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The controllable preparation of Co_3O_4 nanostructure for designing optimal mechanical and magnetic properties of graphite/kaolin based compounds

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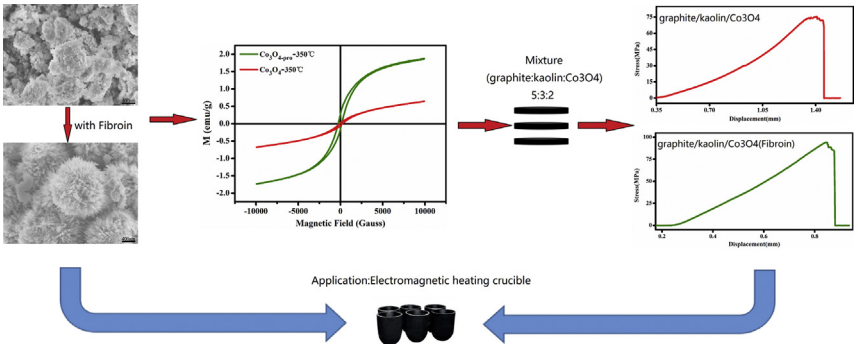
HIGHLIGHTS

- Co_3O_4 microstructures are tuned by adding silk fibroin under hydrothermal reaction and mixed with kaolin and graphite.
- Silk fibroin optimizes the morphology of Co_3O_4 and increases its magnetism from 0.68 to 1.95 emu/g.
- Co_3O_4/graphite/kaolin (5:3:2) compounds show desired magnetic and mechanical properties.
- The addition of Co_3O_4 improves the electromagnetic heating efficiency of graphite crucible in industry.

GRAPHICAL ABSTRACT



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ABSTRACT

Low heating efficiency of graphite crucible limits the application in electromagnetic induction heating system because of the diamagnetism of graphite. In the present work, Co_3O_4 nanostructures were successfully prepared by means of a hydrothermal method, and introduced them into graphite and kaolin as raw material of crucible to improve their electromagnetic heating efficiency. The morphology of Co_3O_4 was adjusted by introducing silk fibroin. The microstructures and morphology of the silk-fibroin-Co_3O_4 composites were characterized by XRD, SEM, TEM, and Raman. The magnetic and mechanical properties of these compounds were also evaluated. Adding silk fibroin can optimize the morphology of Co_3O_4 and increase its magnetism. The addition of Co_3O_4 calcined at 350 °C (with silk fibroin) to graphite increases its magnetism without sacrificing its compressive strength. Co_3O_4/graphite/kaolin (5:3:2) compounds show desired magnetic and mechanical properties.

1. Introduction

In recent years, transition metal oxides have attracted considerable attention with regard to their physical properties [1–3]. Nanostructured cobalt oxide with spinel crystal structure prepared by various techniques is known as a promising material due to its use as catalysts, electrochromic films, and magnetic materials. Co_3O_4 (magnetic Co^{2+} ions in tetrahedral sites and non-magnetic Co^{3+} ions in octahedral sites) is relatively stable in the natural environment and useful in lithium-ion batteries, gas sensors, and catalysts [4]. Research interest/effort has contributed to prepare cobalt oxide by different methods such as reduction/oxidation route [5], sol-gel [6], thermal treatment

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[7], and chemical precipitation method [8]. The magnetic properties of nanosized Co_3O_4 materials are affected by the shape, size, and crystallization conditions of the nanoparticles [9–12]. Nanostructured Co_3O_4 with variable morphology including nanowires (~60 nm) [13], nanoparticles (20–40 nm) [14,15], and nanotubes (diameter < 20 nm, length < 1 μm) [16] have been prepared. The large size distribution of nanostructured Co_3O_4 results in anomalous magnetic properties. It is reported that the morphology of nanostructure is largely determined by the surfactant added during the whole reaction. Silk fibroin, as a natural protein produced by the silkworm with high molecular weight and unique self-assembly behavior, has been successfully applied in the energy storage and biomedical field by acting as a template for several decades [17]. Especially in recent years, silk fibroin as template has shown promising future in regulating metal oxide nanomaterials. Shen et al. reported the use of silk fibroin with specific nanostructures employed to tune the synthesis of Fe_3O_4/C hollow nanomaterial as anode materials for lithium ion batteries [18]. Multifunctional iron oxide/silk-fibroin microspheres were also synthesized as the carriers in drug delivery system in cancer cells [19]. Silk fibroin hydrogels can be formed directly by reacting with water, which is involved with hydrogen bonding and electrostatic interaction, etc. [20,21]. Using of these factors can effectively control the morphology of nanostructure.

Graphite exists as one of the giant covalent structures in nature and its applications as electrodes and heating container were found due to the good electrical and thermal conductivity [22]. Graphite crucible containing a significant amount of crystalline graphite is usually used in electromagnetic induction heating system. However, the current drawback of graphite crucible is that it has low heating efficiency when temperature rises rapidly in the initial heating process. This is mainly because of the diamagnetism of graphite. Therefore, incorporation of ferromagnetic magnetic oxides into graphite is supposed to be a practical strategy in improving the magnetic properties of graphite. Thus, in the present work, Co_3O_4 structures were selected as the additive and the effect of silk fibroin on the structural and magnetic properties of Co_3O_4 structures were studied as well. Herein, the hydrothermal method was used for preparation of Co_3O_4 microstructures. Furthermore, the as-prepared Co_3O_4 microstructures were introduced into the ingredient of crucible which is composed of graphite and kaolin to evaluate the magnetic and mechanical properties of the compounds.

