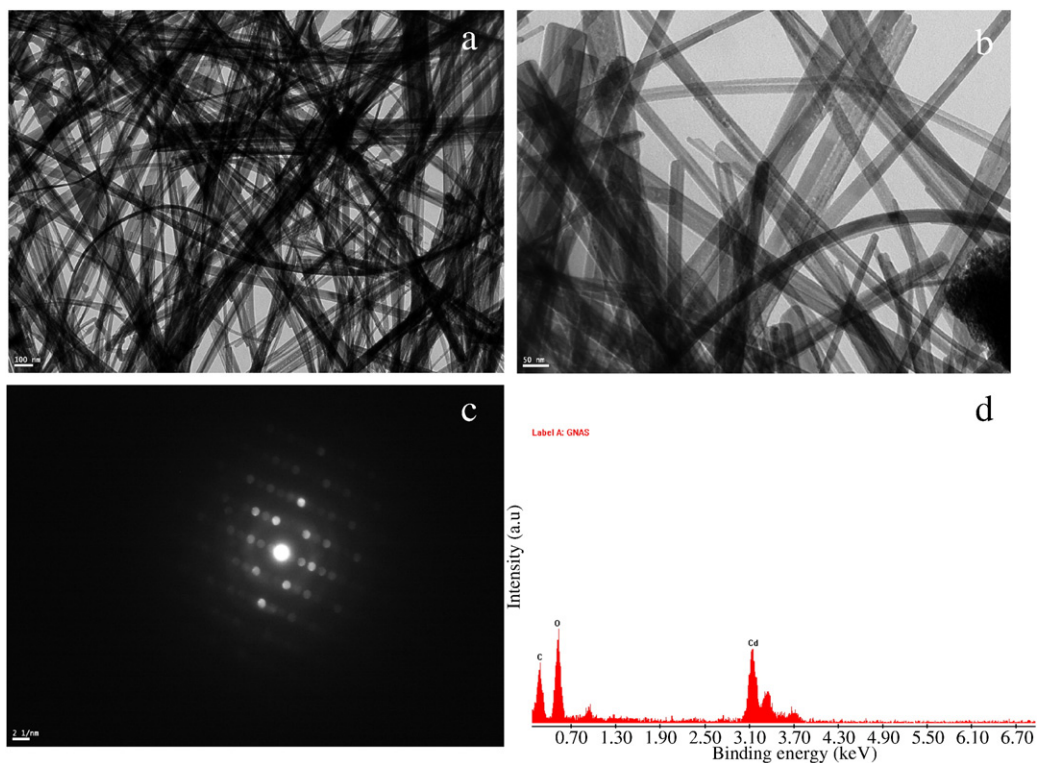

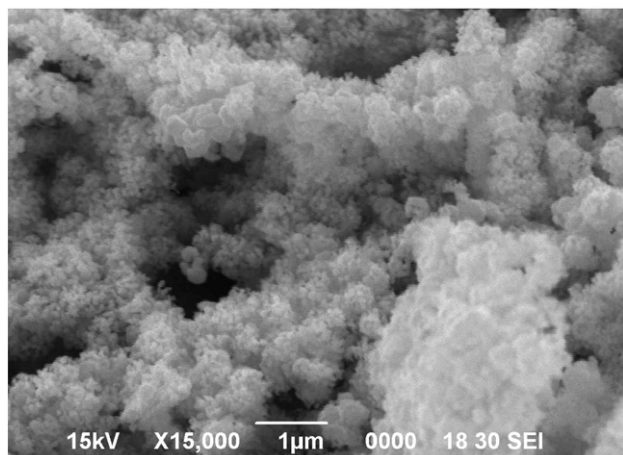**Fig. 3.** TEM images (a, b), SAED pattern (c) and EDX spectrum (d) of CdCO$_3$ nanowires.

Fig. 4. SEM image of CdO products prepared by thermal decomposition of CdCO₃ at 450 °C for 0.5 h.
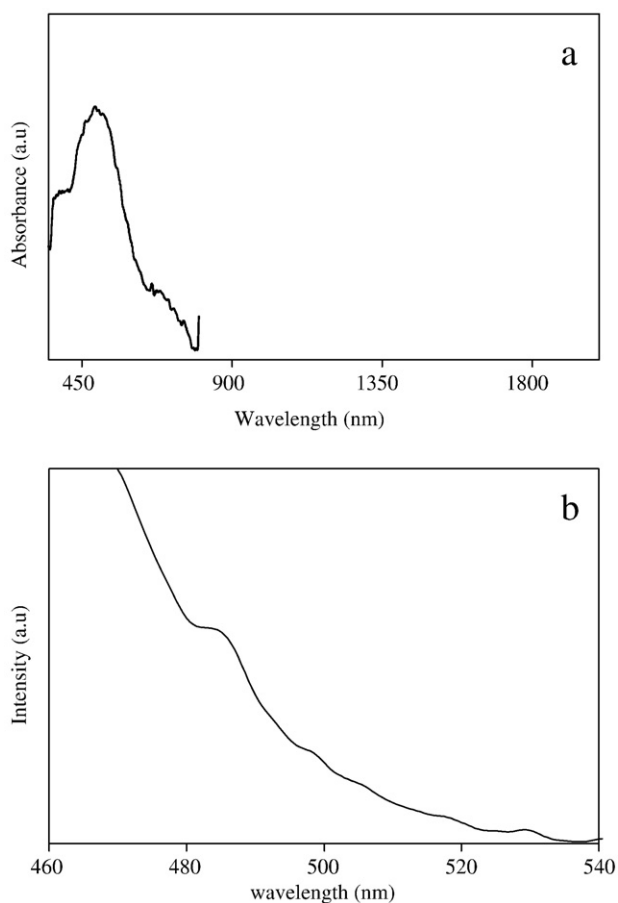

Fig. 5. (a) UV–Vis and (b) room temperature PL spectra of CdO product.

product is formed due to the self conversion of cadmium acetate in presence of ethanol during hydrothermal process. Simply by calcining the $CdCO_3$ product at 450 °C, porous CdO powder was obtained.

Acknowledgements

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4. Conclusions

In conclusion, $CdCO_3$ nanowires have been successfully prepared by a simple hydrothermal route at 160 °C and 180 °C for 1d. $CdCO_3$