



Sonochemical Syntheses of a New Nano-Plate Cadmium (II) Coordination Polymer with Pyridinecarboxylate and Azide Ligands

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ABSTRACT: Nanoplates of three-dimensional coordination polymer, $[Cd_3(3\text{-pyc})_4(N_3)_2(H_2O)]_n$ (1), (3-pyc⁻=3-pyridine carboxylate), have been synthesized by sonochemical method. The CdO nanoparticles were obtained by heating of $[Cd_3(3\text{-pyc})_4(N_3)_2(H_2O)]_n$ nanoplates at 500°C. The $[Cd_3(3\text{-pyc})_4(N_3)_2(H_2O)]_n$ and CdO nanoparticles were characterized by scanning electron microscopy, X-ray powder diffraction (XRD), thermal gravimetric analyses (TGA), differential thermal analyses (DTA) and IR spectroscopy. Results show that size and morphology of CdO nanoparticles are depending on particles size of compound (1) and thermolyses temperature.

Key Words: Nano-Structure, Cadmium(II) Oxide, Coordination Polymer, Crystal Structure

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INTRODUCTION

Nanostructured materials have attracted the attention of researchers not only by their unique chemical and physical properties but also by their potential application in many fields, which has stimulated the search for new synthetic methods for these materials. These materials consist of small grains with sizes below 100 nm. Coordination polymers are a very important topic of modern solid state chemistry. Especially porous compounds have attracted a lot of attention due to their potential as heterogeneous catalysts or adsorbents for gases like hydrogen [1]. But besides porosity there are also attractive aspects of non-porous coordination polymers, e.g. magnetic, luminescent, vaporochromism or conducting properties to name a few [2].

On the other hand cadmium oxide ($E_g \sim 2.3$ eV) is an n-type degenerate semiconductor with high electrical conductivity [3]. Due to its large linear refractive index ($n=2.49$) it is a promising candidate for optoelectronic applications and other applications including solar cells, photo transistors, photodiodes, transparent electrodes and gas sensors [4]. There are several methods reported for the preparation of the CdO nanoparticles, but most of these methods only describe the thin film formation of CdO [5]. There is very little literature available on the synthesis of the particles as a free-standing powder. Pan et al. reported a formation of several nanobeltes at high temperatures from a number of metal oxides, one of them being CdO [6]. The formation of CdO nanoparticles using the thermal treatment of cadmium acetate has been recently described by [4]. Because of possibilities of these interesting applications, there have been some efforts to prepare nanoparticles of CdO and some different methods have been reported for preparing the CdO nanoparticles. Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 KHz-10 MHz) [7]. In the present work we have developed a simple sonochemical [8].

Method to prepare CdO nanoparticles, where in compound 1 is synthesized as a precursor compound by the reaction of cadmium acetate dihydrate, sodium azide and 3-pyridinecarboxylic acid (3-Hpyc) in an ultrasonic bath and is converted to CdO by heating at 500°C in a furnace. The $[Cd_3(3\text{-pyc})_4(N_3)_2(H_2O)]_n$ nanoplate and CdO nanoparticles have been characterized by XRD, TGA, DTA and IR spectroscopy and also morphology and size of the nanoparticles have been observed by SEM.

The structure of compound (1) has been reported by Morsy [9] and the complex in the solid state is a 3D polymeric framework that consists of trinuclear units in which the three Cd centers are held together by four bridging $\mu\text{-N,O,O'}$ -tridentate 3-pyc- anions, two bridging $\mu_{1,1}\text{-N}_3$ - anions and two aqua molecules. The title complex crystallizes in monoclinic with space group P1.

MATERIALS AND METHODS

Experimental Materials: All reagents for the synthesis and analysis were commercially available and used as received. Double distilled water was used to prepare aqueous solutions.

