

Syntheses and Characterization of Cadmium (II) Oxide Nanostructure from two Nano-sized Cadmium (II) Coordination Polymers

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Abstract

Two nano-sized mixed-ligand Cd(II) coordination polymers; [Cd(4,4'-bpy)(C₄H₄O₄)]·1/4 H₂O (1) and [Cd(bpy)_{1.5}(NO₃)₂].3H₂O (2) (bpy=bipyridine) were synthesized by a sonochemical method and characterized by elemental analyses, thermal gravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The crystallinity of these compounds were studied by Powder X-ray diffraction (XRD). CdO nanostructures were obtained by direct calcinations of nano polymers at 400 °C. The cadmium (II) oxidenano-particles were characterized by Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Keywords: Coordination polymer; CdO; Nanostructure; Calcination.

Introduction

Metal oxide nanostructures have now been widely used in many areas, such as ceramics, catalysis, sensors, transparent conductive films, electro-optical and electrochromic devices [1–5]. The synthesis of nano structures of semiconductors has been a rapidly growing area of research due to their important optical, physical and chemical properties [6]. Cadmium oxide (CdO), is an n-type semiconductor with a direct wide band gap (2.27 eV) and a narrow indirect band gap of 0.55 eV [7]. CdO has high transparency in the visible region of the solar spectrum [8]. Coordination polymers are highly crystalline materials that are constructed from molecular building blocks (metal ions, bridging ligands, counter anions and guest molecules). The structure of this sort of polymer is constructed from coordination bonds, and

the polymer could be grown in one, two and three-dimensional networks. The coordination polymers are prepared by some useful crystallization methods such as slow diffusion, hydrothermal and solvothermal. The ligand must have a bridging organic group at least in one extended dimension and the metal atoms must solely be bridged by this organic ligand. The coordination number of most cadmium polymers equals six and they accept octahedral (Oh) symmetry [9–12]. Cadmium (II) as a metal center with spacer and linker ligands can accommodate all kinds of architectures (1D, 2D and 3D polymers), just as other transition metals [13–16]. Till date many methods have been adopted to grow CdO, including chemical bath deposition [17], solvothermal method [18] and vapor phase transport [19–20]. In this paper, we report synthesis of nano-sized cadmium (II) coordination polymers, with two different

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N-donor organic ligands prepared by a sonochemical method. These nano-coordination polymers were used as precursors for the preparation of cadmium (II) oxide nanoparticles.

Materials and Methods

All the reagents were of the commercial available purity. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz was used for the ultrasonic irradiation. All ultrasonication experiments were carried out at ultrasonic power between 100–110 mW measured by calorimetry [21]. Powder X-ray diffraction (XRD) patterns were collected from a diffractometer of Philips Company with X'PertPromonochromatized Cu K radiation ($\lambda = 1.54 \text{ \AA}$). Microscopic morphology of products was visualized by a LEO 1455VP scanning electron microscope (SEM). The thermo gravimetric analysis (TGA) of compound 1 was carried out with Pyris Diamond Perkin Elmer under air atmosphere at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from room temperature to $500 \text{ }^\circ\text{C}$. Fourier transform infrared spectra were performed using KBr pellets on FT-IR spectrometer (Magna-IR, 550 Nicolet) in the range $400\text{--}4000 \text{ cm}^{-1}$.

Synthesis of nano-sized $[\text{Cd}(4,4\text{-bipy})(\text{C}_4\text{H}_4\text{O}_4)]_n \cdot 1/4 \text{ H}_2\text{O}$ (1) and $[\text{Cd}(\text{bipy})_{1.5}(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$ (2) precursors

Nano-Sized $[\text{Cd}(4,4\text{-bipy})(\text{C}_4\text{H}_4\text{O}_4)]_n \cdot 1/4 \text{ H}_2\text{O}$ (compound 1) was prepared by reaction of between 10 ml of 0.1 M solution of Succinic acid which was added drop-wise to a mixed solution of 10 ml of a 0.1 M solution of ligand 4,4'-bipyridine and a 10 ml of 0.1 M

