

Preparation of ZnO Nanocrystals with Desired Morphology from Coordination Polymers through a Solid-state Decomposition Route

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Abstract

One-dimensional (1D) coordination polymer, $[\text{Zn}(4,4'\text{-bpy})(\text{H}_2\text{O})_4](\text{ADC})\cdot 4\text{H}_2\text{O}$ (1) ($4,4'\text{-bpy}$ = 4,4'-bipyridine and H_2ADC = acetylenedicarboxylic acid), and three-dimensional (3D) metal-organic framework (MOF), $\text{Zn}(\text{ADC})_2\cdot(\text{HTEA})_2$ (2) (HTEA = triethylamine) were prepared at room temperature. The compounds were characterized by single-crystal X-ray diffraction and powder X-ray diffraction (PXRD) analyses. The polymers were applied as precursors for the synthesis of ZnO nanocrystals via direct thermal decomposition. The prepared nanocrystals were characterized by PXRD, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). It was found that the nanocrystals of different morphologies such as rods and particles were formed using 1 and 2, respectively.

Keywords: Nanocrystals of zinc oxide; Coordination polymer; Solid-state synthesis; Morphology.

Introduction

There is considerable scientific and technological interest in the synthesis and characterization of transition metal oxide with controlled size and shape owing to their unique applications including catalysis and photoelectronic devices [1-3].

Among metal oxides, ZnO has been intensively studied because of its wide range of applications in the field of catalysis [4], gas sensing [5], optoelectronics [6] and piezoceramics [7]. Zinc oxide nanocrystals have been synthesized using different methods such as vapor phase growth [8], vapor-liquid solid process [9], sol-gel process [10], electrochemical [11] and precipitation methods [12].

Solid-state decomposition of coordination polymers

and metal-organic frameworks (MOFs) have developed as an alternative route for the synthesis of ZnO nanocrystals with diverse morphologies. The advantages of these crystalline precursors are simplicity of processing and long-range ordering that allow the synthesis of ZnO with various morphologies. ZnO nanomaterials with desired morphologies have been obtained by thermal decomposition of appropriate coordination polymers and MOF precursors [13, 14]. For instance, thermolysis of coordination polymers such as $([\text{Zn}(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}3\text{-bpdh})(\text{H}_2\text{O})_2](\text{ClO}_4)_2\cdot(4,4'\text{-bipy})_{0.5})_n$ [15], $[\text{Zn}(3\text{-bpdh})(\text{NO}_2)_2]_n$ [16], $[\text{Zn}(4\text{-bpdb})(\text{NO}_2)_2]_n$ [17], $\text{Zn}(\text{ABDC})(\text{ADC})$ [18] and $[\text{Zn}(\text{ancic})_2]$ (Hanic = 2-aminonicotinic acid) [19] has led to the formation of ZnO with various morphologies.

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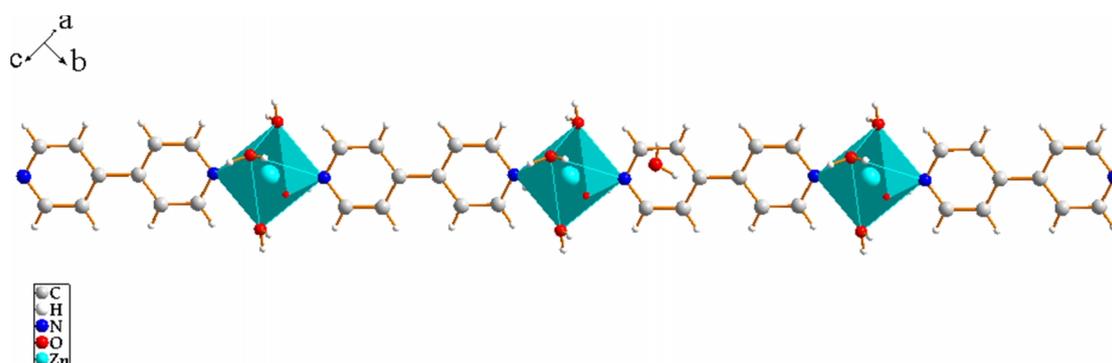