Instruments: An ultrasonic bath (Tecna 6; 50-60 Hz and 0.138 KW) were used for the ultrasonic irradiation. Melting points were measured on an Electrothermal 9100 apparatus. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. The thermal behavior was measured with a PL-STA 1500 apparatus between 35 and 600 °C in a static atmosphere of nitrogen. The simulated XRD powder pattern based on single crystal data were prepared using [10]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu- α radiation. The samples were characterized by a scanning electron microscope with gold coating.

Procedure: To prepare the $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ precursor, a proper amount of the solution of Cd (CH₃COO) 2.2H₂O in water with definite molarity was positioned in an ultrasonic bath, then into this solution, a proper volume of 3-Hpyc and sodium azide solution in water was added in drops, the mole ratios between the 3-Hpyc, NaN₃ and Cd (CH₃COO) 2.2H₂O were different in various batches. The different concentrations of cadmium (II) acetate and ligand 3-pyc⁻, N₃⁻ solution (0.01 and 0.1 M) with same aging time, 1 hr, were tested, however appropriate nano-size of compound 1 obtained under the mentioned conditions with same yield. The obtained precipitates were filtered subsequently washed MeOH and then dried. To form the CdO powders the obtained precipitates were heated at 500°C in a furnace.

RESULTS and DISCUSSION

Fig. 1. A. shows the XRD pattern of a typical samples of $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ prepared by the sonochemical process and Fig. 1. B. shows the XRD pattern of the above samples after heating at 500°C. The obtained patterns match with the standard patterns of $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ and CdO. The crystalline phases of $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ and CdO are respectively triclinic [9] and cubic, with the lattice parameters which are close to the reported values, (JCPDS card number 05- 0640). The broadening of the peaks indicated that the particles were of nanometer scale. Fig. 2 shows the SEM images of the $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ particles. The different concentrations of compound 1 (0.1 and 0.01 M) were tested, however appropriate nano-size (90 nm) of compound 1 obtained under concentration of 0.1 M (Fig. 2. a). According to Fig. 2. B the particles obtained under concentration of 0.01 M in water have been aggregated and its morphology is uniform but at microsize. Fig. 3 shows the SEM image of cadmium (II) oxide nanoparticles with the diameter distribution of 40-60 nm and the average diameter of about 55 nm at 500°C. Fig. 4 shows the DTA and TGA curves of nano-sized compound 1 recorded in static air atmosphere from ambient temperature to 700°C show that the crystalline sample is stable up to 165°C, at which temperature loss one H₂O molecule 1.91% of compound 1. the decomposition of N₃⁻ and 3-pyc⁻ ligands start up to 320°C in one step with four exothermic effects at 372, 390, 405, 420°C and mass loss of 56.2% mass loss calculations of the end residue and XRD pattern of the final decomposition product, shows the formation of CdO. Fig.5 shows the IR spectrum of compound 1 and the spectrum of CdO prepared by heating at 500°C. In the high energy region compound 1 exhibits a strong broad band around 3393 cm⁻¹ corresponding to the water molecules coordinated to the Cd(II) ions and 2055 m V (N₃⁻) and 1609 vs cm⁻¹ V as (-COO⁻) and 1381 after heating vs cm⁻¹, Vs(-COO⁻) disappeared in IR spectra.

