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Perspectives Article

Rapid production of acid-functionalized infinite coordination polymer nanoparticles and their calcination to mineral metal oxide

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ABSTRACT

Zn and Cu based infinite coordination polymers (ICPs) with nanoparticle morphologies have been successfully synthesized through facile precipitation and hydrothermal methods. These infinite coordination polymers are composed of the infinite-chain of the M^{2+} and bi-carboxylic ligand, 4,4′-((1E,1′E)-(1,4-phenylene bis(methanylylidene)) bis(azanylylidene)) dibenzoic acid. The formation of Zn-ICP and Cu-ICP is evidenced by elemental and inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses. The scanning electron microscopy images show the monodispersed particles with diameters about 56 and 76 nm for Cu and Zn-ICPs, respectively. The possible mechanism for the ICP formation is proposed. Subsequently, these infinite coordination polymers were used as precursors for the preparation of crystalline metal oxide particles by calcination route.

1. Introduction

Coordination compounds have attracted great interest in materials science and modern chemistry. These compounds can be made in many forms, including nanocomplexes, crystalline Metal Organic Frameworks (MOFs) [1] and Infinite Coordination Polymer (ICP) nano- and microparticles [2–11]. These materials show promise in many applications, including catalysis [5,12,13], ion exchange [14,15], gas storage [16–20], small molecule detection [21,22], separation processes [23,24], optoelectronics [25], antisense gene regulation [26], and drug delivery [27,28]. The properties of the coordination polymers and their potential applications highly depend on their bulk and microscopic structures.

For the first time, two groups introduced the concept of amorphous infinite coordination polymers (ICPs), which are prepared from metal-organic ligands [2] or organic ligands [6] as linker and metal ion connecting nodes. There are now a variety of ways for preparing ICP particles from a broad class of metal nodes and both organic and metal-organic ligands [2,29–31]. Similar to MOFs, these compounds are assembled via coordination chemistry principles; however, the resulting materials are typically amorphous, not crystalline. The ICP particles are attractive for many applications because of their high degree of tailorability through choice of transition metal nodes and ligand precursors, high thermal stability in many cases, and the ability to readily access their interior sites, at least in solution [9].

Herein, we have succeeded to report the formation of novel ICP nanoparticles from the metal nodes (Zn^{2+} and Cu^{2+}) and a bidentate organic ligand 4,4′-((1E,1′E)-(1,4-phenylene bis(methanylylidene)) bis(azanylylidene)) dibenzoic acid. We have also demonstrated that the choice of solvent and reaction method could have an impressing effect on the size of the products. Furthermore, the nitrogen adsorption-desorption analysis (BET method) shows the mesoporosity in the prepared coordination polymer. To survey the effect of metal-ICP as precursor on the size and morphology of the obtained metal oxides, the calcination of these products was also investigated.

2. Experimental

2.1. Chemicals and instruments

Benzene-1,4-dicarboxaldehyde, 4-Aminobenzoic acid, $Zn(CH_3COO)_2.2H_2O$, $Cu(CH_3COO)_2.2H_2O$, and all solvents were bought from acroschemical company and used as received.

^1H NMR spectra were recorded on a Bruker Avance 300 spectrometer. The ^1H NMR chemical shifts in ppm are reported from tetramethylsilane (TMS) as internal reference. The elemental analyses were carried out on a Perkin-Elmer 2400 SERIES II. Fourier-transform infrared spectra were recorded using Perkin-Elmer Spectrum RXI FT-IR spectrometer with 2 cm^{-1} spectral resolution; using pellets of the materials diluted with KBr. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses were conducted on a Perkin Elmer Optima 8000 ICP-OES by dissolving 5 mg of powders in 0.5 mL hot HNO_3 and bringing the volume of solution to 10 mL (5 points were used to draw calibration plot). SEM images were taken on a KYKY-EM3200 scanning electron microscope with Secondary Electron (SE) detector. Thermogravimetric analysis (TGA) measurement was conducted on a SETARAM-SETSYS

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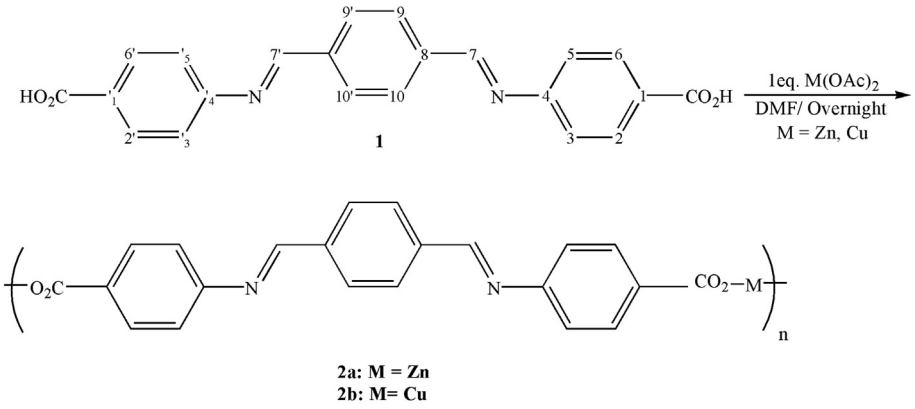

Scheme 1. Synthetic route of the Schiff base ligand and its ICP.

