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#### CEPTED MANUSCRI

# Simple preparation of amorphous infinite coordination polymer nanoparticles and solid state

### transformation to ZnO nanoparticles

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**Abstract:** A novel organic-inorganic hybrid materials comprised from infinite-chains of Zn(II) and bicarboxylic acid linker (4-Carboxy-1-{3-[(4-carboxy-phenylimino)-methyl]-4-hydroxy-benzyl}pyridinium chloride) was successfully formed by precipitation from the mixture of precursor solutions. Thermogravimetric and elemental analyses, energy dispersive X-ray (EDX) and Fourier-transform infrared (FT-IR) spectroscopies approved the existence of two well-defined coordinating sites (N,O and COO sites) coordinated to zinc ions. Coordination of the linker N,O site to  $Zn^{2+}$  ion generated the metalo-ligand units and further addition of  $Zn^{2+}$  ion resulted in the attachment of these units to each other via carboxylic acid groups. Time-dependent SEM analysis demonstrated that the optimum time for preparing the smallest particles is 5 min. Calcination of the prepared zinc based coordination polymer achieved uniform ZnO nanoparticles with larger band gap in comparison with bulk counterpart.

Keywords: Band gap; Growth mechanism; Precipitation; Zinc coordination polymer; Zinc oxide

#### Introduction

Coordination polymers are a kind of organic-inorganic hybrid materials composed of metallic nodes connected by repeating units of ligands extending in one, two or three dimensions and have attracted great attentions [1-3]. Bailar reported the first series of procedures for constructing inorganic polymers based on coordinative bonds [4]. While the researchers have been concerned in metal-organic frameworks (MOFs), the first examples of nano- or microscale coordination polymer particles were reported by Mirkin [5] and Wang [6]. Recent studies revealed great interest in two new types of coordination polymers i.e. metal-organic frameworks (MOFs) and infinite coordination polymers (ICPs) [7-10].

**ACCEPTED MANUSCRIP** 

In contrast to crystalline MOF, ICPs with amorphous nanostructures constructed from self-assembly of metal ions and organic linkers [11-13]. By addition of nonpolar solvent to the mixture of metal ions  $(Zn^{2+}, Cu^2+, Ni^{2+})$  and carboxylate functionalized binaphthyl bis-metallo-tridentate Schiff base (BMSB) linker, micro/nanoparticles of ICPs was prepared [5]. Depending on the desired application, the ICPs particles with specific physiochemical properties such as color, luminescence, and redox properties can be achieved either by exchanging the metal ions and ligands or adjusting their interactions.

Recently, some researchers have developed the approaches to manufacture ICPs by using various methods. Mirkin's group reported the preparation of adjustable ICPs by using precipitation process [14-16]. The preparation of micro-sized cubic ICPs via microwave-assisted solvothermal revealed by Masel [17]. Lin's group reported the formation of ICP nanorods via the water-in-oil microemulsion method [18]. Oh and his coworkers developed the preparation method of ICPs with different morphologies and sizes by utilizing solvothermal method [19-21]. ICPs particles have also been used as precursors for producing metal oxides by Oh [19, 22, 23] and our groups [24-26].

In this paper, a new bi-carboxylic acid Schiff base linker was synthesized from p-aminobenzoic acid and functionalized salicylaldehyde with iso-nicotinic acid. We describe a simple precipitation method to fabricate zinc coordination polymer with bi-carboxylic acid Schiff base linker and used obtained ICP for preparing ZnO by calcination.

#### **Experimental Section**

#### Materials and apparatus

Solvents and all other chemicals were obtained from Acros, Merck and Alfa-Aesar commercial sources and used as received unless otherwise noted.

