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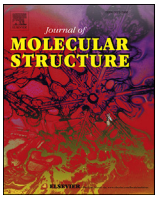

Amine ligand-based hydrothermal synthesis of Co_3O_4 nanoparticles, characterization and magnetic study

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ABSTRACT

Cobalt(II,III) oxid (Co_3O_4) nanostructures have been successfully synthesized using $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ (en: ethylenediamine) as the single precursors via hydrothermal method, and $CoCl_2 \cdot 6H_2O$ through a facile ammonia-assisted approach. Indeed, ammine and en ligands, as well as ammonia vapor, act as the sources of hydroxide ion in the preparation of Co_3O_4 nanoparticles. The structure of products was confirmed by X-ray diffraction (XRD) technique and Fourier-transform infrared (FT-IR) spectroscopy and their morphologies were examined by scanning electron microscopy (SEM). The optical study of the as-prepared Co_3O_4 nanostructures using UV–Vis diffused reflectance spectroscopy (DRS) exhibited their semiconducting property by revealing one optical band gap in 3.3 eV. Moreover, the vibrating sample magnetometry (VSM) measurements showed a weak ferromagnetic behavior that could be attributed to uncompensated surface spins and/or finite-size effects. Further, the effects of the nature of the precursor, its concentration, temperature and reaction time on the size and morphology of the samples were studied in detail.

1. Introduction

Cobalt(II,III) oxid (Co_3O_4) comes from a Co(II) and two Co(III) cations that occupy tetrahedral and octahedral sites in a unique normal spinel structure, respectively, and is a semiconductor matter [1,2]. Co_3O_4 nanomaterials have high potential in gas sensors, rechargeable batteries, magnetic materials and use for ceramics as pigments, heterogeneous catalysts, energy storage and electrochemical devices [3–7]. This prospect of Co_3O_4 has led to substantial research and efforts developing synthetic routes for various types of its nanostructures. Therefore, Co_3O_4 nanostructures such as nanoparticles, nanoplates, nanowires, nanotubes, nanoflowers and nanosheets have recently received remarkable attention and many applications, because of their novel and interesting transport, optic and magnetic properties that are not observed by their bulk materials [8]. Among these structures, Co_3O_4 nanoparticles has been extensively prepared of using the physical and chemical techniques such as sol-gel [9], solvothermal [10,11], combustion [12], chemical vapor deposition [13,14], microemulsion [15], thermal decomposition of cobalt precursors [16–20], ionic liquid-assisted [21], sonochemical [22], microwave-assisted [23,24] and mechanochemical [25] methods. The hydrothermal method because of its effectiveness on synthesizing different materials with various morphologies has attracted much attention recently. In addition, the hydrothermal method is one of the simplest and least expensive techniques for preparation of the nanosize transition metal oxides with relatively high specific surface areas at low temperature.

Among the numerous methods developed for preparing metal oxide nanostructures, the molecular precursor route has been regarded as one of the most convenient and practical techniques. By choosing a proper molecular precursor, nanocrystalline products could be obtained usually under conditions significantly milder than those employed in other synthesis. Because of their low cost, easy preparation and mild decomposition, metal-ammine complexes have been employed as ideal precursors for preparing metal oxide nanostructures [6,26,27]. Herein, we report a facile and surfactant-free hydrothermal method to synthesize Co_3O_4 nanoparticles from two simple complexes of Co(III) with amine ligands, hexaamminecobalt(III) chloride and tris(ethylenediamine)cobalt(III) chloride, and Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$). Also, the characterization of the obtained products by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, ultraviolet–visible diffused reflectance

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spectroscopy, and magnetic measurements is studied.

2. Materials and methods

All of the chemical reagents were of analytical grade (Merck) and used without further purification. The precursor complexes, $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$, were synthesized by chemical precipitation method before use, according to literature reported methods [28,29].

2.1. Preparation of Co_3O_4 nanostructures

2.1.1. Using hexaamminecobalt(III) chloride

In a typical procedure, the stainless steel autoclave (capacity 300 ml) including a beaker containing 25 mL aqueous solution of hexaamminecobalt(III) chloride (0.01 or 0.1 M) was sealed and transferred to an oven at 75 °C. After an appropriate time (1 or 6 h), the autoclave was cooled naturally to room temperature, then the resultant precipitate was collected by centrifugation and washed with distilled water and absolute ethanol for several times. After drying in oven at 70 °C, black powders were obtained. The reactions were repeated at 150 °C.

2.1.2. Using tris(ethylenediamine)cobalt(III) chloride

In the similar procedure, a 25 mL solution 0.1 M of $[Co(en)_3]Cl_3$ was obtained and transferred into the stainless steel autoclave, and then hydrothermally treated at 150 °C for 24 h. The produced precipitate was collected by centrifugation, washed with distilled water and absolute ethanol, respectively, and then dried at 70 °C to give black powder.

