

Synthesis of Cd(OH)₂ and CdO nanoparticles via a PEG-assisted route

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Nano cadmium hydroxide has been synthesized using PEG400 as the template at room temperature. Then this nano cadmium hydroxide recrystallizes into nano cadmium oxide at 400 °C for 2 h. The products were characterized by X-ray diffraction (XRD), IR, optical absorption measurement, scanning electron microscopy (SEM) and EDAX. The effect of reaction time, temperature, solvent and molecular weight of the PEG on the formation of nanostructures CdO was investigated in detail.

Key words: CdO, X-ray diffraction, PEG, Nanostructure.

Introduction

The synthesis of nano structures of semiconductors in a nano powder form has been a rapidly growing area of research due to their important optical, physical and chemical properties [1]. Cadmium oxide (CdO), an n-type semiconductor with a direct wide band gap (2.27 eV) and a narrow indirect band gap of 0.55 eV [2] is widely used in applications such as the preparation of cadmium-coated baths and manufacturing of paint pigments. It has a cubic (NaCl type, fcc) crystal structure with alternating Cd and O atoms located at lattice points, with a high density (8150 kg m⁻³) and melting point (1500 °C) [3]. It is widely used in applications such as photodiodes [4], phototransistors [5], gas sensors [6], photovoltaic cells, and paint pigments. For these applications, particle size, porosity, and specific surface area are of major importance. Recently, various one-dimensional CdO nanostructures such as nanowires, nanoneedles, nanobelts and nanorods have been synthesized by different methods such as solid-state transformation metal-organic framework [7], vapor phase transport [8], template-assisted [9] and solvothermal method [10].

Generally, long chain polymers help the growth of 1D nanostructure, but their practical uses are very limited. It is feasible that short chain polymers can also promote the formation of nanostructures [11]. Therefore, we can use short chain polymers to selectively control synthesis of nanostructures. In the present study, a short-chain polymer, poly (ethylene glycol) (average molecular weight 400, abbreviated as PEG400) is found to selectively promote the formation of Cd(OH)₂ nanoparticles. The nanopowders obtained were calcinated

to 400 °C for 2 h to recrystallize to CdO nanoparticles. This method develops a new route to synthesize other nano scale particles.

Experimental

All the reagents were of analytical grade and were used without any purification. In a typical experimental procedure, Cd(CH₃COO)₂·2H₂O was dissolved in distilled water to form a 0.5 M solution. The precursor solution obtained (4 ml) was added to a 100 ml conical flask containing mixed solutions of 50 ml distilled water, 2.8 gr NaOH, 10 ml of PEG400 and were blended well by stirring for 10 minutes subsequently, the mixed solution was placed for a certain times at room temperature (Table 1). After each synthesis white crystalline products were collected by centrifugation, washed with distilled water and ethanol several times and dried at 60 °C in a vacuum for 10 h.

Cadmium hydroxide nano particles in white powder form which transformed into brown cadmium oxide nano particles after being in a furnace at 400 °C for 2 h. By changing the temperature, we could vary the particle size. Different reaction conditions and products are summarized in Table 1.

The products were characterized by X-ray diffraction

Table 1. Summary of experimental conditions and corresponding products

Furnace Reaction time (h)	Mw of PEG	solvent	Vol. of PEG (ml)	Heating Temperature °C	Reaction time (day)	Reaction number
5	400	H ₂ O	10	250	2	1
5	400	H ₂ O	10	250	6	2
5	400	EtOH	10	250	6	4
2	400	H ₂ O	10	400	4	5
2	400	H ₂ O	10	600	4	6

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(XRD) with Cu K α ($\lambda = 1.5418 \text{ \AA}$) incident radiation. XRD patterns were recorded from 4° to 100° (2θ) with a scanning step of 0.04° .

The optical absorption was examined on a Perkin Elmer, lambda UV-Vis by dispersing Cd(OH) $_2$ and CdO powder in anhydrous alcohol and using anhydrous alcohol as the reference. IR spectra was obtained using KBr discs ($4000, 500 \text{ cm}^{-1}$) on a Bruker tensor 27 FTIR spectrophotometer. The SEM images were made on a Philips XL30, EDAX connected to SEM was employed to perform the elemental analyses of the nanostructures materials.

