

## Sonochemical Synthesis of a Cobalt(II) Coordination Polymer Nano-structure with azo ligand: A New Precursor for Preparation Pure Phase of $\text{Co}_3\text{O}_4$ Nanostructure

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### Abstract

A new nano-sized cobalt(II) coordination polymer,  $(\text{CoL}_1)_0.5\text{DMF} \cdot 1.5\text{CH}_3\text{OH}$  (**1**); [ $\text{H}_2\text{L}_1 = 5\text{-(4-Carboxy phenyl azo) salicylic acid}$ ] has been synthesized by a sonochemical method. The thermal stability of compound **1** was studied by thermo- gravimetric and differential thermal analyses. Nano-structure of this coordination polymer was characterized by elemental analyses, IR spectroscopy, powder X-ray diffraction and scanning electron microscopy. Nano-particles of  $\text{Co}_3\text{O}_4$  were obtained by calcination of compound **1** at  $550^\circ\text{C}$ . The  $\text{Co}_3\text{O}_4$  nano-particles were characterized by powder X-ray diffraction and scanning electron microscopy.

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## 1. Introduction

Design and synthesis of metal–organic coordination polymers are of great interest due to their special properties and potential applications in sorption, electrical conductivity and catalysis [1–12]. Chemical and physical properties of solid materials strongly depend on both the size and the shape of the microscopic particles they are made up from. This is especially true for materials with morphological features smaller than a micron in at least one dimension, which are commonly called

nano-scale materials, or simply nano-materials. Nano meter-sized particles of metal coordination polymers are fascinating to explore, since their unique properties are controlled by the large number of surface molecules, which experience an entirely different environment than those in a bulk crystal. Nano-structured materials have been prepared by a variety of synthetic methods, including gas phase techniques, liquid phase methods and mixed phase approaches. Among a variety of approaches, the utilization of ultrasound

has been extensively examined over many years [13]. The powerful ultrasound radiation used in this method (20 kHz–10 MHz) induces physical or chemical changes during cavitation (the formation, growth, and implosive collapse of bubbles in a liquid) which can generate local hot spots having pressures of about 1000 bar, temperatures of roughly 5000 K, and heating and cooling rates of about  $10^{10} \text{ K s}^{-1}$ . These extreme conditions permit access to a range of chemical reaction space normally not accessible, which allows for the synthesis of nano-structured materials [14-19]. In recent years, there has been an increasing interest in the synthesis of large surface areas, unusual adsorptive properties, surface defects and fast diffusivities.  $\text{Co}_3\text{O}_4$  is a very important material extensively used in catalysis, gas sensors, electrochromic films, battery cathodes, heterogeneous catalytic materials and magnetic materials [20-21]. Due to their small size, nanoparticles exhibit novel material properties that are significantly different from those of their bulk counterparts.  $\text{Co}_3\text{O}_4$  nanoparticles have been synthesized by various methods like sol-gel, surfactant-mediated synthesis, thermal decomposition, polymer-matrix assisted and spray-pyrolysis [22-23]. In this paper we describe a simple synthetic sonochemical preparation of a cobalt(II) coordination polymer nano-structure,  $(\text{CoL}_1)_0.5\text{DMF} \cdot 1.5\text{CH}_3\text{OH}$  (**1**); and the use of this new compound as a precursor for preparation of  $\text{Co}_3\text{O}_4$  nano-particles by calcination method.

## 2. Experimental

### 2.1. Materials and characterization

All reagents and solvents for the synthesis and analysis were commercially available and used as received. X-ray powder diffraction (XRD) measurements were performed using an X'pert

diffractometer of Philips Company with monochromated  $\text{CuK}_\alpha$  radiation. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating. IR spectra were recorded on a SHIMADZU- IR460 spectrometer in a KBr matrix.