2.1.3. Using $CoCl_2·6H_2O$

In third procedure, one beaker containing 10 mL of 0.01 M $CoCl_2·6H_2O$ aqueous solution together with another beaker containing 10 ml ammonia solution 0.1 M were transferred into the stainless steel autoclave of 300 ml in capacity, which was then heated in an oven at 100 °C for 24 h. After that the autoclave was air-cooled to room temperature, the black products were collected by centrifugation and washed with distilled water and absolute ethanol for several times, followed by drying at 70 °C. The experimental conditions of all the obtained products have been summarized in Table 1.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were obtained on a Phillips X'Pert Pro X-ray diffractometer equipped with Ni-filtered Cu Kα source at scan range of $10 < 2\theta < 80$. The FT-IR spectra were recorded on a magna 550 FT-IR instrument with KBr pellets in the range of 400–4000 cm^{-1}. The morphology of the synthesized nanostructures was observed by means of an AIS 2100 scanning electron microscope. The particle size distribution of the products was measured by the diameter of 50 particles on the magnified SEM images using Digimizer software. UV–Vis spectra of Co_3O_4 nanostructures were recorded using a Shimadzu 180 spectrophotometer. Magnetic measurements were carried out at room temperature by a vibrating sample magnetometer, Meghnatis Daghigh Kavir Co. with the maximum magnetic field of 8 kOe.

Table 1
Summary of the experimental conditions for the synthesis of Co_3O_4 nanostructures.

Row	Precursor	Precursor concentration (M)	Temperature (°C)	Reaction time (h)	Sample
1	$[Co(NH_3)_6]Cl_3$	0.01	150	1	S_1
2	$[Co(NH_3)_6]Cl_3$	0.1	150	1	S_2
3	$[Co(NH_3)_6]Cl_3$	0.01	150	6	S_3
4	$[Co(NH_3)_6]Cl_3$	0.1	75	6	S_4
5	$[Co(NH_3)_6]Cl_3$	0.1	150	6	S_5
6	$[Co(en)_3]Cl_3$	0.1	150	24	S_6
7	$CoCl_2·6H_2O$	0.01	100	24	S_7

3. Results and discussion

3.1. Precursor characterization

To identify the synthesized precursor complexes, $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$, the FT-IR analysis was used in comparison to the literature reported values [30]. Fig. 1a presents the FT-IR spectrum of hexaamminecobalt(III) chloride. The strong band in the range of 3300–3100 cm^{-1} is attributed to N–H stretching vibrations. The asymmetric and symmetric bending modes of HNH are observed at 1584 and 1326 cm^{-1}, respectively, and its cradle vibration appears at 830 cm^{-1}. The FT-IR spectrum of $[Co(en)_3]Cl_3$ is shown in Fig. 1b. The bands assigned to the stretching and bending vibrational modes of NH_2 groups in the ethylenediamine ligands are observed at 3432 and 3202 cm^{-1}, and 1564 and 1462 cm^{-1}, respectively. The adsorption peaks at around 3200-3100 cm^{-1} are due to C–H stretching vibrations of CH_2 groups. The C–N vibration band appears at 1058 cm^{-1}. The N–H stretching frequencies for $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ are red shifted compared to the pure NH_3 and ethylenediamine. Upon coordination, the N–H band is weakened and the NH_3 stretching frequencies are lowered.

3.2. Characterization of Co_3O_4 nanoparticles

The products obtained using hexaamminecobalt(III) chloride, tris(ethylenediamine)cobalt(III) chloride and cobalt(II) chloride hexahydrate as the precursors were first examined by XRD. Fig. 2 shows the XRD patterns of the typical samples S_2, S_6 and S_7. The products are identified as the single phase Co_3O_4 with a suitably crystalline cubic structure (JCPDS card No. 43–1003) and the space group of Fd-3m. The lattice constants are a = b = c = 0.8084 nm, in a good consistent with the standard values of Co_3O_4 (a = b = c = 0.8065 nm) [31]. Compared with the standard X-ray

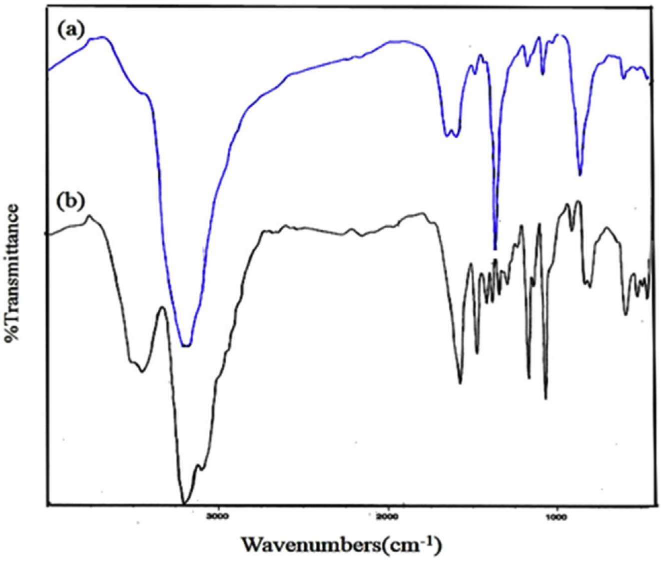

Fig. 1. FT-IR spectra of the precursor complexes, (a) $[Co(NH_3)_6]Cl_3$ and (b) $[Co(en)_3]Cl_3$.