Result and discussion

Fig. 1 shows a typical XRD pattern of the synthesized products prepared at 400°C . Peaks at $2\theta = 32.99^\circ$, 38.29° and 55.26° correspond to (111), (200) and (220) Bragg's reflection planes of cubic CdO respectively (JCPDS card No. 5-640) [12]. Sharp and intense peaks prove the synthesis of good quality crystalline CdO with a 24.5 nm average diameter calculated by using Scherrer's formula $D = (0.9)\lambda / \beta \cos\theta$; where D is the crystal diameter, λ is the X-ray wavelength, β is the full width half maximum (FWHM) at a selected 2θ . No peak attributable to possible impurities was observed during this procedure. The surface morphology of the as-synthesized dried powder was studied using SEM and is illustrated in Fig. 2a-b. Fig. 2a shows a top view

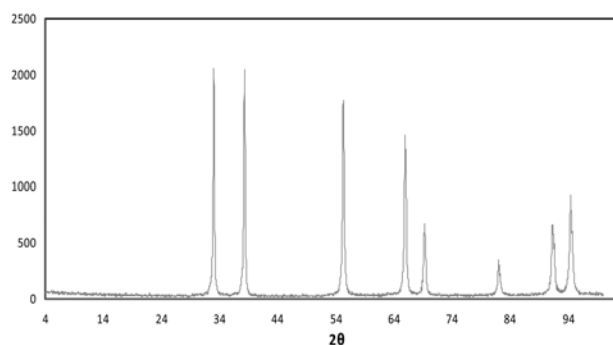


Fig. 1. Powder XRD pattern of the CdO nanoparticles from reaction no. 5. The positions of the (111), (200), (220), (311) and (222) peaks are at $33.00, 38.27, 55.26, 65.92$ and $69.28, 2\theta$ respectively, using the Cu K α radiation at $\lambda = 1.5405 \text{ \AA}$. The presence of Cu K α radiation at $\lambda = 1.5443 \text{ \AA}$ possibly resulted in the appearance of the (220), (311) and (222) peaks at $55.45, 66.12$, and $69.50, 2\theta$.

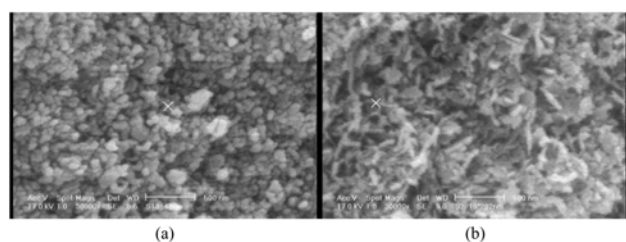


Fig. 2. (a) SEM image of Cd(OH) $_2$ reaction no. 1 before calcination (b) SEM image of the top CdO reaction no. 1

of an SEM image of the Cd(OH) $_2$ nanopowder reaction no. 1 before calcination. Fig. 2b shows a top view of an SEM image of the CdO nanopowder reaction no. 1 which formed rod-type nanoparticles. In order to investigate the effect of both time of aging and temperature on the formation of nano powder of the products, parallel experiments were carried out, see Table 1 Fig. 3a shows a top view of an SEM image of nano granular CdO prepared for 4 days, reaction no. 5 in this reaction uniform nanoparticles were formed. Fig. 3b shows the top view of an SEM image of nano granular CdO prepared for 6 days, reaction no. 2. Fig. 3c illustrates the CdO nanostructure at 600°C , reaction no. 6.

To study the solvent effect the experiment was also carried out in ethanol, reaction no. 4 (Fig. 4). The particle size of Cd(OH) $_2$ which formed in this reaction was uniform but when this hydroxide transfers into CdO the particle size was not uniform.

Fig. 5 displays the EDAX spectrum of the CdO nanostructure measured with the same SEM system. It shows that CdO is a component of the crystals.

UV-Vis absorption spectrum of nano CdO by dispersing the powder in ethanol is shown in Fig. 6. The as-synthesized solution of nano CdO illustrates a

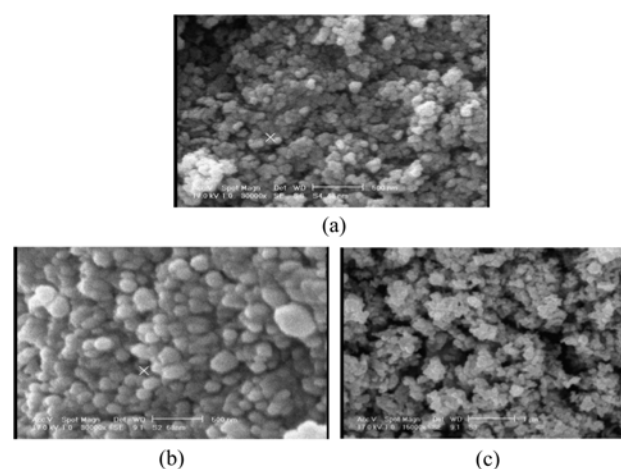


Fig. 3. SEM images of CdO nano particles (a) at 400°C reaction no. 5 (b) 6 days reaction no. 2 and (c) 600°C reaction no. 6