The CHN elemental analysis was done on a Perkin-Elmer 2400 SERIES II. Inductively coupled plasmaoptical emission spectroscopy (ICP-OES) was conducted on SPECTRO ARCOS FHE 12 ICP-OES analyzer. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 300 spectrometer. Fourier-transform infrared spectra of solid samples (KBr pellets) were obtained on a Perkin-Elmer-RXI FT-IR spectrometer. The elemental composition and surface morphology of the samples were studied using energy dispersive X-ray analysis (EDX) equipped with a high resolution MIRA3-TSCAN-XMU field emission scanning electron microscope (FE-SEM). Atomic force microscopy (AFM) was carried out to study the topology of the surface of coordination polymer using Ara-Research AFM full plus in the non-contact mode and at ambient air. Thermogravimetric analysis (TGA) was conducted on TGA 1-Mettler Toledo thermogravimeter in the temperature range from room temperature to 700°C at a heating rate of 10°C min<sup>-1</sup> in static air. XRD pattern was recorded on a Rigaku D-max CIII X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation. The electronic spectra were taken on a Cintra 101 spectrometer. The emission spectra were taken on a Jasco FP-6500 spectrofluorometer. The specific surface area and pore size distribution were determined by the nitrogen adsorption method using Belsorp-mini II instrument with 23 points for evaluation. Before performing the adsorption experiments the sample was outgassed under vacuum at 150°C.

#### Synthesis of the ligand

All of the steps of the synthesis process are shown in Scheme 1. 5-(chloromethyl)-2hydroxybenzaldehyde (**A**) was prepared according previous report [26, 27].

#### 4-Carboxy-1-(3-formyl-4-hydroxy-benzyl)-pyridinium chloride (B)

As a typical procedure, in a 100 mL round bottom flask, 9.23 g (75mmol) of isonicotinic acid in methanol was added to the warm methanolic solution of 3 g NaOH. After 2h, the solution was exposed to air to evaporate solvent. The precipitated white powder of sodium isonicotinate was collected and washed with methanol (9.5 g; 87% yield).

5 g (35 mmol) of sodium isonicotinate was suspended in 25 mL of THF. A solution of 6 g (35 mmol) 5-(chloromethyl)-2-hydroxybenzaldehyde (**A**) in 15 mL THF was added to this suspension and the reaction mixture was refluxed for 48 h. The solvent was removed by filtration and the residue was washed with THF several times. The product taken up in a small volume of distilled hot water (30 mL), acidified with 6 M HCl and stirred for 30 min to achieve pH = 2. After concentrating the solution to about a half volume in a hot water bath, the formed solid product was collected by filtration. To remove the NaCl impurity, the white residue was treated with a small volume of methanol (20 mL), the mixture was filtered, and an excess volume of diethyl ether was added to the filtrate to precipitate the desired compound. The product was collected and dried under vacuum (4 g; 38% yield) [28]. Elemental anal. Calc. for  $C_{14}H_{12}NO_4Cl.1.2H_2O$ : C, 53.33; H, 4.60; N, 4.44. Found: C, 52.96; H, 4.30; N, 4.50. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta = 11.25$  (s, 1H, OH<sup>10</sup>), 10.28 (s, 1H, CH<sup>9</sup>O), 9.34 (d, 2H, H<sup>1,4</sup>), 8.46 (d, 2H, H<sup>2,3</sup>), 7.91 (d, 1H, H<sub>aromatic</sub>), 7.73 (dd, 1H, H<sub>aromatic</sub>), 7.13 (d, 1H, H<sub>aromatic</sub>), 5.88 (s, 2H, C<sup>5</sup>H<sub>2</sub>Cl) ppm. FT-IR (KBr, cm<sup>-1</sup>): 3198 (v<sub>O-H, H2O</sub>), 3059 (v<sub>C-H-aromatic</sub>), 2926(v<sub>C-H-aliphatic</sub>), 2865 (v<sub>C-H-aldehyde</sub>), 1711 (v<sub>C=O-acid</sub>), 1671 (v<sub>C=O-aldehyde</sub>), 1617, 1491 (v<sub>C=C</sub>).

## Synthesis of Schiff base ligand, 4-Carboxy-1-{3-[(4-carboxy-phenylimino)-methyl]-4-hydroxybenzyl}-pyridinium chloride (L)