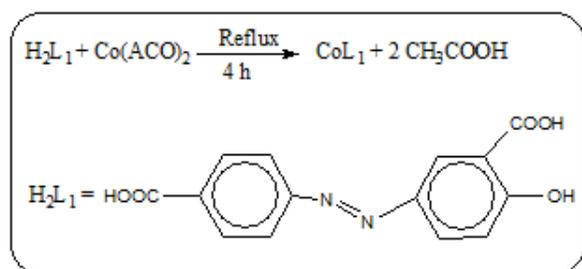
### 2.2. Synthesis of Ligand 5-(4-Carboxyphenyl azo) salicylic acid ( $\text{H}_2\text{L}_1$ )

In 250 mL conical flask, 4-aminobenzoic acid (3.14 g, 20 mmol) was dissolved in a mixture of concentrated hydrochloric acid (24 mL) and water (100 mL). The solution was cooled with stirring in an ice bath to  $0^\circ\text{C}$  until it become clear, then a solution of sodium nitrite (1.38 g, 20 mmol) in water (7 mL) was added dropwise during 10 minutes, then the reaction mixture was further stirred for 20 minutes in an ice bath at  $0-5^\circ\text{C}$ . The solution was added dropwise to coupling component involve salicylic acid (2.74 g, 20 mmol), in 10% sodium hydroxide solution (30 mL) with stirring in an ice bath for one hour. The product was collected by filtration and washed with water and dried under vacuum at room temperature overnight. Yield 80%, m.p. $>300^\circ\text{C}$  decomposed; orange powder.  $^1\text{H NMR}$ (400 MHz, DMSO): 8.08-8.1 (dd, H-2), 7.4-7.5 (t, H-4), 8.36-8.37 (d, H-1), 7.15–7.17 (d, H-3), 7.92-7.94 (H-5), 11.3 (s, H-6). IR (KBr): 3236 (O-H), 1660-1578 (C=O carboxyle), 1483 (N=N). Elemental analysis calcd. (%) for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_5$ : C 58.7, H 3.49, N 9.79; found: C 58.5, H 3.43, N 9.65.

### 2.3. Synthesis of $(\text{CoL}_1)_0.5\text{DMF} \cdot 1.5\text{CH}_3\text{OH}$ (**1**)

Compound **1** was prepared using the following method: The cobalt(II) acetate (10 mmol, 2.86 g) dissolved in 20 ml methanol. After heating up to reflux, the ligand (10 mmol 2.48 g) dissolved in 4 ml DMF was added dropwise under stirring, Where upon a suspension of the cobalt complex

dyeobtained. The precipitated solid was collected by filtration, washed with methanol and then vacuum dried to obtain the cobalt(II) azo complex (Scheme 1). Elemental analysis calcd. (%) for  $C_{17}H_{17.5}N_{2.5}O_7$  CO: C 47.7, H 4.09, N 8.18; found: C 45.4, H 3.88, N 8.3.

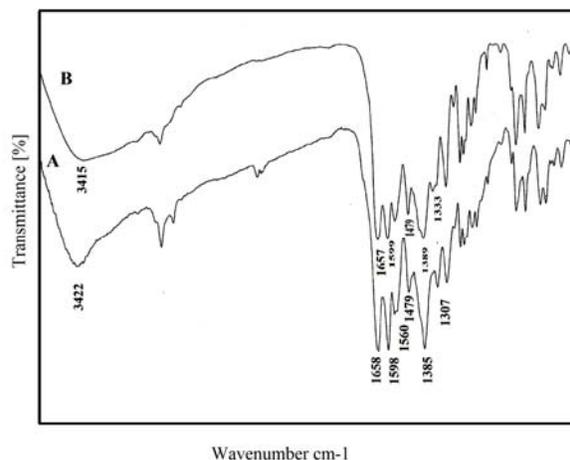


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**Scheme 1.** The produced compound **1** from the reaction of  $H_2L_1$  with cobalt(II) acetate by reflux method.

#### 2.4. Synthesis of nano-sized $(CoL_1).0.5DMF.1.5CH_3OH$ (1) by sonochemical method

To prepare the nanostructure of compound **1** by sonochemical process, we used an ultrasonic bath with 0.01M concentrations of metal and ligand solutions and the power of 40 KHz for 1 hour. To the prepared  $Co(CH_3COO)_2.4H_2O$  solution (50 ml) in methanol, a proper volume of ligand ( $H_2L_1$ ) solution in DMF (50 ml) was added in drop wise manner under the ultrasonic irradiation. The obtained precipitates were filtered, subsequently washed with double distilled methanol and then dried.



**Fig.1.** The IR spectra of (A) as synthesized bulk materials of compound **1** and (B) compound **1** nano-structure prepared by sonochemical method.

