

Facile synthesis of cobalt doped hematite nanospheres: Magnetic and their electrochemical sensing properties

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ABSTRACT

Nanocrystalline pure α -Fe₂O₃ and Co-doped α -Fe₂O₃ powders were synthesized by the hydrolysis method. The structure and the morphology of the samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The magnetic property of the samples was studied by vibrating sample magnetometer (VSM) at room temperature, which showed that the Co-doped α -Fe₂O₃ have a weaker ferromagnetic behavior than the pure α -Fe₂O₃. The electrochemical sensing ability of ascorbic acid (AA) and uric acid (UA) by pure α -Fe₂O₃ and Co-doped α -Fe₂O₃ modified glassy carbon electrode (GCE) exhibited higher anodic current response with a shift in positive potential than the bare GCE. Compared with pure α -Fe₂O₃, Co-doped α -Fe₂O₃ showed enhanced electrochemical sensing performance.

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1. Introduction

Functional metal oxide nanocrystals have been extensively investigated in the recent decade for their outstanding new properties suitable for a broad spectrum of downstream application [1–3]. Among them, nanoparticles of iron oxides are important materials due to their biocompatibility, catalytic activity and low toxicity. They have significant application in various fields such as drug delivery system [4], cancer therapy [5], magnetic resonance imaging [6], high density magnetic storage devices [7], ferro-fluids [8], rechargeable lithium batteries [9], catalysis [10], gas sensor [11] and biosensor [12], etc. Iron oxide mainly occurs in three different forms namely FeO, Fe₂O₃ and Fe₃O₄. Fe₂O₃ has four crystallographic phases namely, α -Fe₂O₃ (hematite), β -Fe₂O₃, γ -Fe₂O₃ (maghemite) and ϵ -Fe₂O₃ [13]. The γ -Fe₂O₃ and Fe₃O₄ have inverse spinel structure and superparamagnetic property. The α -Fe₂O₃ is the most stable iron oxide which has antiferromagnetism with canting ferromagnetic responses at room temperature. It has a complex defect structure in which three types of defect species namely, oxygen vacancies, Fe³⁺ and Fe²⁺ interstitials are present [14]. It has a wide range of applications such as photocatalyst for N₂ fixation

[15], sorbents [16] and sensors [17], etc. As motivated by the novel properties and potential application of nanosized iron oxide, synthesis of α -Fe₂O₃ in nanometer scale has attracted more attention [18,19]. Many methods have been reported for the synthesis of α -Fe₂O₃ including forced hydrolysis [20], combustion [21], anhydrous solvent [22], sol-gel [23], wet chemical synthesis [24], microwave-hydrothermal synthesis [25–27], and spray pyrolysis [28,29], etc. Among them, forced hydrolysis of Fe³⁺ plays an important role in natural system. This method does not need the addition of any precipitator. Doping of different metal ions or metal oxides into Fe₂O₃ will find new application or improve the performance of existing applications. For instance, Niu et al. [30] found that the material mixed with rare earth oxides through a sol-gel method in citric acid system presented high gas sensitivity to gasoline. Jing et al. [31] also reported that the Co-doped γ -Fe₂O₃ exhibits higher gas sensitivity and better selectivity to acetone and ethanol than the pure γ -Fe₂O₃. It is noted that until now most of the researchers focused mainly on doping of metal ion into γ -Fe₂O₃ while doping of metal ion in α -Fe₂O₃ and their electrochemical sensing properties have not been reported yet.

In this paper, we have reported the preparation of Co-doped α -Fe₂O₃ nanopowder, by using simple hydrolysis of FeCl₃ method. The prepared nanoparticles have been used to modify the GCE and remarkable enhancement in the current response with shift in anodic peak potential is observed for electrochemical oxidation of AA and UA when compared to the bare electrode.

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2. Experimental

2.1. Synthesis of α -Fe₂O₃ and Co-doped α -Fe₂O₃ nanospheres

Anhydrous ferric chloride (FeCl₃), hydrated cobaltous chloride (CoCl₂·6H₂O) and potassium chloride (KCl) were purchased from Qualigens and used without further purification. Ascorbic acid and uric acid were purchased from Sigma and used as received. Doubly distilled water was used as the solvent.

Co-doped α -Fe₂O₃ powders were prepared as follows [32]. The aqueous solution of anhydrous FeCl₃ was heated to 100 °C for 16 h. Then the yellow product obtained, FeOOH, was separated from the mother liquor with an ultra-speed centrifuge and washed with distilled water three times. The obtained yellow powder was annealed at 600 °C for 6 h, and the product α -Fe₂O₃ was obtained. Co-doped α -Fe₂O₃ nanostructures were synthesized by the same method. For the preparation of Co-doped α -Fe₂O₃, CoCl₂ salt was added to the aqueous solution of FeCl₃ in four different molar percentages, 5%, 10%, 15%, and 20%, respectively. The solutions were refluxed for 16 h at the temperature of 100 °C. The obtained yellow powders were annealed at 600 °C for 6 h. Thus we obtained 5–20% Co-doped α -Fe₂O₃ nanostructures.

2.2. Characterization details

The prepared samples were studied by FTIR spectroscopy using a Shimadzu FT-IR 8300 series instrument in the range of 400–4000 cm⁻¹. One milligram of each powder sample was diluted with 200 mg of vacuum-dried IR-grade KBr powder and subjected to a pressure of 10 tons. The Raman spectroscopy used in this study was the BRUKER RFS 27: Stand alone FT-Raman Spectrometer equipped with Nd: YAG 1064 nm as an excitation source.