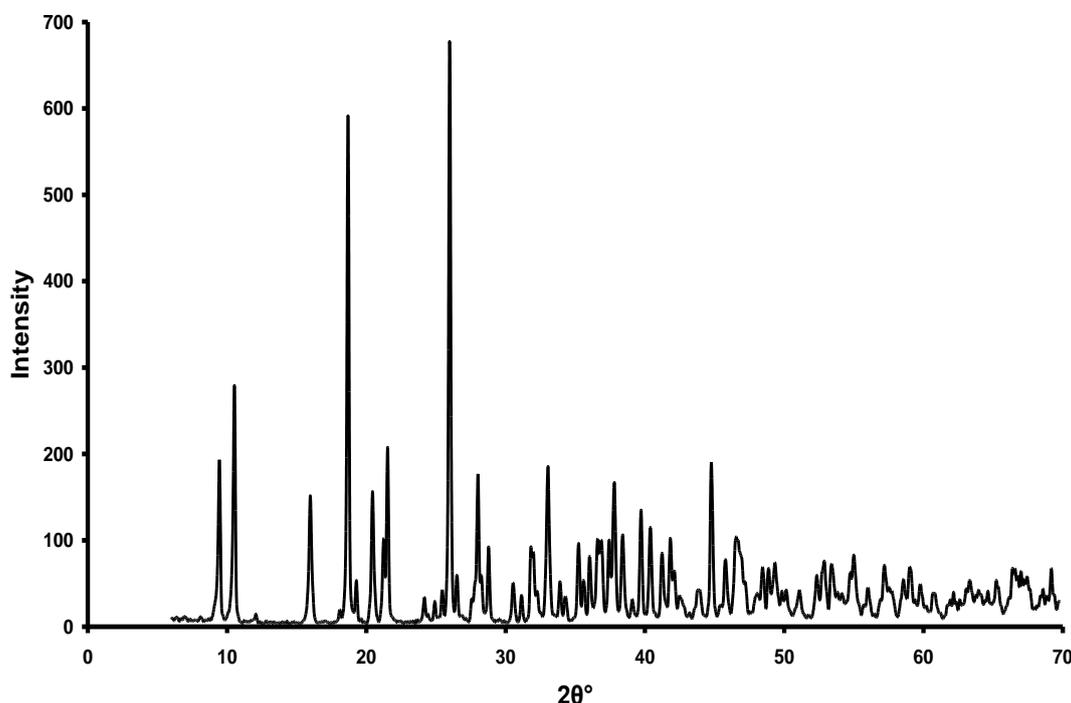


Figure 1. a) The XRD pattern of $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ nanoplates