Evolution TGA-DTA/DSC in the temperature range from room temperature to 700 °C at a heating rate of 10 °C min^{-1} in air. Nitrogen adsorption-desorption analysis was performed using Belsorp mini2 instrument with 24 points for evaluation. Before performing the adsorption experiments the samples were outgassed under vacuum at 150 °C. XRD patterns were recorded on a Rigaku D-max CIII X-ray diffractometer using Ni-filtered Cu Kα radiation.

2.2. Synthesis of the 4,4′-((1E,1′E)-(1,4-phenylene bis(methanylylidene)) bis(azanylylidene)) dibenzoic acid

For the synthesis of ligand, a solution of benzene-1,4-dicarboxaldehyde (2 g, 150 mmol) in ethanol was added dropwise to a solution of 4-aminobenzoic acid (4.085 g, 300 mmol) in 70 mL warm ethanol. A large amount of precipitate appeared during the addition of 4-aminobenzoic acid. The produced suspension was filtered and the precipitate washed with ethanol several times. Yellow solid (4.12, 74% yield); Elemental anal. Calc. for $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.33; N, 7.52. Found: C, 70.60; H, 4.06; N, 7.78. ^{1}H NMR (D_2O): δ = 12.89 (s, 2H, COOH), 8.74 (s, 2H, N═CH), 8.11 (s, 4H, $H^{9,9',10,10'}$), 8.01 (d, 4H, $H^{2,2',6,6'}$), 7.39 (d, 4H, $H^{3,3',5,5'}$) ppm. FT-IR (KBr, cm^{-1}): 2400–3200 (υ_{O-H}), 3023 ($\upsilon_{C-H-aromatic}$), 2872 ($\upsilon_{C-H-imine}$), 1679 ($\upsilon_{C=O}$), 1591 ($\upsilon_{C=N}$).

2.3. Synthesis of ICP by precipitation method

For the synthesis of ICP nanoparticles, a solution of metal precursor was added slowly to the spacing ligand dissolved in *N,N*-dimethylformamide (DMF). In a typical synthesis, an exact amount of $M(CH_3COO)_2$ (1.34 mmol; M = Zn, Cu) was added slowly to 150 mL DMF solution of spacing ligand (0.5 g, 1.34 mmol). A cloudy solution was observed and a large amount of precipitate appeared within several

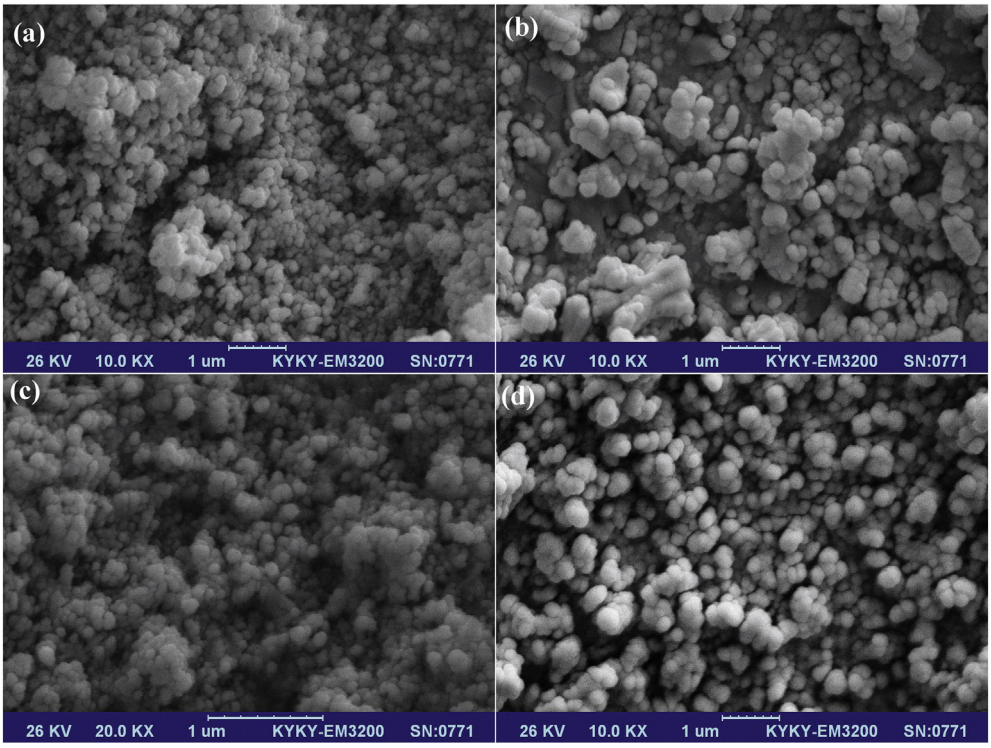

Fig. 1. Scanning electron microscopy images of the prepared polymers in a) Zn-ICP by precipitation, b) Zn-ICP by hydrothermal, c) Cu-ICP by precipitation, d) Cu-ICP by hydrothermal methods.