

# Synthesis and Characterization of Zinc(II) Oxide Nanoparticles by Thermal Decomposition of Two Zinc(II) Nitrite Coordination Polymer Precursors

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**Abstract** Two zinc(II) coordination polymers,  $\{[\text{Zn}(3\text{-bpdb})(\text{NO}_2)] \cdot 0.5\text{H}_2\text{O}\}_n$  (**1**) and  $[\text{Zn}(4\text{-bpdb})(\text{NO}_2)_2]_n$  (**2**), 3-bpdb = 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene and 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene, have been synthesized and characterized by elemental analyses and IR spectroscopy. Nanoparticles of zinc(II) oxide have been prepared by thermolyses of two different zinc(II) coordination polymers, **1–2**. The nano-materials were characterized by scanning electron microscopy, X-ray powder diffraction and IR spectroscopy. The thermal stability of ZnO nano-particles was studied by thermal gravimetric and differential thermal analysis and showed that there is no loss of weight, which indicates that the products were zinc(II) oxide. This study demonstrates the coordination polymers may be suitable precursors for the preparation of nanoscale materials.

**Keywords** Nanoparticles · Zinc(II) oxides · Thermogravimetric analysis · Coordination polymer

## 1 Introduction

In recent years, the synthesis of inorganic materials with specific size and morphology has attracted significant attention due to their possible use in different fields [1–4]. ZnO is a polar inorganic crystalline material with many applications due to its unique combination of interesting properties such as non-toxicity, good electrical, optical and piezoelectric behavior, stability in a hydrogen plasma atmosphere and low price [5–8]. ZnO is a well known semiconductor with a wide direct band gap (3.37 eV) and a large exciton binding energy of 60 meV at room temperature [9, 10]. In addition, it has a wide range of applications as solar cells, luminescent, electrical and acoustic devices, in gas and chemical sensors, as coatings, catalysts, micro-lasers, memory arrays and in biomedical applications [8, 11].

Many methods have been developed to synthesize zinc(II) oxide nano-crystals including vapor phase growth [12], vapor- liquid- solid process [13], soft chemical method [14], electrophoretic deposition [15], sol-gel process [16], homogeneous precipitation [17, 18], etc. The use of coordination polymers as precursors for the preparation of inorganic nanomaterials such as zinc(II) oxide has not been investigated thoroughly. Coordination polymers represent an important interface between synthetic chemistry and materials science. During the past decade, considerable interest has been focused on new coordination polymers based on polydentate organic ligands due to their novel structural topologies and potential applications in sensing, catalysis, ion exchange, separations and gas storage [2–40]. In this paper we describe the preparation of two zinc(II) coordination polymers,  $\{[\text{Zn}(3\text{-bpdb})(\text{NO}_2)] \cdot 0.5\text{H}_2\text{O}\}_n$  (**1**) and  $[\text{Zn}(4\text{-bpdb})(\text{NO}_2)_2]_n$  (**2**), as well as their use in preparing ZnO nanoparticles.

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## 2 Experimental Section

### 2.1 Materials and Physical Techniques

With the exception of the ligands 3-bpdb and 4-bpdb, which were prepared according to literature procedures, all reagents and solvents for the synthesis and analysis were commercially available from Merck Company and used as received.

IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips company with monochromated  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). TGA and DTA curves were recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating.

### 2.2 Preparation of $\{[\text{Zn}(3\text{-bpdb})(\text{NO}_2)]\cdot 0.5\text{H}_2\text{O}\}_n$ (**1**) and $[\text{Zn}(4\text{-bpdb})(\text{NO}_2)_2]_n$ (**2**)

Compounds **1–2** were prepared using reported methods. To a magnetically stirred methanolic solution of  $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$  (1 mmol) was added dropwise a mixture of 3-bpdb or 4-bpdb (1 mmol) and of  $\text{NaNO}_2$  (2 mmol) in methanol and a little water at room temperature over 30 min. The reaction mixture was stirred for 1 h at room temperature. Pure **1–2** were obtained by slow evaporation of this solution at room temperature. The products were filtered, washed with acetone and dried in air.

#### 2.2.1 Compound **1**

Yellow crystals, m.p. 185 °C. Found (%) C: 38.40, H: 2.50, N: 22.60; Calcd. for  $\text{C}_{24}\text{H}_{22}\text{N}_{12}\text{O}_9\text{Zn}_2$ ; C: 38.23, H: 2.92, N: 22.30. IR ( $\text{cm}^{-1}$ ), selected bands:  $\nu = 665(\text{s}), 862(\text{m}), 1023(\text{s}), 1044(\text{m}), 1185(\text{vs}), 1266(\text{vs}), 1307(\text{m}), 1415(\text{vs}), 1454(\text{m}), 1623(\text{s}), 2913(\text{w})$  and  $3042(\text{w})$ .