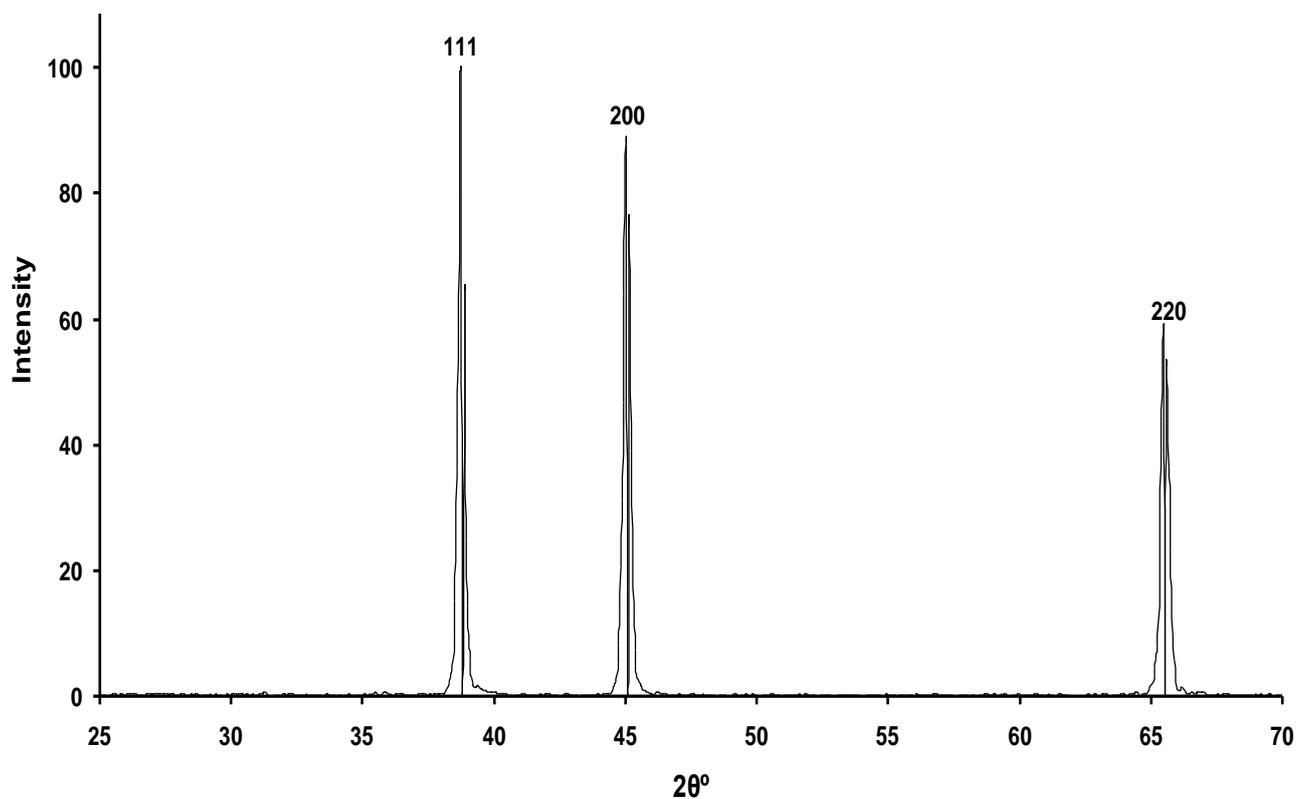


Figure 2. b) The XRD pattern of CdO nanoparticles

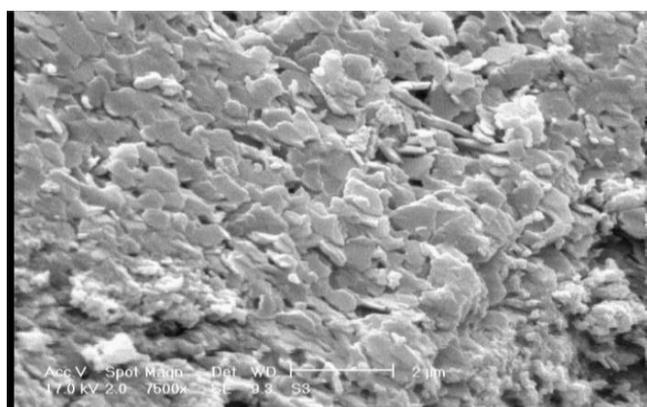


Figure 3. SEM photographs of $[Cd_3(3-pyc)_4(N_3)_2(H_2O)]_n$ a) 0.1 M

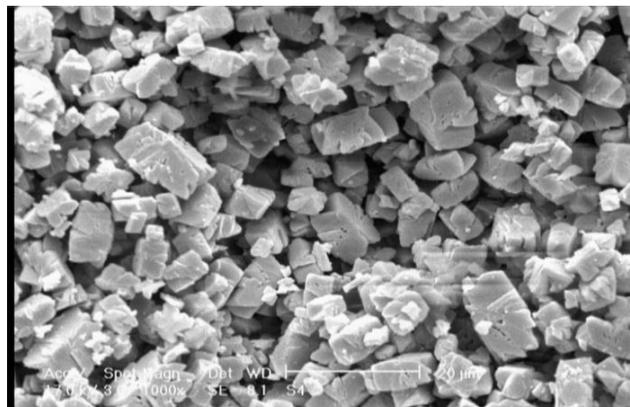