Figure 1. Structure of coordination polymer $[\text{Zn}(4,4'\text{-bpy})(\text{H}_2\text{O})_4](\text{ADC}).4\text{H}_2\text{O}$ (1)

Here, we report the preparation of ZnO nanocrystals from thermal decomposition of $[\text{Zn}(4,4'\text{-bpy})(\text{H}_2\text{O})_4](\text{ADC}).4\text{H}_2\text{O}$ (1) and $\text{Zn}(\text{ADC})_2(\text{HTEA})_2$ (2). The morphology of ZnO nanocrystals could be controlled by applying these two crystalline precursors.

Materials and Methods

All chemicals were of commercial reagent grade and used without further purifications. X-ray powder diffraction (XRPD) data were recorded using a Philips PW1800 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) was performed on a KYKY EM-3200. EDX (energy dispersive X-ray) analysis was carried out on Ametek Prime.

Synthesis of $[\text{Zn}(4,4'\text{-bpy})(\text{H}_2\text{O})_4](\text{ADC}).4\text{H}_2\text{O}$ (1) nanorods

A solution of 4,4'-bipyridine (0.16 g, 1 mmol) in ethanol (10 ml) was mixed with an aqueous solution (10 ml) of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.25 g, 1 mmol) and acetylenedicarboxylic acid (0.11 g, 1 mmol). The crystals of 1 were formed at room temperature after 5 days followed by filtering, washing with distilled water and drying in air. The solid was then annealed at 400, 500 and 600 °C.

Synthesis of $\text{Zn}(\text{ADC})_2(\text{HTEA})_2$ (2) nanoparticles

To prepare compound 2, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.118 g, 0.40 mmol) and H_2ADC (0.092 g, 0.80 mmol) were dissolved in ethanol (20 mL) and placed in a vial that was then inserted in another large vial containing triethylamine/ethanol (0.2 mL/4.0 mL). After filtration, the crystals washed with ethanol and dried in air. The nanoparticles were obtained by annealing the crystals at 600 °C for 2 h.

Results and Discussion

Coordination polymer 1 and MOF 2 were synthesized at room temperature. The X-ray structure determination shows that compound 1 contains ZnN_2O_4 octahedra that link together to form 1D coordination polymer exhibited in Figure 1 [20]. The X-ray single crystal analysis of compound 2 reveals that this structure contains tetrahedral zinc centres linked with acetylene units. The 3D structure of 2 is shown in Figure 2 [21].

Zinc oxide nanocrystals were prepared by direct thermal decomposition of coordination polymer 1 and MOF 2 under air atmosphere. As shown in Figure 3, the PXRD patterns obtained by annealing coordination polymer 1 at 600, 500 and 400 °C were similar. The morphology of the obtained nanocrystals was characterized by SEM (Figure 4). The SEM images exhibited nanorods with 30-60 nm in diameter and a

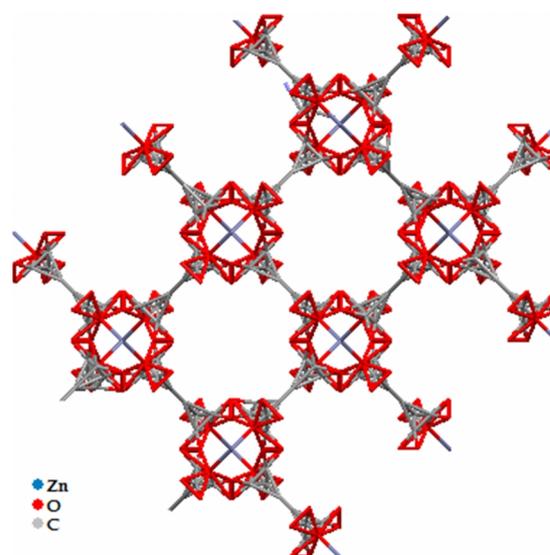


Figure 2. Structure of MOF $\text{Zn}(\text{ADC})_2(\text{HTEA})_2$ (2)