The structures of the samples were analyzed by a Rich Siefert 3000 diffractometer with Cu-K α_1 radiation ($\lambda = 1.5406$ Å). The UV–Vis absorption spectra were obtained on a CARY 5E UV–VIS–NIR Spectrophotometer. The morphology of the materials was analyzed by SEM and FE-SEM using a HITACHI S600N scanning electron microscopy and a HITACHI SU6600 field emission-scanning electron microscopy, respectively. The BET specific surface area (S.S.A.) was measured using a Micromeritics (ASAP 2020) analyzer. The magnetic studies were carried at room temperature using VSM: EG & G Princeton, Applied Research Model 4500 instrument. The electrochemical experiments were performed on a CHI 600A electrochemical instrument using the as-modified electrodes and bare GCE as working electrode, a platinum wire was the counter electrode, and saturated calomel electrode (SCE) was the reference electrode.

2.3. Preparation of the Co-doped α -Fe₂O₃ modified GCE is as follows

Ultrasonic agitation for 30 min was used to disperse 1 mg of Co-doped α -Fe₂O₃ into 5 mL of acetone to make a reddish brown and homogeneous suspension. The polished GCE was coated with 5 μ L of the above reddish brown suspension. The modified electrode was activated in a 0.1 M KCl solution by successive cyclic scans between 0 and +1.2 V. Before and after each experiment, the modified electrode was washed with distilled water and reactivated by the method mentioned above.

3. Results and discussion

3.1. Structural characterization

The FTIR spectrum of the pure α -Fe₂O₃ and α -Fe₂O₃(5%Co) are given in Fig. 1(a) and (b), respectively. Fig. 1(a) and (b) shows the

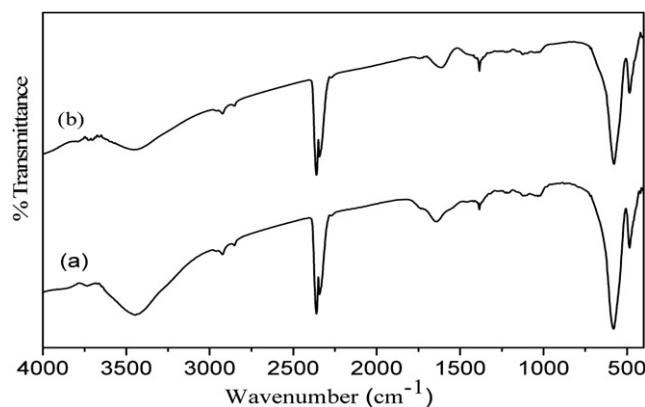


Fig. 1. FTIR spectrum of (a) pure α -Fe₂O₃ and (b) α -Fe₂O₃(5%Co).

absorption band in the region of 3461, 1642, 1580, 1383, 574, 579, 481 and 485 cm⁻¹. The general range of 3600–3100 cm⁻¹ may be assigned for water of hydration. Hydrate also absorbs in the range of 1670–1600 cm⁻¹ [33]. This later band can be taken as another important means of identifying water of crystallization. In Fig. 1(a), the band associated with the lattice water molecule is broad, and is observed in a region of 3461 and 1642 cm⁻¹. The simultaneous presence of these two bands indicates that the water of crystallization is present in the sample. The bands at 574 and 481 cm⁻¹ in Fig. 1(a) and at 579 and 485 cm⁻¹ in Fig. 1(b) are due to the Fe–O stretching vibrational modes [34]. These two bands are sharp and are of strong intensity. The intensity of the broad peaks at 3600–3000 cm⁻¹ is found to be decreasing from Fig. 1(a) to (b). The shifts observed for the above samples may be due to the particle size effect [35].

The Raman spectrum of the pure α -Fe₂O₃ and α -Fe₂O₃(5%Co) are shown in Fig. 2(a) and (b), respectively. Fig. 2(a) shows the peaks at 225, 242, 294, 411 and 499 cm⁻¹ correspond to the α -Fe₂O₃ phase [36], namely two A_{1g} modes (225 and 499 cm⁻¹) and three E_g modes (242, 294 and 411 cm⁻¹). Fig. 2(b) is similar to that of Fig. 2(a). However, it shows additional peaks at 488, 519 and 680 cm⁻¹ which are characteristic of cobalt oxide [37]. It suggests that the cobalt oxide may be well dispersed in the lattices of α -Fe₂O₃.

Fig. 3(a) and (b) represents the XRD pattern of pure α -Fe₂O₃ and α -Fe₂O₃(5%Co), respectively. In Fig. 3(a), the diffraction peaks are all closely matched with the standard α -Fe₂O₃ reflections (JCPDS No. 33-0664). It revealed that the synthesized α -Fe₂O₃ has an orthorhombic structure. In the case of 5%Co doped sample (Fig. 3(b)), no

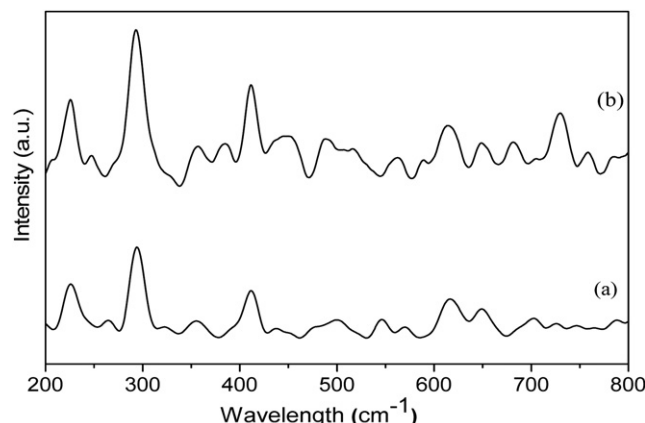


Fig. 2. Raman spectrum of (a) pure α -Fe₂O₃ and (b) α -Fe₂O₃(5%Co).

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