Co$_3$O$_4$ nanoplates: Synthesis, characterization and study of optical and magnetic properties

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A R T I C L E   I N F O

Article history:
Received 8 June 2013
Received in revised form 22 October 2013
Accepted 31 October 2013
Available online 9 November 2013

Keywords:
Transition metal oxides
Cobalt-ammine complex
Nanostructures
Nanoplates
Thermolysis

A B S T R A C T

The selective synthesis of spinel-type Co$_3$O$_4$ nanostructure with nanoplates morphology was successfully achieved by solid-state thermal decomposition of the [Co$^6$(NH$_3$)$_6$]$_3$(C$_2$O$_4$)$_2$H$_2$O complex at 350 °C without employing any solvent, surfactant and complicated equipment. The product was characterized by thermal analysis (TG/DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, UV–visible spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and magnetic measurements. The TEM images show that the product has a plate-like shape with length of 50–200 nm and thickness of 10–20 nm. FT-IR, XRD, EDX and VSM results suggest the as-prepared Co$_3$O$_4$ nanoplates are pure and single-phase with a weak ferromagnetic behavior. The optical spectrum indicated two direct band gaps at 2.18 and 3.55 eV with a blue shift compared with the bulk samples. The plausible pathway for the formation of Co$_3$O$_4$ nanoplates was also proposed. Under the present reaction conditions, the decomposition of other cobaltammine complexes and CoC$_2$O$_4$2H$_2$O led to the Co$_3$O$_4$ nanoparticles and nanorods, respectively.

1. Introduction

Nano-scale transition metal oxides with different shapes and morphologies have attracted great interest because of their unique electronic, optical and other physical and chemical properties and potential technology applications [1–3]. The properties of nanomaterials depend not only on their chemical composition and size but also on their shape, so particular structure is required for obtaining specific property and realizing specific application [4]. In recent years, the synthesis of Co$_3$O$_4$ nanomaterials with special morphologies have attracted considerable attention due to their broad range of applications in gas sensors [5,6], heterogeneous catalysts [7–9], electrochemical devices [10], Li-ion batteries [11], magnetic materials [12,13] and photocatalysts [14,15]. Various physical and chemical methods have been successfully used to prepare one-dimensional Co$_3$O$_4$ nanostructures such as nanotubes [16,17], nanowires [18], nanorods [19], nanoneedles [20] and nanoparticles [21]. However, the shape-controlled synthesis of two-dimensional Co$_3$O$_4$ nanoplates has been seldom reported. For example, Sun et al. prepared Co$_3$O$_4$ nanoplates with an edge length of about 200–300 nm by a solvothermal method via the reaction of Co$_3$(OH)$_6$(CO$_3$)$_2$H$_2$O with concentrated aqueous ammonia in the presence of surfactant CTAB [22]. In addition, Kim and Huh synthesized Co$_3$O$_4$ hexagonal plate-like via the thermal oxidation of the Co(OH)$_3$ precursor at 600 °C in air. The hexagonal plates had a side length of approximately 3.5 μm and 1 μm in thickness [23]. Increasing attention has been focused on two-dimensional nanomaterials not only for their basic scientific richness, but also for their potential applications in nano-scale electronic and optical devices. Two-dimensional nanostructures are promising building blocks for nanodevices with controlled crystal orientation owing to their anisotropic structures. Therefore, there is a need for more effort toward the preparation of metal oxide nanoplates.

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 [24–27]. By choosing a proper molecular precursor, nanocrystalline products could be obtained usually under the conditions significantly milder than those employed in the conventional solid-state synthesis. Because of their low cost, easy preparation and mild decomposition, metal-ammine complexes have already been employed as ideal precursors for preparing metal oxide nanostructures [28,29]. However, to our knowledge, the synthesis of Co$_3$O$_4$ nanoplates by using a metal-ammine complex as a precursor was not attempted up to date.