2. Experimental sections

2.1. Material synthesis

All chemicals and materials were of analytical grade and used directly without any further purification. As shown in Scheme 1, the synthesis process for the Co_3O_4 microstructures was as follows. $Co(NO_3)_2 \cdot 6H_2O$ (0.7 g) and fibroin (0.25 g) were dissolved in deionized water (35 ml). Then, the resulting solution was maintained at room temperature after magnetic stirring for 30 min and forming homogeneous solution. After that, NH_4F (0.18 g), Sodium potassium tartrate ($C_4H_4KNaO_6$) (0.4 g), and urea (CH_4N_2O) (0.75 g) were successively added into the as-prepared solution which was under vigorous stirring. The resultant mixture solution was then transferred into a 60 ml Teflon-lined autoclave and kept in an oven at 120 °C for 5 h. The obtained pink precipitation was collected by centrifugation and washed several times with deionized water and anhydrous ethanol. After drying in oven at 60 °C for 12 h, pink powder was obtained. For comparison, the same experimental steps as above were conducted except adding fibroin. For the preparation of Co_3O_4, the as-prepared products were calcined at 300 °C, 350 °C, 450 °C, 550 °C, and 650 °C for 60 min. Then, ten samples were obtained, and named as $Co_3O_{4\text{-pro}}$-300 °C, $Co_3O_{4\text{-pro}}$-350 °C, $Co_3O_{4\text{-pro}}$-450 °C, $Co_3O_{4\text{-pro}}$-550 °C, and $Co_3O_{4\text{-pro}}$-650 °C, Co_3O_4-300 °C, Co_3O_4-350 °C, Co_3O_4-450 °C, Co_3O_4-550 °C, Co_3O_4-650 °C ('Pro' is the abbreviation of protein, and $Co_3O_{4\text{-pro}}$ represents the samples which were prepared by adding fibroin during chemical precipitation). To endow ferromagnetic property of graphite, we measured the composition of commercial graphite crucible, and found that the weight ratio of graphite and kaolin is close to 3:1. According this basic proportion, we made a series of raw material prescription as Table 1. The graphite, kaolin and $Co_3O_{4\text{-pro}}$-350 °C compounds were mixed mechanically and tableted as wafers with the diameter of 5 mm by a tablet machine. Afterwards, their magnetic and mechanical properties were characterized.

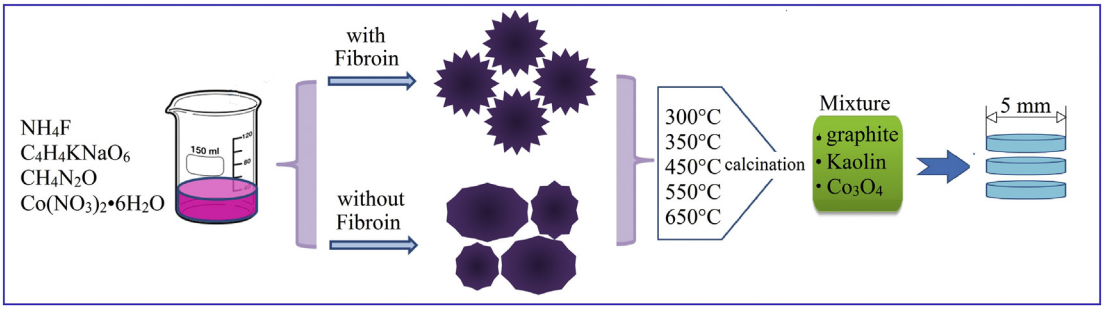
2.2. Characterization

The morphologies of the as-prepared products were studied by scanning electron microscopy (SEM, Hatchi S-4800, Japan) and transmission electron microscopy (TEM, JEM-2100F, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX) with an accelerating voltage of 200 keV. The crystal structure was investigated by X-ray diffraction (XRD, RIGAKU/DMAX). Raman spectrum was collected at room temperature by using DXR Microscope (Thermo Electron Corporation) at ambient conditions, using the radiation of 532 nm. The thermal behaviors of precursors were studied by Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the precursors of Co_3O_4-350 °C and $Co_3O_{4\text{-pro}}$-350 °C were measured by using SDT Q600TGA thermal gravimetric analyzer under air atmosphere in the temperature range of 0–800 °C. The magnetization measurements of the synthesized samples were carried out using Vibrating Sample Magnetometer (VSM, Lakeshore7404, Lakeshore Company). The deformation behaviors of the samples were characterized by Micro control electronic universal testing machine (WDW-20) and Nanomechanical Test Instrument (Nano DMA II/III transducer, Hysitron company).

3. Results and discussion

3.1. Formation of Co_3O_4 with the silk fibroin

Fig. 1 exhibits the SEM images of the six samples which were calcined at different temperature ranging from 300 °C to 450 °C. After addition of fibroin, the samples show the morphology of microspheres structure with various diameters which are composed by needle-like tips, as shown in Fig. 1(a, c, e). While the samples in Fig. 1(b, d,



Scheme 1. Schematic illustration of the synthesis process for the Co_3O_4 microstructures.