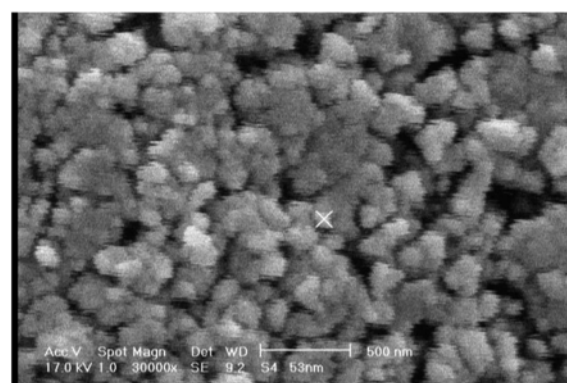


Fig. 4. SEM image of Cd(OH) $_2$ prepared in ethanol.

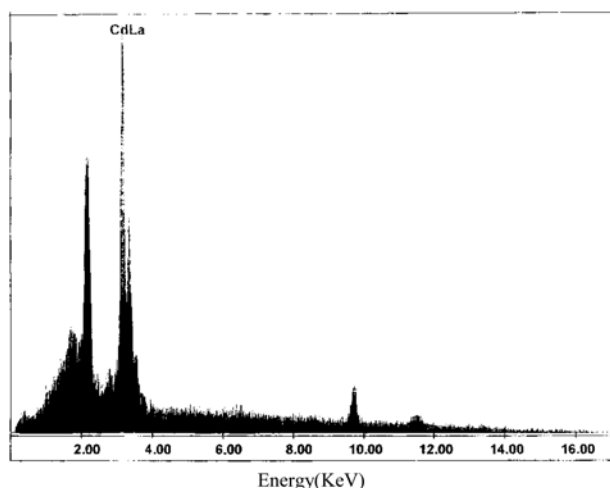


Fig. 5. EDAX spectrum of the CdO nano particles.

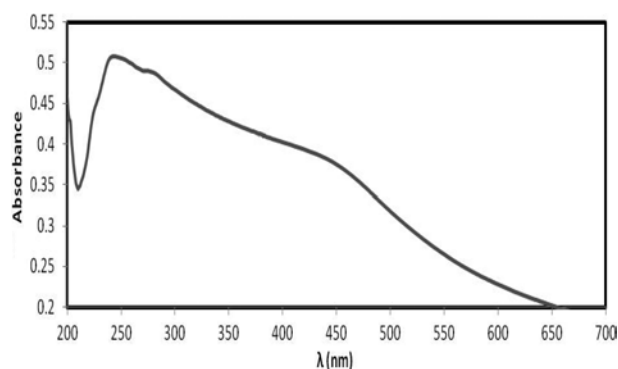


Fig. 6. UV-Vis spectrum of CdO nanostructure.

wide absorption peak centered at 280 nm with a long tail towards a higher wavelength side [13].

With the FTIR spectrum of the as-synthesized powder dispersed in KBr, there is a resolved shoulder in the IR spectrum at 455 cm^{-1} due to the characteristic vibration of Cd-O [14].

Conclusions

This study demonstrated a new method for synthesis of $\text{Cd}(\text{OH})_2$ and CdO nano crystals using a short chain polymer PEG400. PEG400 plays a crucial role in the growth of $\text{Cd}(\text{OH})_2$ nano particles. Therefore by first adding PEG400 to the solution of NaOH and then to the aqueous solution of cadmium acetate it modifies

the growth kinetics of the growing cells, which finally leads to the anisotropic growth of the crystals and forms $\text{Cd}(\text{OH})_2$ nanostructures. This transforms into CdO through heating at 400°C for 2 h.

This method does not need a complicated procedure. The reaction time, temperature and molecular weight of the PEG are important factors in determining the size of CdO .

The method brings forward a new idea of using short polymer chain to synthesize nanostructures of hydroxide, and then this hydroxide under the proper temperature transforms into the desire oxide.

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