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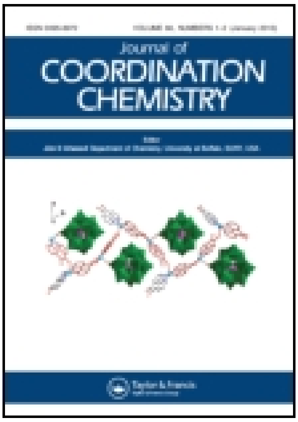

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Zn-nicotinate complex – a precursor for ZnO nanoparticles

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A zinc-nicotinate complex has been prepared by direct reaction of zinc acetate and nicotinic acid in the presence of template tetramethylethylenediamine and is characterized by elemental analysis, FTIR, and TGA/DTA. The Zn complex was a precursor for the synthesis of ZnO nanoparticles. A correlation of the thermal and spectral properties of the precursor complex with its structure has been discussed. Thermolysis under air was studied by thermogravimetry, and the resulting ZnO product was characterized by XRD and TEM, showing compact particles with a diameter of about 17–50 nm.

Keywords: Zinc-nicotinate complex; Structural characterization; ZnO nanoparticles

1. Introduction

Zinc oxide (ZnO) is one of the earliest materials studied as a gas sensor, primarily due to high mobility of conduction electrons in material and good chemical and thermal stability under operating conditions [1]. ZnO nanostructures have been the subject of interest due to their potential wide-ranging applications [2]. ZnO is a wide band gap semiconductor, used in electronics, photoelectrochemstry, and sensor technology [3]. A mixed catalyst containing copper and ZnO is used in methanol synthesis. Recent studies indicate that the Cu–ZnO interface plays an important role under reducing reaction conditions [4].

Different synthetic methods have been devised, including sol-gel technique [5], microemulsion synthesis [6], mechanochemical processing [7], spray pyrolysis and drying [8], plasma synthesis [9], hydrothermal processing [10], sonochemical or microwave-assisted synthesis [11], direct precipitation [12], etc. However, formation of the Zn–O–Zn bond among the nanoparticles due to the existence of water results in hard agglomerates, which impede applications of ZnO nanoparticles. Therefore, removal of water in precursors is a key process for reducing hard agglomerates.

The preparation of ZnO nanoparticles by thermolysis of organometallic [13] or molecular precursors and metal-organic framework precursors [14] has been reported. Guo *et al.* [15] reported the formation of ZnO nanoparticles [100–300 nm size] by thermolysis of [Zn

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(en)$_3$][Zn(CN)$_4$]. Recently Hosseinian *et al.* [16] and Akbari *et al.* [17] reported the synthesis of ZnO nanoparticles using metal-organic framework and coordination polymers as starting materials.

The present study prepares ZnO nanoparticles by thermolysis of [Zn(nicot)$_2$·4H$_2$O] at moderate temperature. This process was followed by thermogravimetry and the product was characterized with respect to its crystallinity and morphology. Loss of the ligands leads to yield a fine particulate ZnO phase.

2. Experimental

2.1. *Chemicals*

Zn(Ac)$_2$·4H$_2$O was purchased from Loba Chemie. Nicotinic acid and tetramethylethylenediamine (TMED) were purchased from Sigma Aldrich. All reagents and solvents were of commercial grade and used without purification.

2.2. *Synthesis of precursor complex and ZnO nanoparticle*

2.2.1. Precursor complex [Zn(nicot)$_2$·4H$_2$O]. Nicotinic acid (0.32 g) was dissolved in 50 cm^3 of hot water (80 °C) and then cooled to room temperature. This solution was added dropwise to zinc acetate (0.23 g). The reaction mixture was stirred for about 10 min and TMED (0.39 mL) was added dropwise to the reaction mixture; then the reaction mixture was stirred for 30 min. The white crystalline material obtained was washed with distilled water and methanol and dried under vacuum. Anal. Calcd for $C_{12}H_{18}N_2O_8Zn$: C, 37.82; H, 4.23; N, 7.34; Zn, 17.15%. Found: C, 38.50; H, 3.89; N, 6.91; Zn, 17.37%.

2.2.2. ZnO nanoparticle. Thermal decomposition of the as-synthesized precursor complex was carried out up to 500 °C until the decomposition of the organic moiety was reflected by an intense exothermic effect in the DTA curve with maximum at 490 °C. The final product of the decomposition, ZnO, was obtained as white powder.

3. Results and discussion

3.1. *IR spectra and structure correlation of [Zn(nicot)$_2$·4H$_2$O]*

The IR spectra confirmed the presence of water as well as organic moieties in the precursor complex. The IR spectral data are listed in table 1.

The difference between the asymmetric and symmetric carboxylate stretches ($\Delta = \upsilon_{as}(COO^-) - \upsilon_s(COO^-)$) is used for correlation of infrared spectra with the structure. For ionic carboxylate, not coordinated with a metal ion, it is 170 cm^{-1} [18].

The asymmetric carboxylate stretch $\upsilon_{as}(COO^-)$ shifts to higher wavenumbers in comparison to ionic group because in monodentate coordination the redistribution of electron density takes place, which consequently shifts the Δ value to higher wavelength. Bidentate coordination

Table 1. Characteristic IR absorption bands in [Zn(nicot)$_2$·4H$_2$O].