solution of Cadmium (II) acetate under strong magnetic stirring at room temperature. Then the solution was irradiated with an ultrasonic horn for 30 min. After cooling to room temperature, the precipitates were centrifuged, washed by distilled water and ethanol in sequence and dried in vacuum at $60 \text{ }^\circ\text{C}$. Elemental analysis calculated for $\text{C}_{14}\text{H}_{12.5}\text{CdN}_2\text{O}_{4.25}$: C, 49.12; H, 3.67; N, 8.17. Found: C, 49.14; H, 3.73; N, 8.10 %. Nano-sized $[\text{Cd}(\text{bipy})_{1.5}(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$ (compound 2) was prepared by reaction between 10 ml of 0.1 M solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in MeOH which was added drop-wise to a mixed solution of 10 ml of ligand 4,4'-bipyridine in MeOH under strong magnetic stirring at room temperature. Then the solution was irradiated with an ultrasonic horn for 30 min. After cooling to room temperature, the precipitates were centrifuged, washed by distilled water and ethanol in sequence and dried in vacuum at $60 \text{ }^\circ\text{C}$. Elemental analysis calculated for $\text{C}_{15}\text{H}_{18}\text{N}_5\text{O}_9\text{Cd}$: C, 34.28; H, 3.29; N 13.23; Found: C, 34.73, H, 2.94; N, 12.84:

Synthesis of CdO nanoparticles

For preparation of CdO nanoparticles calcinations of Nano compounds 1 and 2 were done at $400 \text{ }^\circ\text{C}$ in static atmosphere of air for 3h. IR spectrum and powder XRD diffraction show that calcination was completed and pure CdO was produced.

Results and Discussion

Figure 1 shows the FT-IR spectra of compound 1. The IR spectra of compound 1 show absorption bands at around 1566 cm^{-1} due to the C–H of 4,4'-bipy. The C–O modes of Succinic acid were revealed at 1007 and 1044 cm^{-1} . The characteristic bands of the C–N in the pyridine

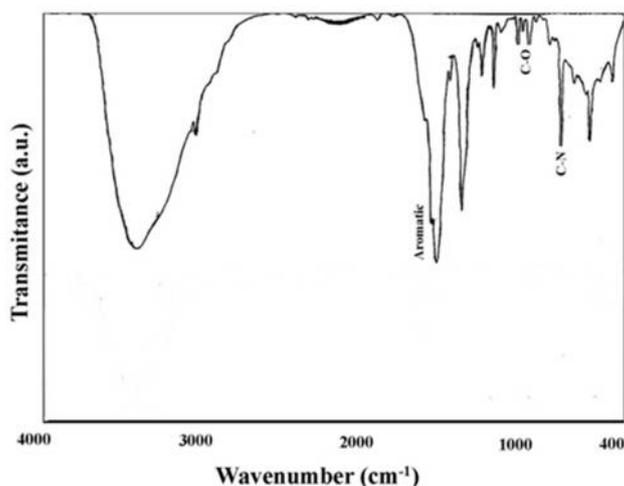


Figure 1. FT-IR spectra of compound 1

ligand was appeared at 807cm^{-1} . The broad absorption band at 3414cm^{-1} was assigned to H_2O modes.

Figure 2 illustrates the IR spectra of compound 2. The IR spectra of compound 2 show relatively weak absorption bands at around 3108cm^{-1} due to the C–H modes involving the aromatic ring. Absorption bands with variable intensity in the frequency range $1490 - 1611\text{cm}^{-1}$ correspond to the C–H mode of 4,4-bipy

ligand. The characteristic band of the NO_3^- was appeared at 1384cm^{-1} .

Figures 3a and 3b illustrate thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of compound 1. TGA and DTA were carried under nitrogen flow. $[\text{Cd} (4,4\text{-bipy}) (\text{C}_4\text{H}_4\text{O}_4)] \cdot 1/4 \text{H}_2\text{O}$ is stable and do not decompose up to 39.5C . Decomposition of the compound 1 occurred in six