#### 2.4. Synthesis of nanoparticles $(CoL_1).0.5DMF.1.5CH_3OH$ (1) by surfactant.

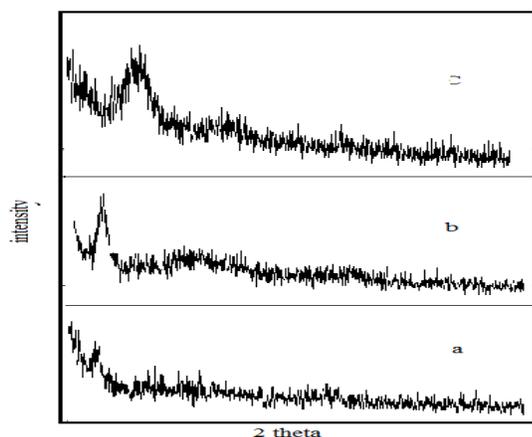
The precursor  $(CoL_1).0.5DMF.1.5CH_3OH$  (1) 0.855 (1 mmol) was dissolved immediately in 1.42 g (5 mmol) oleic acid. This solution was degassed for 20 minutes and then heated to  $180^\circ C$  for 2 hours. At the end of the reaction, a black precipitate was formed. A small amount of toluene and a large excess of EtOH were added to the reaction solution and precipitate of Compound **1** nanoparticles were separated by centrifugation. The solids were washed with EtOH and dried under air atmosphere.

#### 2.5. Synthesis of $Co_3O_4$ nanoparticles by calcinations in $550^\circ C$

$Co_3O_4$  nano-particles were synthesized by calcination of compounds **1** under air atmosphere. The morphology and size of the as-prepared  $Co_3O_4$  samples were further investigated using Scanning Electron Microscopy (SEM). Bulk powder of the precursor **1** produces regular shape of  $Co_3O_4$  nano-particles with the diameter about 51 nm (Figure6).

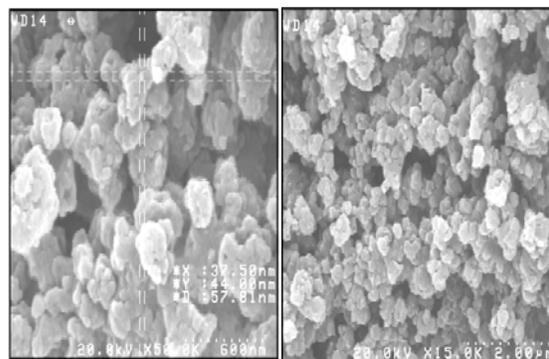
### 3. Results and discussion

The reaction of 5-(4-Carboxy phenyl azo) salicylic acid ( $H_2L_1$ ) and cobalt(II) acetate leads to the formation of a new cobalt coordination polymer ( $CoL_1$ ).  $DMF_{0.5} \cdot CH_3OH_{1.5}$  (**1**). Nano-sized structure of compound **1** was obtained by ultrasonic irradiation in a DMF: MeOH (with 1:1 molar ratio) solution. IR spectrum of the nano-structure of compound **1** shows more similarity with the IR spectrum of the complex (Figure 1). Figure 2 shows the XRD pattern of compound **1** bulk sample (Figure 2a) in comparison with the XRD pattern of a typical sample of compound **1** prepared by the sonochemical process (Figure 2b) and by using surfactant (Figure 2c).



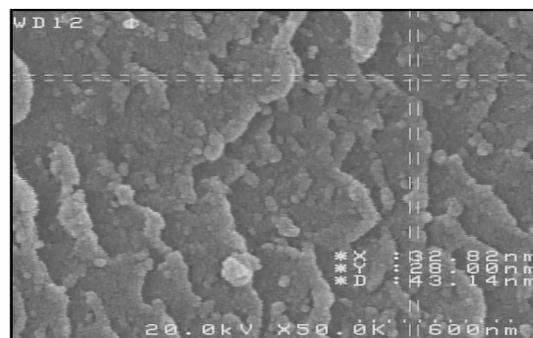
**Fig. 2.** The XRD patterns of (a) compound **1** prepared by reflux method, (b) nano-sized structure of compound **1** prepared by sonochemical method and (c) nano-sized structure of compound **1** prepared by oleic acid as a surfactant at 453 K.