#### 2.2.2 Compound **2**

Yellow crystals, m.p. 283 °C. Found (%) C: 39.50, H: 2.50, N: 22.55; Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_6\text{O}_4\text{Zn}$ ; C: 39.23, H: 2.72, N: 22.88. IR ( $\text{cm}^{-1}$ ), selected bands:  $\nu = 666(\text{s}), 814(\text{s}), 1015(\text{s}), 1054(\text{m}), 1164(\text{vs}), 1264(\text{vs}), 1305(\text{m}), 1416(\text{s}), 1445(\text{w}), 1604(\text{vs}), 2923(\text{w})$  and  $3064(\text{w})$ .

### 2.3 Synthesis of ZnO Nanoparticles

The precursors **1** or **2** (80 mg) were dissolved in oleic acid (1.35 mL) to form a greenish black solution. This solution was heated to 240 °C for 2 h in air. At the end of the reaction, a black precipitate was formed. A small amount of toluene and a large excess of MeOH were added to the reaction solution and ZnO nano-structures were separated by centrifugation. The dark solid was washed with EtOH and dried under nitrogen.

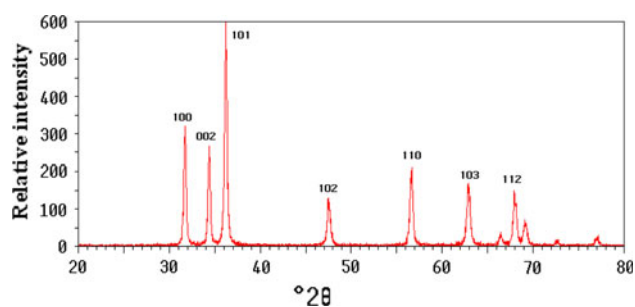
## 3 Results and Discussion

Reaction between two flexible organic nitrogen donor-based ligands, 3-bpdb and 4-bpdb, and mixtures of zinc(II) acetate with sodium nitrite yielded crystalline materials formulated as  $\{[\text{Zn}(3\text{-bpdb})(\text{NO}_2)]\cdot 0.5\text{H}_2\text{O}\}_n$  (**1**) and  $[\text{Zn}(4\text{-bpdb})(\text{NO}_2)_2]_n$  (**2**). The IR spectra display characteristic absorption bands for the ligands and the nitrite anions. The relatively weak absorption bands at  $3080 \text{ cm}^{-1}$  are due to the C–H modes involving the aromatic ring hydrogen atoms. The C–H modes involving the aliphatic hydrogen atoms of the ligands in **1** and **2** occur at  $2920 \text{ cm}^{-1}$ . The absorption bands with variable intensity from  $1400$  to  $1580 \text{ cm}^{-1}$  correspond to ring vibrations of the py moiety of the ligands. Characteristic bands of the nitrite anions appear at  $1174$  and  $1236 \text{ cm}^{-1}$ . The structure of compounds **1** and **2** were previously reported [6] and are 1D polymers with distorted octahedral  $\text{ZnN}_2\text{O}_4$  coordination environments with two *N*-donor ligands where the nitrite ligands *cis* to each other, thus generating angular nodes of metal moieties. Compounds **1–2** crystallize in the monoclinic with space groups of  $\text{C}2/c$  and  $\text{P}2_1/c$ , respectively.

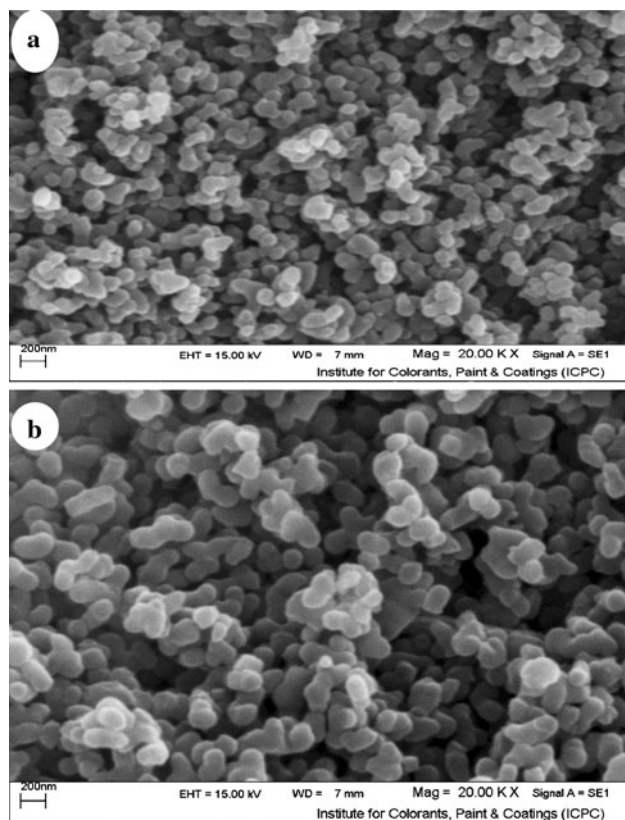
Nanoparticles of ZnO were generated by thermolysis of **1** and **2**. The final products in each case upon thermolysis at 200 °C is ZnO based on their IR spectra, XRD patterns and TGA/DTA analysis.