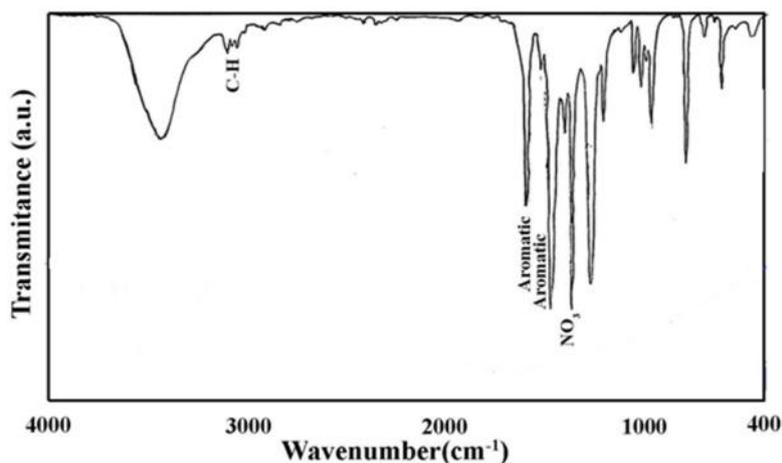


Figure 2. FT-IR spectra of compound 2

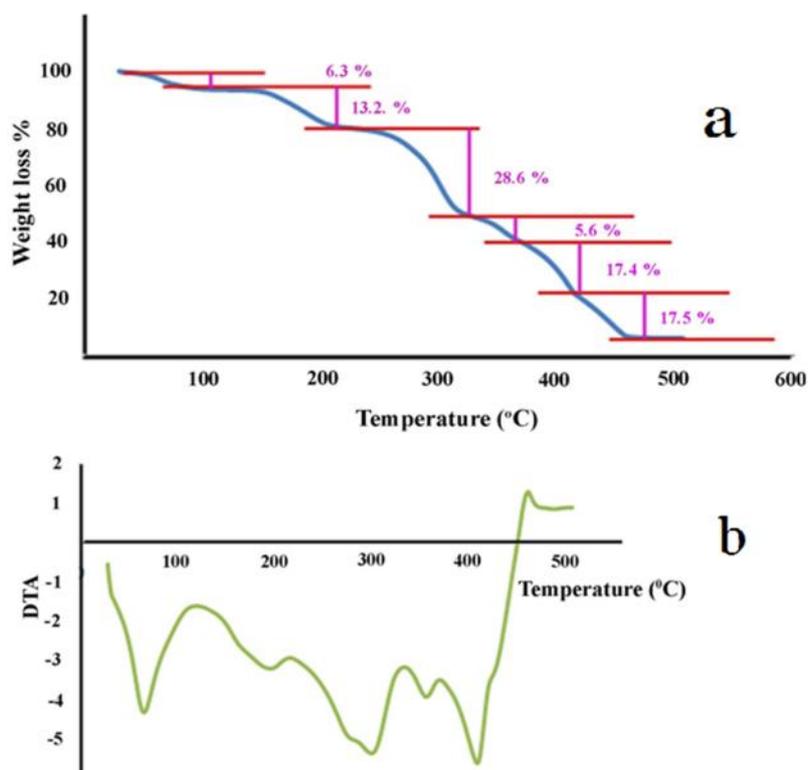


Figure 3. (a) TGA (b) DTA curve of compound 1

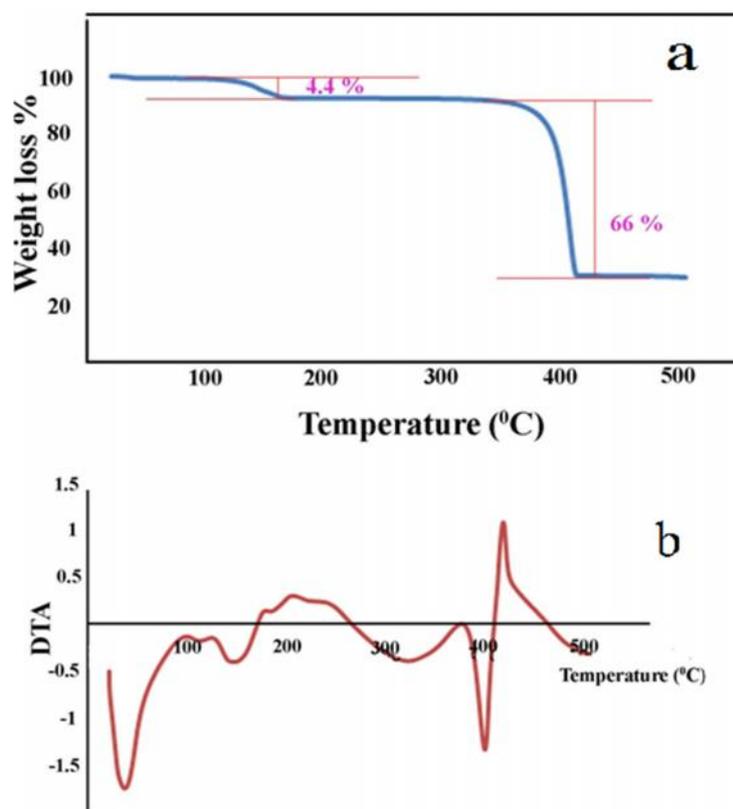


Figure 4. (a) TGA (b) DTA curve of compound 2

weight-loss steps. The first corresponding to 6.3% weight loss, occurred in the range of 39.5 C, which is related to the elimination of H_2O molecules due to its previous exposure to air; other weight losses (13.2%, 28.6%, 5.6%, 17.4%) beginning at 135.8 C are related to the decomposition of 4,4 -bipy and $C_4H_4O_4$. Final weight loss shown (17.5%) at 496 C was related to the decomposition of CdO [22]. DTA curve displays five endothermic effects at 61.2, 183.1, 289.6, 349.4, 403.9 C and five exothermic effects at 106, 204, 324, 363 and 457.6 C. Figures 4a and 4b depict TGA and DTA curves of compound 2, respectively, which was carried out between 30 and 500 °C in air. In the TGA curve, two weight loss steps were observed. According to TGA results, the first weight loss occurred in 117 °C (4.4%) is related to the elimination of H_2O molecules, and another weight loss (66%) shown at 394.1 °C was related to $[Cd(bipy)_{1.5}(NO_3)_2]$ decomposition to CdO. DTA curve displays three endothermic effects 32.1, 138.1 and 397.8 C and six exothermic effects at 88.0, 113, 172, 195, 366 and 416 C.