Figure 3 shows the SEM images of compound **1** nano-structure with the average diameter of 50 nm obtained by sonochemical process with multi wave ultrasonic generator.



**Fig.3.** SEM photographs of compound **1** nanoparticles produced by sonochemical method by 0.01:0.01 M concentration of initial reagents in two scale.

Treatment of compound **1** nanostructures with oleic acid as a surfactant at 453 K results in formation of compound **1** nanostructures aggregates from nanoparticles of this compound with the diameter of about 30-50 nm, which can be observed in Figure 4.



**Fig.4.** SEM photograph of compound **1** nano-structure prepared by thermal treatment of compound **1** with oleic acid at 453 K.

To examine the thermal stability of the compound **1**, thermogravimetric (TG) and differential thermal analyses (DTA) were carried out between 50 and 900 °C under Argon flow (Figure 5). The compound **1** is stable up to 400 °C. Decomposition of compound **1** occurs between 400 and 450 °C with a mass loss of 52.82%. Mass loss calculations

show that the correct final decomposition product can be  $\text{Co}_3\text{O}_4$ . The DTA curve displays one distinct endothermic peak at 420 °C (Figure 5).

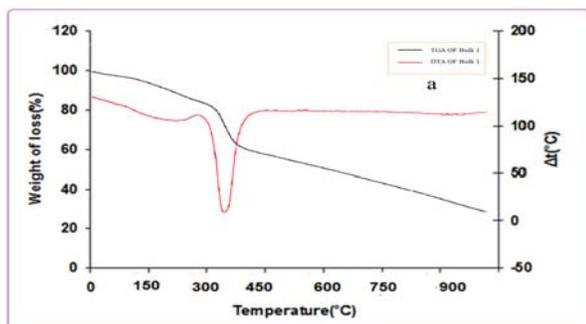


Fig. 5. TGA and DTA diagrams of compound 1.

Figure 2-c attributed to the XRD pattern of the residue obtained from calcination of compound 1 nano- structures at 673 K. SEM image (Figure 6) of the residue obtained from calcination of compound 1 nano-structure at 823 K shows that nanoparticles of  $\text{Co}_3\text{O}_4$  with the diameter about 51 nm.



Fig. 6. SEM photographs of  $\text{Co}_3\text{O}_4$  nanoparticles produced by calcination of precursor 1 at 550°C.

The final product after decomposition process of compound 1 is, based on their XRD patterns (Figure 7), cubic  $\text{Co}_3\text{O}_4$ . The phase purity of the as-prepared cubic  $\text{Co}_3\text{O}_4$  nano-particles are completely obvious and all diffraction peaks are perfectly indexed to the cubic  $\text{Co}_3\text{O}_4$  structure with the lattice parameters of ( $a = 8.084 \text{ \AA}$  and  $z = 8$ )

which are close to the reported values, (JCPDS card number 43-1003).

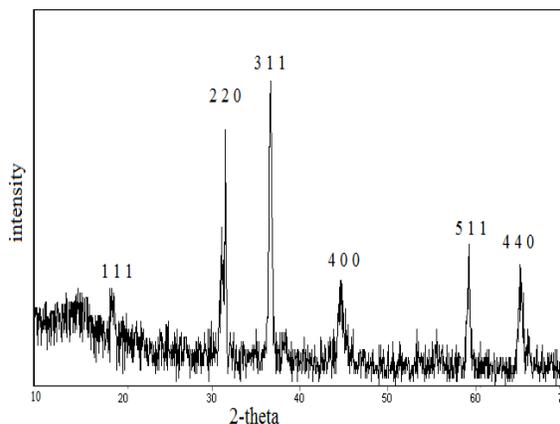


Fig. 7. XRD patterns of  $\text{Co}_3\text{O}_4$  prepared after calcination of compound 1.

#### 4. Conclusion

A new cobalt(II) coordination polymer,  $(\text{CoL}_1)_0.5\text{DMF} \cdot 1.5\text{CH}_3\text{OH}$  (**1**) has been synthesized using a reflux approach and by sonochemical irradiation. Calcination under air atmosphere produces nano-sized particles of  $\text{Co}_3\text{O}_4$ . This study demonstrates that the coordination polymers may be suitable precursors for the preparation of nanoscale materials and it does not need special conditions like high temperature, long time and pressure controlling.

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