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Preparation and characterization of Co₃O₄ nanoparticles by solid state thermal decomposition of cobalt(II) macrocyclic Schiff base complexes

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Nanoparticles of Co_3O_4 were successfully synthesized by solid state thermal decomposition of the cobalt(II) macrocyclic Schiff base complexes [CoL¹] (1) and [CoL²] (2) as novel precursor at 450 °C for 3 hrs without employing toxic solvent or surfactant and complicated equipment. The products were characterized by Fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy (UV-Vis), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results show that the Co_3O_4 products are pure and single phase and have plate-like. The optical spectra of the Co_3O_4 products indicated two direct band gaps at about 1.4 and 2.5 eV.

Key words: Nanoparticles, Cobalt(II) macrocyclic Schiff base, Thermal decomposition, XRD, SEM, TEM.

Introduction

Macrocyclic Schiff base compounds containing nitrogen and oxygen donor atoms play key role in understanding the coordination chemistry of transition metal ions and have received much attention in recent years [1-7]. Macrocyclic complexes have been received much attention because of their potential applications in applied science and bioinorganic chemistry [8-10]. The cobalt complexes play important roles as catalyst and also as oxygen carriers [11, 12]. Recently, several groups used cobalt complexes as new precursor for preparation of cobalt oxide nanoparticles by various methods [13-22]. Although considerable effort has been dedicated to the controlled synthesis of Co₃O₄ nanoparticles from various precursors [13-26], only little attention was focused on cobalt(II) Schiff base complexes [19, 21]. Among various techniques for preparation of cobalt oxide nanoparticles, such as microwave assisted, hydrothermal, chemical precipitation and reverse micelles [23-26], thermal decomposition is one of the best [13-22, 27-30], because it is inexpensive and don't used toxic solvent and surfactant.route where of process conditions, particle size, particle crystal structure and purity can be easily controlled.

Recently, our group has been synthesized metal oxides nanoparticles via thermal decomposition method of transition metal Schiff base complexes [31-37]. Herein, we report the synthesis and characterization of



Scheme 1. The chemical structures of $[CoL^1]$ (1) and $[CoL^2]$ (2).

Co₃O₄ nanoparticles by solid state thermal decomposition of cobalt(II) macrocyclic Schiff base complexes [CoL¹] (1) and $[CoL^2]$ (2) (Scheme 1).

Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Dialdehydes, 1,2-bis (2-formylphenyl) propane and 1,2-bis (2-formyl-3-methoxyphenyl) propane, used in the synthesis were prepared by the reaction of salicylaldehyde or 3-methoxysalicylaldehyde and 1,3dibromopropane in the presence of K₂CO₃ at 80 °C according to the literature [38].

Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. Optical absorption spectra were recorded on a Cary 100 UV-Visible Spectrophotometer, VARIAN EL 12092335 in a wavelength range of 200-700 nm at room temperature. The sample for UV-Vis studies was well dispersed in distilled water by sonication for 10 min to form a homogeneous suspension. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-K α radiation with nickel beta filter in the range $2\theta = 10^{\circ}$ - 80°. The FT-

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IR (Perkin-Elmer spectrophotometer) spectra were recorded as a KBr disk. The transmission electron microscopy (TEM, Jeol JEM 1400 with an accelerating voltage of 120 kV) and scanning electron microscopy (SEM, Philips XL-30E) images were obtained.

To a stirred solution of dialdehydes, 1,2-bis (2-formylphenyl)propane and 1,2-bis (2-formyl-3-methoxyphenyl) propane (2 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (2 mmol) in methanol (50 mL) was added dropwise 1,3phenylenediamine (2 mmol) in methanol (10 mL). After the addition was completed, the stirring was continued for 2 hrs. The microcrystalline powder of the complexes were filtered and washed with cold methanol and then dried in air for 2 days.