1.7 g (5.79 mmol) of 4-Carboxy-1-(3-formyl-4-hydroxy-benzyl)-pyridinium chloride (**B**) was dissolved in 40 mL hot methanol, and 10 mL methanolic solution of *p*-aminobenzoic acid (0.794 g; 5.79 mmol) was added to above solution slowly. Fine yellow crystal of the product was formed spontaneously and the reaction mixture was stirred for 2h. After this time, the products were isolated, and subsequently washed with methanol several times via centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh methanol. The product was collected and dried under vacuum (1.4 g; 59% yield). Elemental anal. Calc. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>5</sub>Cl: C, 61.10; H, 4.15; N, 6.79. Found: C, 61.49; H, 4.32; N, 6.43. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  = 12.68 (s, 1H, OH<sup>10</sup>), 9.02 (d, 2H, H<sup>1.4</sup>), 8.92 (s, 1H, N=CH<sup>9</sup>), 8.20 (d, 2H, H<sup>2.3</sup>), 8.00 (d, 2H, H<sup>12,13</sup>), 7.85 (d, 1H, H<sub>aromatic</sub>), 7.60 (dd, 1H, H<sub>aromatic</sub>), 7.45 (dd, 2H, H<sup>11,14</sup>), 7.05 (d, 1H, H<sub>aromatic</sub>), 5.78 (s, 2H, C<sup>5</sup>H<sub>2</sub>Cl) ppm. FT-IR (KBr, cm<sup>-1</sup>): 3381 (v<sub>O-H</sub>), 3121 (v<sub>C-Haromatic</sub>), 2926 (v<sub>C-H-aliphatic</sub>), 1708 (v<sub>C=O-acid</sub>), 1625 (v<sub>C=N</sub>).

#### Synthesis of Zn-ICP by precipitation method

A solution of  $Zn(OAc)_2.2H_2O$  (1.50 g; 6.83 mmol, 6 mL) in DMSO was added slowly to a 10 mL hot DMSO solution of Schiff base ligand (L) (1.30 g, 3.15 mmol). Immediately, large amount of precipitate was observed in the solution. The colloidal solution was further stirred and 4 mL taken from the reaction mixture at various times (5, 10, 30, 60 min). The yellow precipitate was isolated by centrifugation and washed with DMSO and ethanol several times (0.91 g; 48% yield). Elemental anal.

Calc. for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>7</sub>ClZn<sub>2</sub>.2H<sub>2</sub>O: C, 46.07; H, 2.86; N, 4.67; Zn, 21.81. Found: C, 46.42; H, 2.81; N, 4.96; Zn, 22.02. FT-IR (KBr, cm<sup>-1</sup>): 3427 (v<sub>O-H, H2O</sub>), 3051 (v<sub>C-H-aromatic</sub>), 2893 (v<sub>C-H-aliphatic</sub>), 1620 (v<sub>C=N</sub>), 1568 (v<sub>C=O-asymmetric</sub>), 1470 (v<sub>C=O-symmetric</sub>).



Scheme 1. Illustrative preparation steps of the ligand preparation and proposed structure for Zn-ICP infinite coordination polymer.

#### **Results and Discussion**

To fabricate **Zn-ICP**, the 4-Carboxy-1-{3-[(4-carboxy-phenylimino)-methyl]-4-hydroxy-benzyl}pyridinium chloride (**L**) containing carboxyl groups were designed to act as ligand for coordination of the metal ion (Scheme 1). For this purpose, functionalized salicylaldehyde (**B**) was synthesized by nucleophilic substitution of chloro group of 5-(chloromethyl)-2-hydroxybenzaldehyde (**A**) with sodium isonicotinate followed by acidification of the mixture to protonate the carboxylate group. In the next step, ligand (**L**) was prepared from 4-Carboxy-1-(3-formyl-4-hydroxy-benzyl)-pyridinium chloride (**B**) and p-aminobenzoic acid by Schiff base condensation reaction. As shown in Scheme 1, the mixing of DMSO solutions of prepared ligand (**L**) and Zn(OAc)<sub>2</sub> at room temperature achieved the **Zn-ICP** as light yellow precipitate. To study the chemical composition of obtained **Zn-ICP**, ICP-OES and CHN elemental analysis were carried out which indicated the existence of two zinc ions per one ligand in each monomeric unit of **Zn-ICP** and confirmed the proposed structure. One equivalent of  $Zn^{2+}$ ions was coordinated by N,O site of the ligand. Second equivalent of zinc cations acted as node to connect metal-organic building blocks together through the carboxylate groups. The existence of one acetate anion is required in each unit for the neutrality of prepared **Zn-ICP**.

The chemical composition of product was also explored by energy dispersive X-ray (EDX) spectroscopy (Fig. 1). It can be deduced from EDX spectrum that the product is composed of C, N, O, Cl and Zn elements. The 1.486 eV signal of Al is related to the coating material.