The IR spectrum of ZnO the nanoparticles after thermolysis in oleic acid as a surfactant shows absorption bands at  $\sim 500 \text{ cm}^{-1}$ , which are attributed to the Zn–O stretching mode. The weak bands from  $1380$  to  $3425 \text{ cm}^{-1}$  are probably due to the presence of water in the KBr matrix.

Figure 1 shows X-ray powder diffraction pattern of ZnO nanoparticles after thermolysis **1** and **2**. The XRD patterns of ZnO nanoparticles are the same and are in agreement with the typical ZnO wurtzite structure (i.e., hexagonal phase, space group  $\text{P}6_3\text{mc}$ , with lattice constants  $a = 3.24982(9) \text{ \AA}$ ,  $c = 1.6021 \text{ \AA}$ ,  $Z = 2$ , JCPDS No.



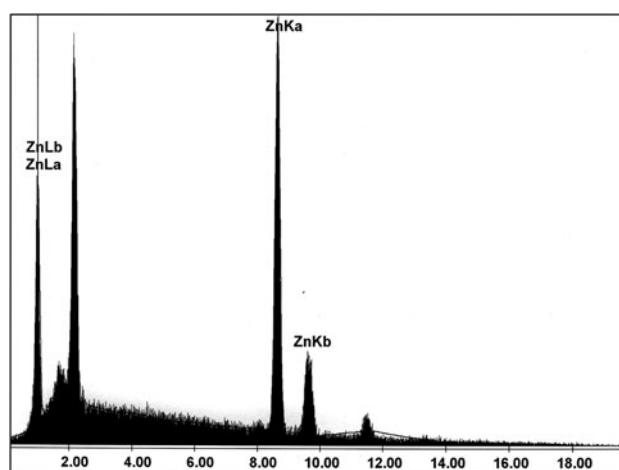
**Fig. 1** X-ray powder diffraction pattern of ZnO nanoparticles after thermolyses of compounds 1–2



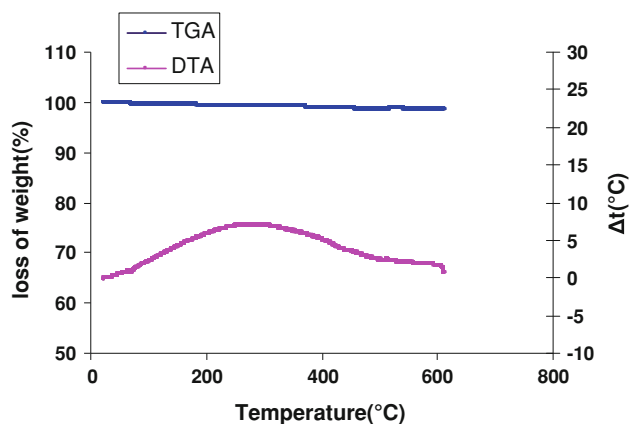
**Fig. 2** SEM photographs of ZnO nanostructure produced by thermolyses of **a** compound 1 and **b** compound 2

36–1451). Sharp diffraction peaks indicate a good crystallinity for the ZnO nanoparticles. No impurity was observed. The broadening of the peaks indicated that the particles were at the nanometer scale, which is in agreement with that observed from SEM images (Fig. 2a, b).

The EDAX SPECTRA of **1** and **2** were performed on the ZnO nanoparticles after thermolysis (Fig. 3). The spectra show the presence of Zn as the only element component. The TGA was carried out to show that there was no impurity in products **1** and **2** after thermolysis. There is no



**Fig. 3** EDAX analysis of ZnO after thermolyses of compounds 1–2



**Fig. 4** TG-DTA curves of the ZnO nanostructures after thermolyses of compounds 1–2

loss of weight, which indicates the existence of zinc(II) oxide (Fig. 4).

#### 4 Conclusions

Two zinc(II) coordination polymers, **1** and **2**, were synthesized and characterized by elemental analysis and IR spectroscopy. Nanoparticles of zinc(II) oxide were prepared by thermolysis of **1** and **2**. The nanomaterials were characterized by SEM, XRD and IR spectroscopy. The thermal stability of the ZnO nanoparticles was studied by TGA and DSC and showed that there is no weight loss, which indicates the presence of zinc(II) oxide. The study demonstrates the coordination polymers may be suitable precursors for the preparation of nanoscale materials.

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