Assignment	[Zn(nicot)$_2$·4H$_2$O]
υ(O–H)$_{\text{water}}$	3300s, broad
υ(C=O)	–
δ(H$_2$O)	1630s
υ_{as}(COO$^-$)	1580s
υ(C=C), υ(C=N)	1630s, 1520 m
υ_{s}(COO$^-$)	1400s
δ(C–H)$_{\text{pyridine}}$	1380s
υ(C–O)	—
	1200w
	1160w, 1060s
y(C–H)$_{\text{pyridine}}$	850 m
	780 m, 650 m

shifts the position of the asymmetric carboxylate stretch to lower wavenumbers in comparison to ionic, and thus lowers the value of Δ. The following order has been observed for carboxylate complexes of divalent metal cations [19].

$$\Delta\ (\text{monodentate}) > \Delta\ (\text{ionic}) > \Delta\ (\text{bridging bidentate}) > \Delta\ (\text{chelating bidentate})$$

Application to spectra of [Zn(nicot)$_2$·4H$_2$O] shows asymmetric and symmetric stretches υ_{as}(COO$^-$) and υ_{s}(COO$^-$) at 1580 and 1400 cm^{-1}, respectively, and with a Δ value 180 cm^{-1}. This value is only slightly higher than expected for ionic carboxylate (170 cm^{-1}) [18]. The higher value can be ascribed to strong hydrogen bonds formed by carboxylate oxygen and the effect of the pyridine ring on carboxylate.

3.2. *Thermal analysis*

3.2.1. Phenomenological aspect. Thermal decomposition of [Zn(nicot)$_2$·4H$_2$O] is shown in Supplementary material (TGA DTA curve). The compound is thermally stable to 80 °C. Above 80 °C, four waters are lost in one step at 80–125 °C (exp. weight loss 20.0%; calcd 18.8%). Release of crystalline water was accompanied by endothermic effect on the DTA curve observed at 110 °C.

Thermal decomposition of zinc nicotinate is shown in scheme 1. The dehydrated Zn (nicot)$_2$ is thermally stable to 390 °C. The thermal stability of the dehydrated product is slightly lower than the stability of anhydrous zinc(II) nicotinate (433 °C) prepared by hydrothermal synthesis [18]. As there is no information concerning gas atmosphere (inert gas or air) [20] further discussion would not be appropriate. The temperature of decomposition of the analogous cobalt complex in air is only slightly higher (415 °C) [21] than the onset of the decomposition of zinc(II) nicotinate. Thermal analysis of [Zn(nicot)$_2$·4H$_2$O]

$$[\text{Zn(nicot)}_2](4\text{H}_2\text{O})] \xrightarrow{\text{80-125 °C}} [\text{Zn(nicot)}_2] + 4\text{H}_2\text{O}$$

$$[\text{Zn(nicot)}_2] \xrightarrow{\text{390-540 °C}} 2\text{nicot} + \text{ZnO}$$

Scheme 1. Thermal decomposition of zinc(II) nicotinate complex.

has also been described elsewhere [22]. Two different temperatures are reported for the decomposition of the complex in the text and table (140 and 210 °C, respectively). However, we think that these values correspond to decomposition of the mixture of nicotinic acid and zinc nicotinate. The thermal analysis study suggests the correct onset of 390 °C for the thermal decomposition of the zinc(II) nicotinate complex.

The pyrolysis of two molecules of organic ligand took place (exp. weight loss 60.0%; calcd 64.2%) at 390–540 °C. The decomposition from 390 to 440 °C is very intense while from 440 to 540 °C the mass loss is less. Decomposition of the organic moiety was

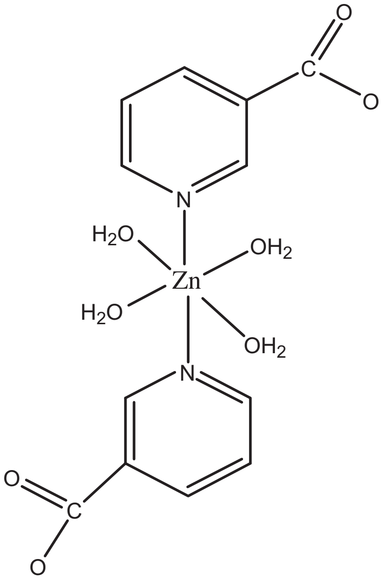

Figure 1. Structure of [Zn(nicot)$_2$(4H_2O)].