The morphology and structure of the products were investigated by SEM images. Figures 5a and 5b show SEM images of nanosized compounds 1 and 2. Figures

5c and 5d show SEM images of CdO synthesized by compounds 1 and 2 as Cd source, respectively. Due to the polymeric structure of Cd (II) coordination polymers, high steric hindrance surrounds the Cd center. The structure around Cd atoms plays the surfactant role [23]. Therefore, since $[Cd(bipy)_{1.5}(NO_3)_2].3H_2O$, has higher steric hindrance than $[Cd(4,4-bipy)(C_4H_4O_4)].1/4 H_2O$, nano sized CdO which was synthesized by calcination of compound 2 was much smaller than the one that synthesized from compound 1.

Figures 6a and 6b show the XRD pattern of compounds 1 and 2. Figures 6c and 6d show the XRD pattern of CdO nanoparticles which were prepared by calcinations of nano powders compounds 1 and 2 respectively. As shown in Figures 6c and 6d, pure CdO phase was formed. The diffraction peaks of the products can be indexed to orthorhombic phase CdO. No remarkable diffractions of other impurities such as, C or N can be found, indicating that pure CdO nanoparticles were synthesized. The sharp diffraction peaks indicate the good crystallinity of the nanoparticles and the peak broadening is due to the small particle size of CdO nanoparticles.