An important issue in the studying of ICP particles is that one should work with amorphous rather than crystalline materials, so the single crystal X-ray analysis cannot be used to study the formation and the exact structures of the obtained ICP particles [11]. XRD analysis of **Zn-ICP** (Fig. 2) indicated that it is amorphous and no crystalline structure was formed during the preparation stages. It means that similar to other examples of ICP particles achieved from the polymerization-precipitation approach [5, 13, 29], this method do not favor slow crystallization which often produces the amorphous structures [11].



Fig. 2. XRD pattern of the amorphous Zn-ICP.

Further evidence for the construction of **Zn-ICP** particles was provided by FT-IR spectroscopy. Coordination of carboxylate groups to Zn<sup>2+</sup> ions was verified by the observation of the shift in the carboxyl stretching frequency from 1708 cm<sup>-1</sup> to 1568 and 1470 cm<sup>-1</sup>. The C=N frequency shift from 1625 cm<sup>-1</sup> in ligand to 1620 cm<sup>-1</sup> in **Zn-ICP** also verified the coordination of N,O site to Zn<sup>2+</sup> ions. The thermal behavior and stability of the **Zn-ICP** was studied by thermogravimetric analysis (TGA/DTA; Fig. 3). The TGA curve exhibited a slight weight loss from room temperature to 150 °C owing to the removing surface adsorbed water [30]. The ligand species started to decompose above 200 °C and the framework collapsed until 450 °C. From the relatively high temperature needed for this decomposition, it can be found that the organic linker is strongly bonded to metal cation. Further weight loss was not observed with heating of the sample to 700 °C. The final residual weight is 25.47% (calculated: 25.60%) attributed to the ZnO formation. TGA analysis clearly indicates the existence of

two water molecules and approves the molecular weight of the monomeric unit of the prepared Zn-ICP.

From the DTA curve it is obvious that the loss of water is endothermic. An intense exothermic

decomposition peak was observed for organic residue burning at about 380 °C.



Fig. 3. TGA/DTA curves of Zn-ICP.

To provide better insight from the **Zn-ICP** morphology, FE-SEM analysis was employed (Fig. 4). The prepared **Zn-ICP** particles have smooth surface with diameters of about 70 nm. **Zn-ICP** nanoparticles formation process was further explored at various reaction times to find evidence for the possible growth mechanism. Three clear evolution steps could be seen as exhibited in Fig. 4. At the primary stages, an investigation of the intermediate product obtained after 5 min indicated that a large number of sphere like nanoparticles are present (Fig. 4a), while the intermediate formed after 30 min comprised from agglomerated nanoparticles (Fig. 4b). It is obvious that the nanoparticles have grown and attached to each other. By increasing the reaction time to 60 min the more agglomerated particles was resulted (Fig. 4c). However, the best time to achieve individual nanoparticles of **Zn-ICP** is 5 min.

From the time-dependent SEM analysis, proposed mechanism was deduced for the particle formation process, which involves nucleation, aggregation and growth. At early stages of the reaction with high concentrations of precursors, fine nanoparticles were produced from nucleation of product. However, with proceeding the reaction, the concentration of precursor decreases and the growth process become dominant and larger ICP particles with deviation from spherical shape were formed. The particle-growth step involves both the coalescence of the nanosized seeds and agglomeration into larger

particles structures along with the next adsorption of additional nanoparticles into the larger particle

cores.



**Fig. 4.** Representative FE-SEM images monitoring the formation of **Zn-ICP** at: a) 5 min, b) 30 min, c) 60 min, and d) high resolution FE-SEM image of (c).

High resolution FE-SEM image (Fig. 4d) shows some porosity in the obtained **Zn-ICP** particles at 60 min. So, N<sub>2</sub> adsorption/desorption analysis was used to study the porosity of prepared sample. Fig. 5 depicts the N<sub>2</sub> adsorption/desorption isotherm of as-prepared **Zn-ICP**. As can be seen, the sample represent type-II isotherm, indicating its nonporous nature. The BET surface area was calculated to be 9.5 m<sup>2</sup>/g. Despite some earlier reports about high porosity and good gas storage ability of ICPs [11, 15, 19, 31], the obtained micro/nano scale coordination polymers did not show well gas storage. Although MOFs have good porosity for gas up-taking due to their well-defined porous framework, there is no any framework or porosity in ICPs for gas up-taking [25].