Anal. calcd for $CoC_{25}H_{24}O_{10}N_4$ [CoL¹] (1): C, 55.55; H, 4.48; N, 10.37%; Found C, 54.56; H, 4.39; N, 10.26%. FT-IR (KBr, cm⁻¹): 3369 (H₂O), 2880-3069 (H aromatic and aliphatic), 1619 (C = N), 1487-1597 (C = C aromatic), 1384 (NO₃).

Anal. calcd for $CoC_{23}H_{26}O_{11}N_4$ [CoL²] (2): C, 51.68; H, 4.90; N, 10.48%; Found C, 51.78; H, 4.83; N, 10.56%. FT-IR (KBr, cm⁻¹): 3378 (H₂O), 2936 (H aromatic and aliphatic), 1622 (C = N), 1476-1578 (C = C aromatic), 1383 (NO₃).

Microcrystalline powder of the mononuclear cobalt(II) macrocyclic Schiff base complexes $[CoL^1]$ (1) and $[CoL^2]$ (2) (about 0.5 g) is loaded into a platinum crucible and then placed in the electrical furnace and heated, at a rate of 10 °C/min in air, up to 450 °C. After 3.5 hours, the resulting nanoparticles of Co₃O₄ are washed with ethanol-at least three times-to remove eventual impurities, and then dried in air for 2 days. FT-IR (KBr pellet, cm⁻¹): 3463, 1654 (H₂O), 662, 567 (Co-O) for Co₃O₄ prepared from $[CoL^1]$ (1) and 3426, 1650 (H₂O), 666, 571 (Co-O) for Co₃O₄ prepared from $[CoL^2]$ (2).

Results and Discussion

The cobalt(II) macrocyclic Schiff base complexes (1 and 2), as novel precursors, were synthesis by methanolic solution of cobalt(II) nitrate, dialdehyde and 1,3-phenylenediamine in molar ration 1 : 1 : 1 at room temperature for 2 hrs. Characterization of the complexes were carried out by FT-IR and elemental analysis (CHN). The proposed structures of the complexes are presented in Scheme 1, and are similar to the macrocyclic complexes that reported by Ilhan and co-workers [1-3].

The complexes are insoluble in most common organic solvents such as methanol, chloroform, ethanol and acetonitrile. Then the suitable crystals could not be obtained for single-crystal X-ray structure determination. The metal-ligand mole ratio was found to be 1:1, according to elemental analysis.

The characteristic infrared spectrum data are given in the experimental section. In the FT-IR spectra of the



Fig. 1. TGA curves of complexes 1 (top) and 2 (bottom).

complexes 1 and 2, a broad band's appear at 3369 and 3378 cm⁻¹, respectively, corresponding to the frequency vibrations of OH group of the uncoordinated water molecules. The bands appeared at 1619 cm⁻¹ (1) and 1622 cm⁻¹ (2) are assigned to the stretching vibration of $v_{C=N}$ group of macrocyclic Schiff base ligand indicating coordination of the azomethine nitrogen to cobalt ion. The stretching frequencies at 1384 (1) and 1383 (2) are corresponding to NO₃ counter ion [1-3].

The TGA curves of the complexes are shown in Fig. 1. The thermal decomposition of the complexes exhibits the presence of two different mass loss steps. Elemental analysis of the complexes indicate the presence of three water molecules in the complex 2. The uncoordinated water molecules were determined using thermal analysis measurements (TGA), in the 25 -400 °C. The TGA results of complexes only showed that the water molecules presence in complex 2 and were removed in the 80-120 °C range. Complex 1 is stable up to 340 °C, and during further heating undergoes decomposition in two steps in the temperature range 340-426, and 426-598 °C, while complex 2 is stable up to 29 °C, and during further heating undergoes decomposition in two steps in the temperature range 29-304, and 304-681 °C. The second decomposition step of the complexes is mainly one of decomposition. The final product may be residual carbon and cobalt oxide that exist at 598 for 1 and 681 for 2.

The Co_3O_4 nanoparticles were obtained by direct calcinations in an air atmosphere of cobalt complexes $[CoL^1]$ (1) and $[CoL^2]$ (2) at 450 °C [20] for 3.5 h.