In this work, we report on the synthesis of Co$_3$O$_4$ nanoplates by direct thermolysis of the [Co$^6$(NH$_3$)$_6$]$_3$(C$_2$O$_4$)$_2$H$_2$O complex at 350 °C in air. The obtained product was characterized by thermal
analysis (TG/DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, UV–visible spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), ultraviolet-visible (UV–Vis) spectroscopy, energy-dispersive X-ray spectroscopy (EDX), and magnetic measurements.

2. Experimental

2.1. Preparation of Co3O4 nanoplates

The \([\text{Co}^{II}(\text{NH}_3)_6]_6\text{Co}_2\text{O}_4\cdot4\text{H}_2\text{O}\) precursor was precipitated by adding an aqueous solution of \(\text{K}_2\text{Co}_3\text{O}_4\) to an aqueous solution of the \([\text{Co}^{II}(\text{NH}_3)_6]\text{Co}_2\text{O}_4\cdot4\text{H}_2\text{O}\) under continuous stirring, according to the method described in literature [30]. The resulting yellowish precipitate was separated and washed with water, ethanol, and diethyl ether and dried at 96 °C in an oven. To prepare Co3O4 nanoplates, the \([\text{Co}^{II}(\text{NH}_3)_6](\text{Co}_2\text{O}_4)\cdot4\text{H}_2\text{O}\) powder was decomposed at various temperatures for one hour in an electric furnace under ambient air. The temperatures for the decomposition of complex were selected from the TG-DTA data. In each temperature, the decomposition product of the complex was collected for characterization.

2.2. Characterization

Thermal analysis (TG/DTA) was carried out with a Netzsch STA 409 PC/PG thermal analyzer at a heating rate of 10 °C/min in air. Infrared spectra were recorded on a Shimadzu FT-IR 160 spectrophotometer using KBr pellets. The XRD patterns were recorded by a Rigaku D−max C II X-ray diffractometer using Ni−filtered Cu Kα radiation (\(λ = 1.5406 \text{ Å}\)) to determine the phases present in the decomposed samples. Raman spectrum measurements was carried out on a Spex 1403 Raman spectrometer. The optical absorption spectrum was recorded on a Shimadzu 1650PC UV–Vis spectrophotometer with the wavelength range of 200–700 nm at room temperature. The sample for UV–Vis studies was well dispersed in distilled water to form a homogeneous suspension by sonication for 25 min. The morphologies particle sizes were determined by a transmission electron microscope (TEM, Philips CM10) and a scanning electron microscope (SEM, Philips XL-30) equipped with a link energy-dispersive X-ray (EDX) analyzer. For the TEM measurements, the powders were sonicated in ethanol and a drop of the suspension was dried on a carbon-coated microgrid. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, Iran Meghnahts Daghigh Kavir Co.).

3. Results and discussion

Thermal behavior of the \([\text{Co}^{II}(\text{NH}_3)_6](\text{Co}_2\text{O}_4)\cdot4\text{H}_2\text{O}\) complex was studied by thermal analysis in the temperature range 25–600 °C in the atmosphere of air. Thermal analysis curves of the complex are illustrated in Scheme 1. This complex undergoes decomposition in three stages. The inset photo shows the color change of the complex during these steps. The first stage occurred in the temperature range of 75–175 °C, shows 11.10% weight-loss which is consistent with the theoretical value of 10.9% caused by the loss of four \(\text{H}_2\text{O}\) molecules. In the second stage, in the temperature range of 175–275 °C, the loss of ammonia molecules takes place. The weight loss calculations (calculated 44.2%, found 44%) show that the six ammonia molecules are removed in this stage, leading to an intermediate probably in the form of \(\text{Co}_6\text{O}_4\). In the third stage, accompanied by a weight loss of 20% (calculated 20.2%), the decomposition of \(\text{Co}_6\text{O}_4\) to the \(\text{Co}_3\text{O}_4\) powder occurs in the temperature range 275–330 °C. After this stage, the weight remained constant, confirming the complete decomposition of the complex. The weight loss of all steps to be about 75.10% which is consistent with the theoretical value (75.60%) calculated for the formation of \(\text{Co}_3\text{O}_4\) from the complex. The DTA curve for the \([\text{Co}^{II}(\text{NH}_3)_6](\text{Co}_2\text{O}_4)\cdot4\text{H}_2\text{O}\) complex gave three characteristic peaks in consistent with TG data. The two small endothermic peaks at about 135 and 230 °C are related to the dehydration and deamination processes of the complex, respectively. The sharp exothermic peak at about 310 °C can be explained via oxidizing \(\text{Co}_2\text{O}_4\) to the \(\text{Co}_3\text{O}_4\) phase by air (\(\text{O}_2\)). According to the above data, the decomposition reactions of the complex can be written as follows:

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\begin{align*}
\text{Co}^{II}(\text{NH}_3)_6(\text{Co}_2\text{O}_4)\cdot4\text{H}_2\text{O}(s) & \rightarrow \text{Co}^{II}(\text{NH}_3)_6(\text{Co}_2\text{O}_4)(s) + 4\text{H}_2\text{O}(g) \\
\text{Co}^{II}(\text{NH}_3)_6(\text{Co}_2\text{O}_4)(s) & \rightarrow \text{Co}_3\text{O}_4(s) + 6\text{NH}_3(g) \\
3\text{Co}_2\text{O}_4(s) + 2\text{O}_2(g) & \rightarrow 3\text{Co}_3\text{O}_4(s) + 6\text{CO}_2(g)
\end{align*}
\]

The FT-IR spectra of the \([\text{Co}^{II}(\text{NH}_3)_6](\text{Co}_2\text{O}_4)\cdot4\text{H}_2\text{O}\) complex and its final decomposition products at different temperatures are shown in Fig. 1. For the complex in Fig. 1(a), the characteristic stretching bands of \(\text{NH}_3\) and \(\text{Co}_2\text{O}_4^–\) groups are observed at about 3500–3000, 1600, 1350 and 800 cm\(^{-1}\) [31]. As shown in Fig. 1(b) and (c), for the complex samples heated at 150 and 200 °C these bands were observed without observable changes. However, for the sample calcined at 250 °C in Fig. 1(d), the characteristic bands of the \(\text{Co}_2\text{O}_4\) phase were observed at about 1625, 1350, 850 and 485 cm\(^{-1}\) which were related to the asymmetric and symmetric \(\text{C–O}\) coordinated to the metal atoms, O–C–O and symmetric C–C–O vibrations, respectively [32]. The broad band at about 3400 cm\(^{-1}\) is assigned to the water of hydration. In addition, there are two small absorption bands (■) at about 665.40 and 582.46 cm\(^{-1}\), which is a clear evidence for the presence of the crystalline \(\text{Co}_3\text{O}_4\) [33]. This observation confirms that the formation of \(\text{Co}_3\text{O}_4\) nanocrystals begins at about 250 °C. As we can see in Fig. 1(e), most bands of the \(\text{Co}_3\text{O}_4\) disappeared with increasing temperature to 300 °C, so for the sample calcined at 350 °C (Fig. 1(f)) only two characteristic strong bands of the spinel-type \(\text{Co}_3\text{O}_4\) structure were observed, confirming complete decomposition of the complex at this temperature in good agreement with the TG/DTA data.

The XRD pattern of the product obtained by calcining the \([\text{Co}^{II}(\text{NH}_3)_6](\text{Co}_2\text{O}_4)\cdot4\text{H}_2\text{O}\) precursor at 350 °C for 1 h is shown in Fig. 2. All the diffraction peaks were in good agreement with the JCPDS file of cubic spinel-type \(\text{Co}_3\text{O}_4\) (JCPDS Card No. 76-1802). This result confirms that the complex was decomposed completely.