Nano-Structures & Nano-Objects 15 (2018) 1–9

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

journal homepage: www.elsevier.com/locate/nanoso

Facile synthesis of quantum sized Co_3O_4 nanostructures and their magnetic properties

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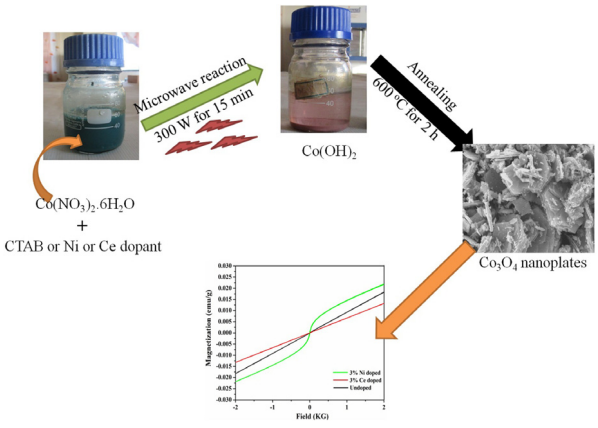
HIGHLIGHTS

- Mesoporous Co_3O_4 nanoplates have been synthesized by a simple microwave route.
- The Co_3O_4 nanoplates with surface defect have finite particle size of 20–40 nm.
- A mesoporous Co_3O_4 hexagonal nanoplate shows excellent magnetic performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 December 2017
Received in revised form 13 February 2018
Accepted 5 March 2018

Keywords:
Nanostructures
Microwave
Photoluminescence
Defects
Paramagnetism
Magnetization

ABSTRACT

We examined the quantum sized Co_3O_4 formation with hexagonal morphology of diameter about 20 nm. The photoluminescence study proved the surface defect-rich Co_3O_4 nanostructures. The combined synergistic effect of quantum sized hexagonal nanoplates structures and surface defects are favorable for the enhanced magnetic properties in Co_3O_4 nanostructures. The addition of surfactants and changing of microwave powers led to the paramagnetic behavior. Room temperature magnetic measurements of Ni-doped Co_3O_4 exhibits weak ferromagnetic nature of Co_3O_4 nanostructures. With practical, environmental friendly and solvent-free microwave strategy provides a brand new promising route for large-scale preparation of metal oxide for outstanding magnetic performance.

1. Introduction

Nanostructured materials are intensively studied due to their excellent physical properties compared to bulk state [1–5]. Moreover, emerging interest in the tuning of material dimensions under nano regime is a big challenge for nanotechnology based applications [6–8]. This feature could be very interesting when reducing the material size toward less than 10 nm system. Most significantly, the amount of atoms within the cluster reduced from few

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https://doi.org/10.1016/j.nanoso.2018.03.005
2352-507X/

thousands to a number of atoms and therefore the quasicontinuous density of states are gradually replaced by a discrete energy level structure [9–12]. This finite size effect still remains a mammoth challenge for the scientific researchers. The precise control over the size and structure of nanostructures might open the gate to a novel invention of electronic and magnetic materials. Therefore, a multitude of efforts has been devoted to develop uniform size and shape of efficient nanostructures supported transition metal oxide nanomaterials.

Most considerably, cobalt oxide (Co_3O_4) has emerged as a promising transition metal oxide for its efficient uses in several applications such as magnetism, super capacitors, gas sensors, batteries, and catalysts [13–23]. Although, many researchers have proposed a number of techniques to synthesize different nanostructures of Co_3O_4, their non-uniformity, the impotency of synthetic ways, larger particle size and uniqueness of morphology render them impractical for widespread use [24–28]. Recently, Ribeiro et al. [29] have briefly investigated the theoretical approach for determining the relation between the morphology and surface magnetism of Co_3O_4 which are well agreed with their experiment results. Furthermore, Zhang et al. [30] have prepared unique morphology and structure of the nanoflakes Co_3O_4 structures shown that the magnetization of magnetic materials is dependent on the morphology and structure of the materials. Hence, the above results induce to design and synthesize well controlled shape and size of nanostructures that are able to deliver high performance in magnetic nature. Therefore, it is imperative to design an inexpensive, environment friendly and convenient synthetic process, particularly for large-scale synthesis of Co_3O_4 nanoparticles with uniform size, shape, and excellent properties.

To develop extremely uniform size and shape of Co_3O_4 nanostructures, microwave heating is an efficient and straightforward route. This method derived high penetration depth over the solution effectively improves surface temperature that benefits for achieving aligned specific structure [31]. Moreover, accelerated internal heating hinders agglomeration and thus helps to form uniform morphology due to directly coupled reaction between applied energy and the molecules [32]. Microwave heating route also results in better reproducibility due to suppressed side reactions [33]. Especially, optimum choice of synthesis power during solution irradiation helps to fluctuate the applied field, friction between molecules and energy loss by heat because of dipole realignment effect [34]. Hence, it is necessary to study the effect of microwave powers for optimization of the crystal size, morphology, and composition of the resultant product [35].