Figure 4. SEM photographs of $[Cd_3(3-pyc)_4(N_3)_2(H_2O)]_n$ b) 0.01 M

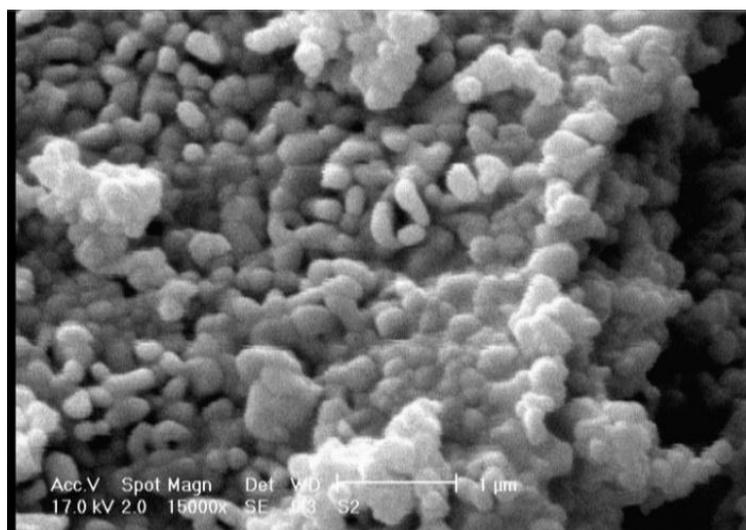


Figure 5. SEM photographs of CdO nanoparticles

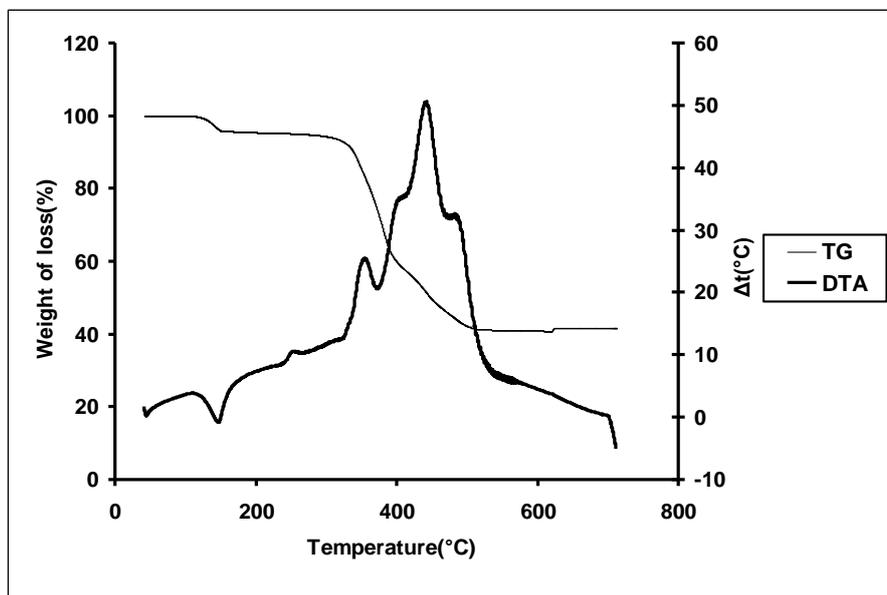


Figure 6. DTA and TGA diagrams of $[Cd_3(3-pyc)_4(N_3)_2(H_2O)]_n$.