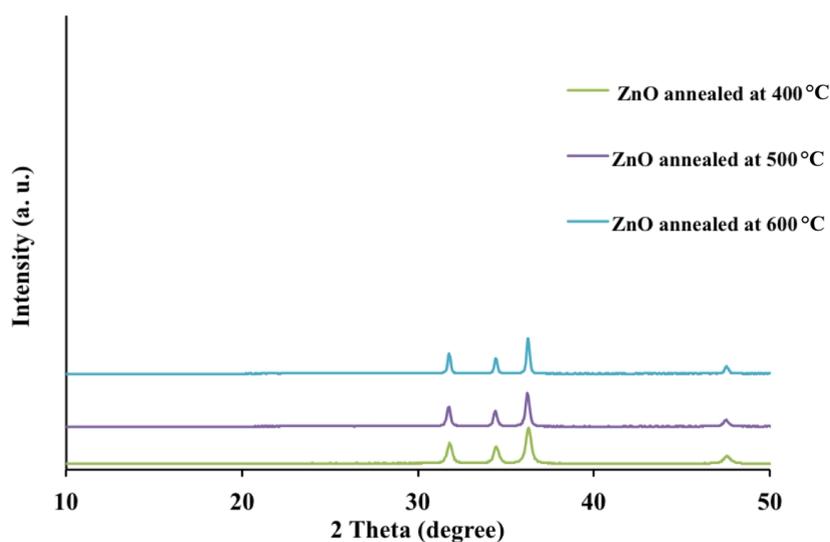


Figure 3. Powder XRD patterns of ZnO nanorods obtained by annealing [Zn(4,4'-bpy)(H₂O)₄](ADC).4H₂O (1) in different temperatures

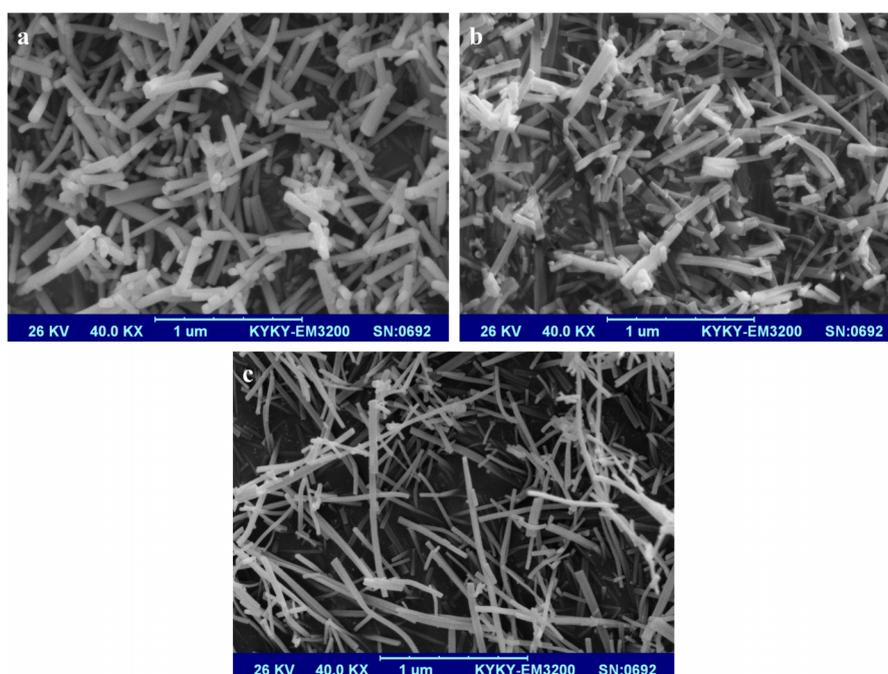


Figure 4. The SEM images of ZnO nanorods obtained by annealing 1 at (a) 400 (b) 500 and (c) 600 °C

few micrometers in length. Inspection of the images reveals that annealing of the coordination polymer 1 at 600 °C resulted in the formation of more uniform rods with longer length (Figure 4c).