Herein, we have prepared Co_3O_4 nanostructures by using efficient and facile microwave synthesis strategy and optimized different synthesis parameters such as surfactants, the variation of microwave reaction powers and dopants (transition metal and rare earth ions), etc. The importance of this study is that the control over the aspect ratio of the cobalt oxide nanostructures and additionally the dimensions and assembly of the nanoparticles. In addition to microwave method, we have additionally compared the influence of hydrothermal synthesis toward particle size and the aspect ratio effect toward the magnetic nature of Co_3O_4 nanostructures.

2. Experimental section

2.1. Material synthesis

2.1.1. Synthesis of Co_3O_4 nanostructures with different surfactants

In a synthesis procedure, the precursors of 0.5 M $Co(NO_3)_2{\cdot}6H_2O$ and 1 g of cetyl trimethyl ammonium bromide (CTAB) surfactant were dissolved in 50 ml distilled water under magnetic stirrer. Then, 3 ml of ammonia solution was added drop wise into above solution to maintain the pH value around 9. After some time, the resultant solution was taken to 100 ml polypropylene capped autoclave bottle. Then, the solution was treated with microwave irradiation at 300 W powers for 15 min. The similar procedure was repeated for citric acid (1 g) and hexamine (1 g) added cobalt nitrate solutions. The brown precipitates were collected in all the three surfactants by centrifugation and then the precipitates were washed with distilled water and absolute ethanol to remove soluble ions and impurities. The precipitate was dried at 80 °C in a hot air oven for 12 h to get the sample of $Co(OH)_2$ architectures. Then, the synthesized powder was calcined under air at 600 °C for 2 h to obtain Co_3O_4 nanoparticles.

2.1.2. Synthesis of Co_3O_4 nanostructures with different microwave power

The same amount of precursors and ammonia was used for the preparation of Co_3O_4 nanostructures without adding any surfactants. The final solution was taken into 100 ml polypropylene capped autoclave bottles. The solution was treated with microwave radiation using different powers from 300 to 900 W for 1 min duration time. After the reaction process was finished, the higher power used (900 and 600 W) autoclave bottles took longer time (45 min) to reach room temperature. This cooling time was lesser (about 25 min) to reach room temperature for 450 and 300 W. After cooled down, same washing, drying and calcinations steps are followed in different surfactants was repeated here to obtain above Co_3O_4 nanostructures.

2.1.3. Synthesis of Co_3O_4 nanostructures with Ni and Ce ions dopant

In addition to above used precursor (without surfactant), 3 wt% of transition metal (Ni) and rare earth ion (Ce) was used for doping. Then, the reaction procedure followed for surfactant assisted Co_3O_4 growth was followed with same microwave power (300 W), drying and calcinations procedures to get Ni and Ce doped Co_3O_4 nanostructures.

2.1.4. Synthesis of Co_3O_4 nanostructures via hydrothermal reaction

In hydrothermal method, same amount of precursors and ammonia was used for the preparation of Co_3O_4 nanostructures. Here, the precursor solution filled autoclave was kept at the temperature of 140 °C for 15 min. The same washing, drying and calcinations steps followed in microwave reaction are repeated here to obtain above Co_3O_4 nanostructures.

2.2. Characterization techniques

The thermal investigation was carried out by using PerkinElmer Thermal Analysis system with a heating rate of 20 °C/min to confirm the transformation of hydroxide phases to the Co_3O_4 nanostructure. The X-ray diffraction analysis is performed to identify the phase structure of Co_3O_4 using PANalytical model X'PERT-PRO X-ray diffractometer system with the Kα radiations from a copper target ($\lambda = 1.5418$ Å). The functional properties were analyzed by Fourier transform infrared (FT-IR) spectrum using Thermo Nicolet 380 FT-IR spectrometer with KBr pellet technique. Raman spectrum was recorded to demonstrate the functional analysis of formed products from laser Raman spectrometer (500 mm focal length, SEKI Japan). The morphological formation of Co_3O_4 was examined using a scanning electron microscopy (SEM) (JSM 6390F, JEOL/EO) and transmission electron microscope (TEM) (JSM 6390F, JEOL/EO). The surface and chemical evolution of Co_3O_4 nanostructures were carried out by using X-ray photoelectron spectrometry (XPS) analysis. The photoluminescence study was traced to study the optical properties of Co_3O_4 nanostructures by the Cary Eclipse PL spectrograph. The vibrating sample magnetometer (Lakeshore mini VSM 3639) is used for the quantification of magnetic nature of calcined Co_3O_4 nanoparticles. All the above measurements were carried out with same instrument setup and temperature for all the samples.