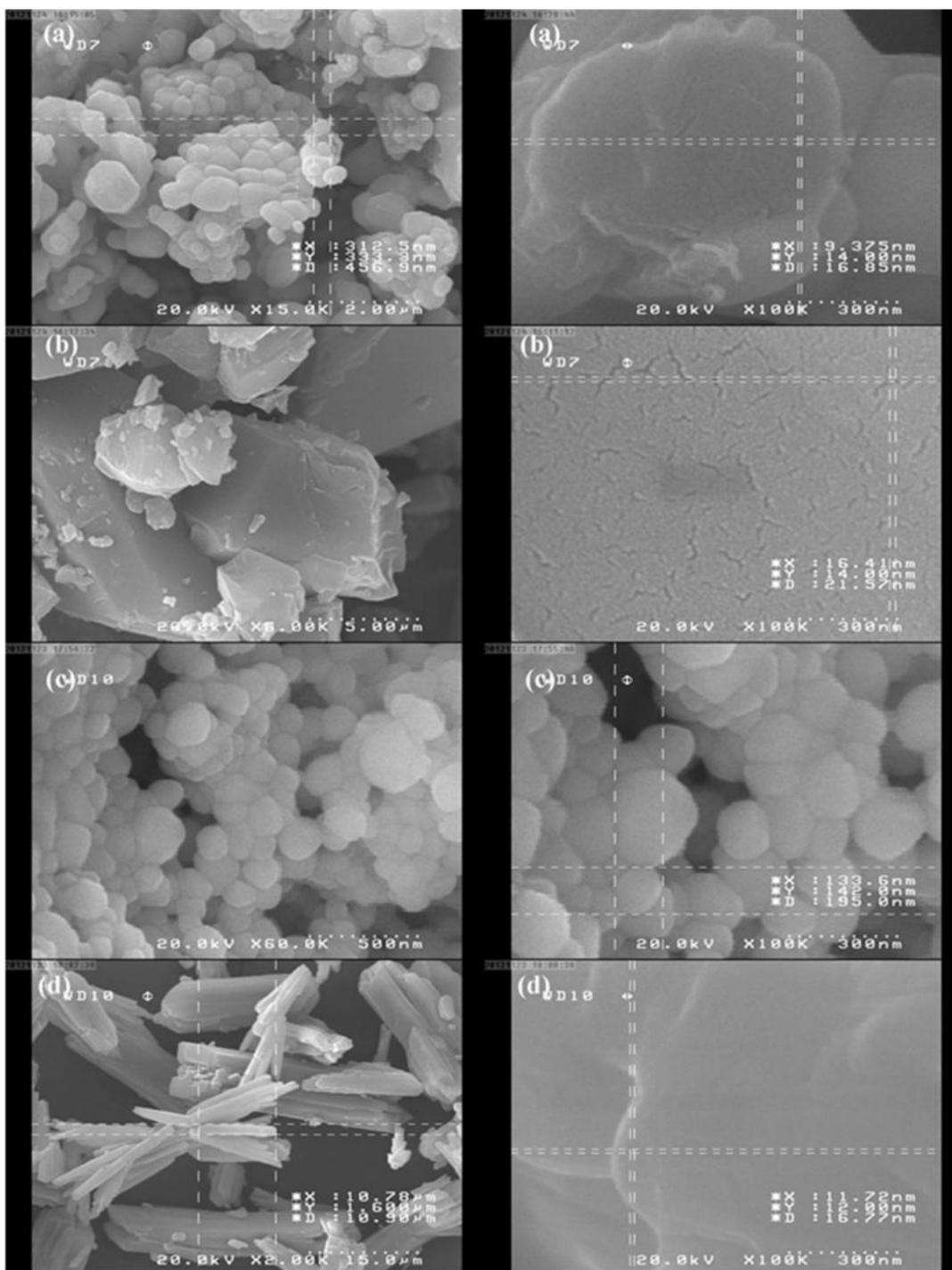


Figure 5. SEM images of (a) nano-sized compound 1, (b) nano-sized compound 2, (c) CdO nanoparticles obtained from calcination of compound 1 and (d) CdO nanorod obtained from calcination of compound 2

Conclusion

In summary, CdO nanoparticles were produced by calcination of nano compounds $[\text{Cd}(4,4\text{-bipy})(\text{C}_4\text{H}_4\text{O}_4)] \cdot 1/4 \text{H}_2\text{O}$ and $[\text{Cd}(\text{bipy})_{1.5}$

$(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$ as starting agents. XRD results indicated that pure CdO nanoparticles have been successfully obtained by this simple route. In this work, we attempted to produce CdO nanoparticles

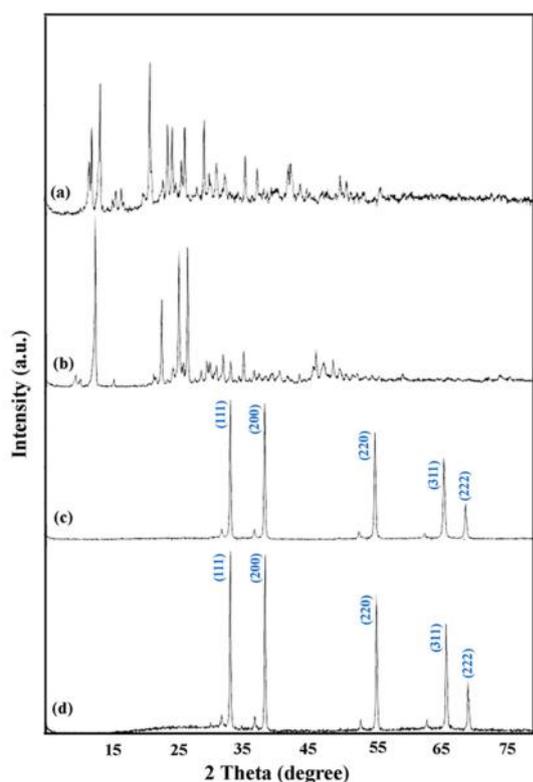


Figure 6. XRD patterns of (a) nano-sized compound 1, (b) nano-sized compound 2, (c) CdO nanoparticles obtained from calcination of compound 1, (d) and CdO nanorod obtained from calcination of compound 2.

without using any capping agent. Hence, we used $[\text{Cd}(4,4\text{-bipy})(\text{C}_4\text{H}_4\text{O}_4)] \cdot 1/4 \text{H}_2\text{O}$ and $[\text{Cd}(\text{bipy})_{1.5}(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$ as new precursors, which can act as surfactant in the reaction medium.

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