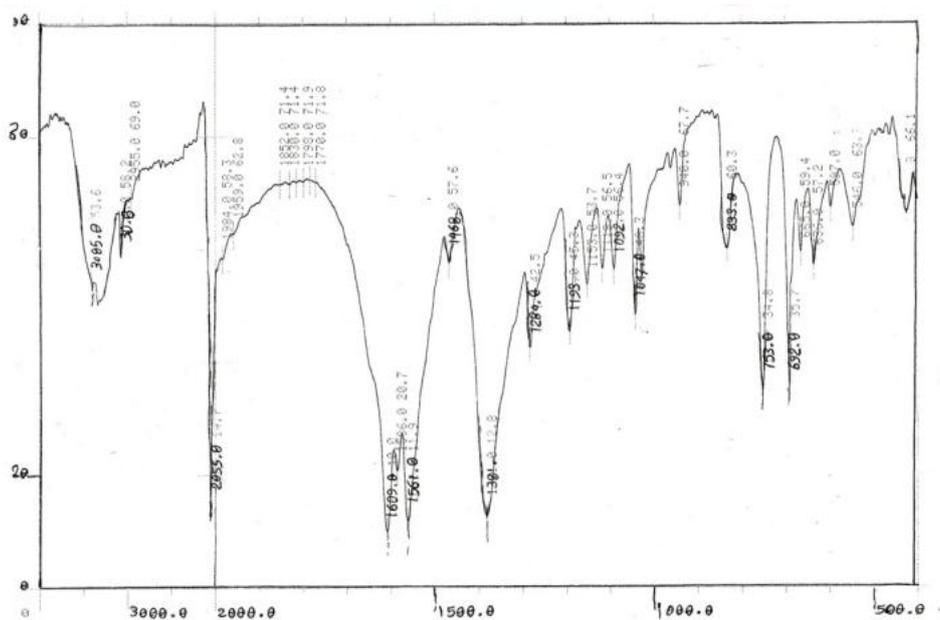


Figure 7. IR -spectra of a) $[Cd_3(3-pyc)_4(N_3)_2(H_2O)]_n$

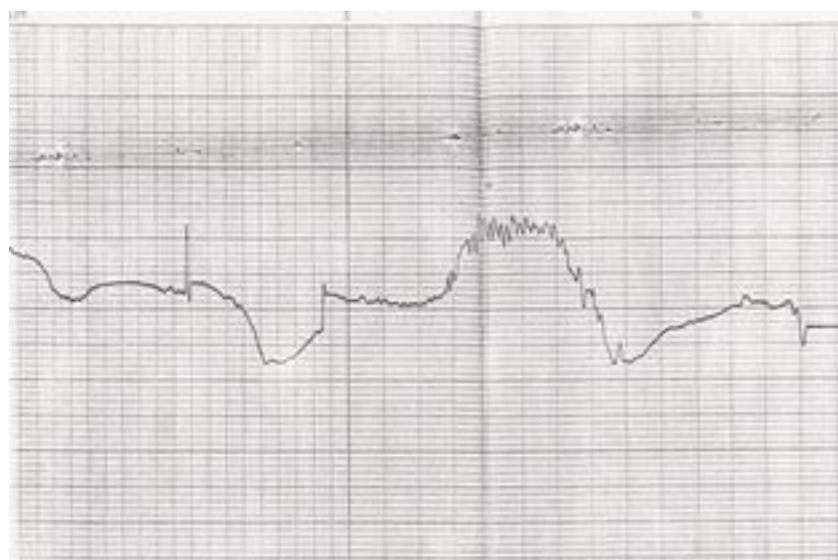


Figure 8. IR -spectra of b) CdO.

CONCLUSION

I have successfully synthesized nano crystalline $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ and CdO through a sonochemical reaction between Cd $(\text{CH}_3\text{COO})_2$, sodim azide and 3-pyridinecarboxylic acid at two different concentrations of initial reagents, 0.1 and 0.01 M, were tested. Of course new nano-sized Cd(II) coordination polymer, $\{[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n\}$ (1), 3-pyc⁻ = pyridine-3-carboxylate) was synthesized by sonochemical irradiation and compared with its crystalline structure that was reported by Morsy A.M. (Abu-Youssef; 2005: 24, 1829-1836). The reactions proceeded under ultrasonic conditions resulting in spherical and uniform CdO and $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ nano crystallites as shown by SEM observations. The recrystallization of CdO from $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ was observed at 420°C in air. By heating $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ at 500°C the CdO nanopowders were obtained and the XRD phase analysis showed the formation of CdO with the cubic symmetry. In our best knowledge, this method in the first one for syntheses of nano particles of $[\text{Cd}_3(3\text{-pyc})_4(\text{N}_3)_2(\text{H}_2\text{O})]_n$ from Cd $(\text{CH}_3\text{COO})_2$ by a sonochemical method. This method can be easily controlled and is expected to be applicable to the fabrication of other nano sized particles.

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