The PXRD pattern of ZnO nanocrystals prepared from MOF 2 is depicted in Figure 5. The morphology of the corresponding ZnO nanocrystals was studied by SEM (Figure 6). It can be seen that the ZnO

nanostructure contains the agglomerated nanoparticles with about 20–40 nm in diameter. The size of the particles was also calculated from the diffraction peaks using Debye-Scherrer equation and the average particle size was about 10 nm. The purity of the obtained ZnO nanomaterials was investigated by EDX analysis presented in Figure 7.

From the SEM images of ZnO nanocrystals (Figure

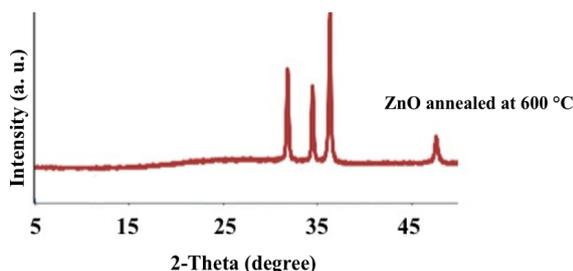


Figure 5. Powder XRD pattern of ZnO nanoparticles obtained by annealing Zn(ADC)₂(HTEA)₂ (2) at 600 °C

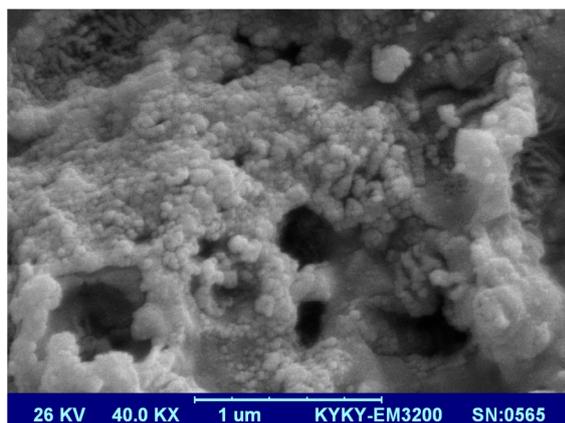


Figure 6. The SEM image of ZnO nanoparticles obtained by annealing 2 at 600 °C

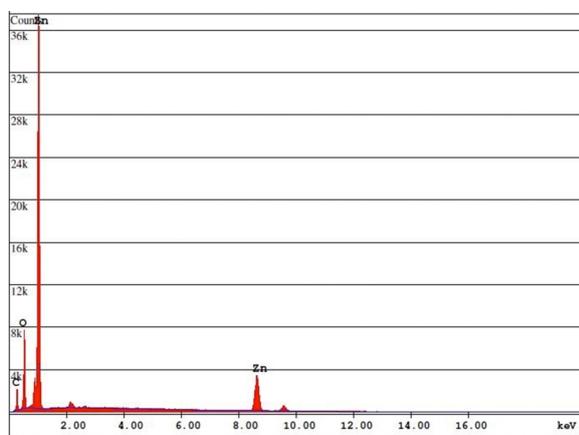


Figure 7. The EDX of nanosized ZnO

4c and 6), it can be seen that changing the precursor from coordination polymer 1 to MOF 2 under the same conditions, affords two different morphologies as rods and spherical with similar XRD patterns.

In conclusion, we have described the synthesis of ZnO nanocrystals through direct decomposition of coordination polymer 1 and MOF 2. Interestingly, changing the precursor from 1D coordination polymer 1 to 3D MOF 2 changes the morphology from nanorods to

nanoparticles. Moreover, the results show that thermolysis temperature can influence the length of ZnO nanorods obtained from coordination polymer 1.

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