Fig. 5. Nitrogen adsorption/desorption isotherm of Zn-ICP nanoparticles prepared by precipitation method at 60 min

AFM was used in non-contact mode under ambient conditions to study the topography and roughness of the **Zn-ICP** in three dimensions (Fig. 6). Crest and trough roughness of the surface was clearly seen in the AFM image. The image confirmed spherical morphology and monodispersed nanoparticles with height of about 77 nm.



Fig. 6. AFM image of Zn-ICP nanoparticles.

Fig. 7 illustrates the absorption and emission spectra of the ligand and **Zn-ICP** nanoparticles. Evidently, despite the similarity in the highest lying transition  $(\pi \rightarrow \pi^*)$  below 350 nm in absorption spectra, prominent differences are seen around 350–500 nm, in which  $n \rightarrow \pi^*$  transition of ligand was disappeared in **Zn-ICP** absorption spectrum and exhibits another absorption band at 442 nm owing to MLCT transition. Upon excitation (at 380 nm and 440 nm for ligand and **Zn-ICP**, respectively), the ligand showed an emission peak at 550 nm. After coordination of the ligand to  $Zn^{2+}$  ion, the intensity of 550 nm emission peak reduced indicating the involvement of nitrogen atom in the coordination to  $Zn^{2+}$  ion. This may be rationalized by incorporation of the  $Zn^{2+}$  ion in the structure of **Zn-ICP** and decreasing the intensity of the  $n \rightarrow \pi^*$  transition.



Fig. 7. UV/Vis (in DMSO) and fluorescence (in the solid state) spectra of ligand ( $\lambda_{ex} = 380$  nm) and Zn-ICP ( $\lambda_{ex} = 440$  nm).

ICP like MOF counterpart and coordination complex could be good precursors for metal oxide preparation [32-38]. Prepared **Zn-ICP** was calcined at 600 °C for 2 h for preparing ZnO nanoparticles. During this process organic ligand was burn gradually and zinc oxide is final product. As show in Fig. 8a, the obtained XRD pattern of the ZnO nanoparticles is completely in compliance with the hexagonal phase of bulk ZnO (JCPDS card no. 80-0075). Absence of any organic residue in FT-IR spectrum (Fig. 8b) confirmed the purity of the obtained ZnO nanoparticles. The FE-SEM analysis (Fig. 8c) illustrates the size and morphology of ZnO nanoparticles. Fig. 8c shows monodispersed nanoparticles with 60 nm average size slightly less than 70 nm in precursor (Zn-ICP) due to the role of organic linker.

The optical absorption spectrum of the obtained ZnO was shown in Fig. 8d. Tauc equation [39] shows the absorption coefficient as a function of photon energy for allowed direct transitions:

 $(\alpha h \upsilon) = C (h \upsilon - E_g)^{1/2}$ 

where  $\alpha$  is absorption coefficient, h is Planck's constant,  $\upsilon$  is the frequency, C is a constant, and E<sub>g</sub> is the band gap energy. From the Tauc plot depicted in the inset of Fig. 8d, the E<sub>g</sub> value was found to be 3.95 eV for ZnO. The larger optical band gap energy of ZnO nanoparticles in comparison with the bulk counterpart (3.3 eV) [40] is due to the quantum confinement effect [41].



**Fig. 8.** (a) XRD pattern, (b) FT-IR spectrum, (c) FE-SEM image, and (d) UV-Vis spectrum (the inset shows Tauc plot) of ZnO product.

#### Conclusion

New bi-carboxylic acid functionalized Schiff base linker and corresponding zinc coordination polymer were prepared and structurally characterized. **Zn-ICP** nanoparticles were obtained immediately after mixing the precursor solutions of the ligand and Zn<sup>2+</sup> ions. The initial formation of sphere like **Zn-ICP** nanoparticles and the aggregation of initial seeds for the final formation of larger nanoparticles were monitored via electron microscopy. The analysis of initial and final products illustrated that they had the same chemical compositions and morphologies but different sizes. Morever, the best time for the formation of individual nanoparticles of **Zn-ICP** is 5 min. Solid state transformation of **Zn-ICP** produced pure ZnO nanoparticles with larger band gap relative to bulk counterpart.

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- Step by step preparation of new bi-carboxylic acid linker.
- Synthesis of new amorphous infinite coordination polymer.
- Represent a reasonable mechanism for growth of crystals.