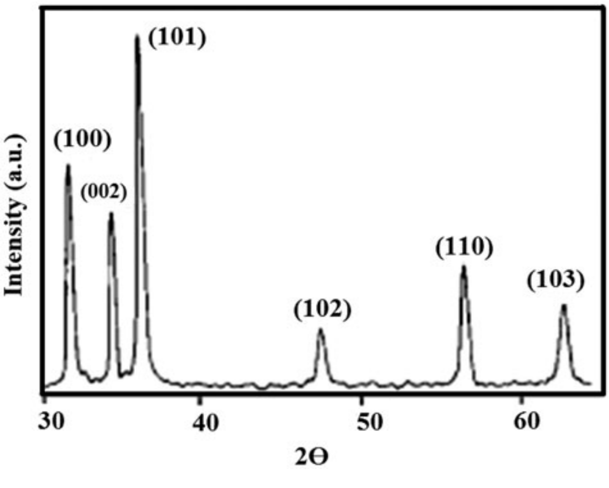

Figure 2. XRD pattern of the as-synthesized ZnO nanoparticle.

reflected by an intense exothermic effect on the DTA curve with maximum at 490 °C, suggesting oxidation of the organic part of the complex occurred in air. The final product of the decomposition, ZnO, was identified by X-ray diffraction.

3.2.2. Thermal stability and structure correlation. In [Zn(nicot)$_2$(4H$_2$O)], all water molecules are coordinated to zinc and situated between mirror planes occupied by nicotinates (figure 1). The water molecules are present in "planes" and due to this structural characteristic the complex dehydrates easily.

3.3. *X-ray diffraction*

X-ray diffraction studies confirmed that the synthesized materials were ZnO of the Wurtzite phase and the structure agreed with the reported JCPDS data (card No. 5-664). Figure 2 shows the powder XRD pattern of the sample. Line broadening of the diffraction peaks is an indication that the synthesized materials are in nanometer range. The crystallite size was calculated from Scherrer formula applied to the major peaks and was 17 nm.

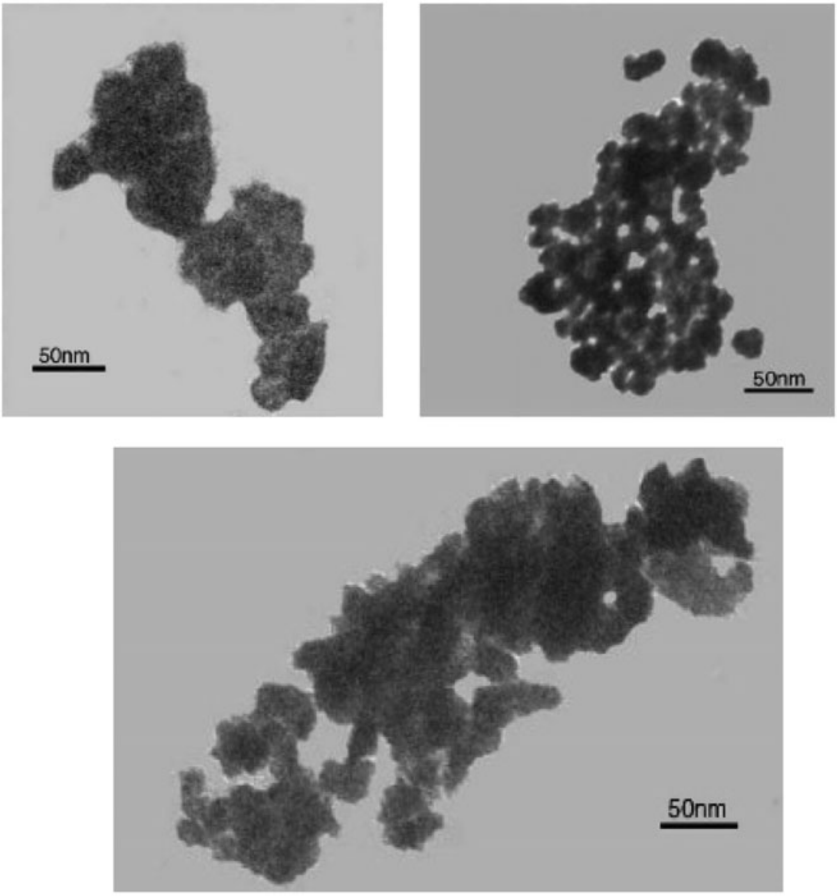

Figure 3. TEM micrographs of the as-synthesized ZnO nanoparticles.

3.4. *Transmission electron microscopy*

Figure 3 gives the TEM micrographs of the ZnO nanoparticles. TEM patterns show that the particles are agglomerated to some extent.

4. Conclusions

[Zn(nicot)$_2$(4H$_2$O)] was prepared and the crystal structure of the compound was determined. Under oxygen thermolysis of [Zn(nicot)$_2$(4H$_2$O)] leads to ZnO nanoparticles with a size of 20–50 nm. There is no correlation between the morphology of the crystals of the parent compound and the ZnO, i.e. the structure completely breaks down during thermolysis. Decomposition of the zinc-nicotinate compound under oxygen occurred in two steps at 80–125 °C and 390–540 °C. Thermolysis of this Zn-based coordination compound is a useful route to nanosized ZnO. The zinc nicotinate complex has been synthesized earlier but functions as a precursor for nanoscale ZnO only when it is synthesized in the presence of TMED, because in aliphatic amine on heating the amount of carbon dioxide evolved is more (due to more no. of carbon atoms) and will restrict further agglomeration. Thus TMED plays an important role for the zinc complex to act as a precursor for nanoscale ZnO.

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