The infrared spectra of the product Co_3O_4 samples, as presented in Fig. 2, that show two absorption bands at 662 and 567 cm⁻¹ for Co_3O_4 prepared from $[CoL^1]$ (1) and 666 and 571 cm⁻¹ for Co_3O_4 prepared from $[CoL^2]$ (2), that are assigned to the Co-O stretching bands of pure normal spinel structure of Co_3O_4 [14-22]. Two distinctive bands around 570 and 663 cm⁻¹ are associated with Co^{III} -O and Co^{II} -O vibration in octahedral and tetrahedral sites of Co_3O_4 lattice, respectively [20].

The XRD patterns of Co₃O₄ nanoparticles prepared



Fig. 2. FT-IR spectra of Co_3O_4 nanoparticles prepared from 1 (left) and 2 (right).



Fig. 3. XRD patterns of Co_3O_4 nanoparticles prepared from 1 (top) and 2 (bottom).

from the thermal decomposition of 1 and 2 at 450 °C for 3.5 h are shown in Fig. 3. The XRD patterns reveals diffraction peaks with 2 theta values of 19, 31, 37, 38, 45, 56, 59 and 65 that are assigned to the 111, 220, 311, 222, 400, 422, 511 and 440 crystal planes of the crystalline phase of Co_3O_4 , respectively. All of the diffraction peaks are in good agreement with the cubic



Fig. 4. SEM images of Co₃O₄ nanoparticles prepared from 1 (left) and 2 (right).



Fig. 5. TEM images of Co_3O_4 nanoparticles prepared from 1 (left) and 2 (right).

 Co_3O_4 phase (JCPDS Card No. 76-1802) [14-19], confirms that the complexes are decomposed completely into the cubic Co_3O_4 phase and are in good agreement with the FT-IR results.

The morphology of the Co_3O_4 products was investigated by SEM. The SEM images of the Co_3O_4 products are shown in Fig. 4. From the SEM micrographs, it was observed that the nanoparticles were similar and uniform sizes but these particles were agglomerates.

Fig. 5 shows the TEM images of the Co_3O_4 nanoparticles prepared at 450 °C. The TEM samples were



Fig. 7. $(\alpha h\nu)^2 \approx h\nu$ curves of Co₃O₄ nanoparticles prepared from 1 (left) and 2 (right).

prepared by dispersing the powder in ethanol by ultrasonic vibration. The uniform of the Co_3O_4 nanoparticles have plate-like shapes with weak agglomeration. The nanoparticles of Co_3O_4 with particle size about 10-100 nm are seen inside TEM images. The SEM and TEM results confirm that the cobalt(II) macrocyclic Schiff base complexes $[CoL^1]$ (1) and $[CoL^2]$ (2) are suitable precursors for the preparation of Co_3O_4 nanoparticles.

Optical properties of the Co_3O_4 nanoparticles were investigated by UV-vis spectroscopy. Fig. 6 shows the UV-Vis spectra of the Co_3O_4 products with two absorption bands in the wavelength ranges of 150-300 and 450-600 nm for nanoparticles prepared from 1 and 2. The first band can be assigned to the O²⁻ Co²⁺ while the second band can be assigned O²⁻ Co³⁺ charge transfer [15, 16, 18].

Cobalt oxide is an antiferromagnetic *p*-type semiconductor with excellent properties and its optical band gap can be obtained by the following equation: $(\alpha hv)^2 = B(hv-E_g)$

The $(\alpha hv)^2 \approx hv$ curves for the Co₃O₄ nanoparticles are shown in Fig. 7. The band gap of the Co₃O₄ products are 2.5 and 1.5 eV for nanoparticles prepared from [CoL¹] (1) and 1.4 and 2.3 eV for nanoparticles prepared from [CoL²] (2), which are similar to the previous reports [19, 21, 22], and also revealing obvious red shift of absorption peaks in comparison with the previous reports [14-16, 18].

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