Research articles

Bifunctional sodium tartrate as stabilizer and reductant for the facile synthesis of Fe$_3$O$_4$/Ag nanocomposites with catalytic activity

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ABSTRACT

In this paper, we have demonstrated a facile and environmentally friendly approach to prepare Fe$_3$O$_4$/Ag nanocomposites (Fe$_3$O$_4$/Ag NPs) by a two-step method. During the preparation process, neither any other reducing agents nor toxic organic solvents were employed. Firstly, Fe$_3$O$_4$ nanoparticles were prepared by co-precipitation and stabilized with the sodium tartrate. Secondly, Fe$_3$O$_4$/Ag composite nanoparticles were synthesized by a simple reflux method, which once more using sodium tartrate as a green reducing agent to reduce the AgNO$_3$ to Ag NPs. The as-prepared NPs were characterized by UV–vis spectrometer, dynamic light scattering (DLS), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and vibrating sample magnetometer (VSM). Both the sodium tartrate stabilized Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$@ST NPs) and Fe$_3$O$_4$/Ag NPs showed well dispersed in water and had high superparamagnetism at room temperature, which can be quickly actuated by a small household magnet. More importantly, the Fe$_3$O$_4$/Ag NPs exhibited excellent catalytic properties both in efficiency and recyclability for the degradation of methyl orange (MO) in the presence of H$_2$O$_2$ and the composition was unchanged after 5 cycle times.

1. Introduction

During past few decades, multifunctional hybrid nanomaterials which contain two or more types of nanoparticles (NPs) have aroused remarkable interest due to their unique functions in catalysis, photography, electronics, antibacterial and optical applications [1–9]. Among various nanoparticles, Fe$_3$O$_4$ NPs and Ag NPs were the most frequently employed inorganic NPs in the synthesis of advanced nanocomposites[2,10–12].Owing to Fe$_3$O$_4$ NPs with good biocompatibility and high superparamagnetism can be used for bio-separations [1,13–15], targeted drug delivery [16–18], and magnetic resonance imaging (MRI) [19]. And Ag NPs due to their excellent catalytic properties [20,21] and antibacterial activity [22,23] have attracted ever-increasing attention.

Fe$_3$O$_4$/Ag NPs composed of these two NPs have been broadly used in diverse fields. Therefore, many efforts have been made to synthesize Fe$_3$O$_4$/Ag NPs. However, in various synthetic methods, the most frequently used reducing agent was NaBH$_4$ [24–27], a few reports employed cellulose [1], oleylamine [28], maltose [29] and chitosan [30] and so on. Among these methods, there were important pitfalls such as higher reaction temperature, longer reaction time, more cumbersome operation and more toxic materials must be recognized and addressed. It is necessary to develop renewable and green materials for the Fe$_3$O$_4$/

Ag NPs because of science and technology is shifting more towards environmentally friendly and sustainable resources and processes.

To the best of our knowledge, the sodium tartrate played a double role; it acted not only as a stabilizer but also as a reducing agent has not been reported. Sodium tartrate as one of the most important renewable reagent was rich in carboxyl group and hydroxyl group. Herein, a facile and environmentally friendly method to prepare Fe$_3$O$_4$/Ag nanocomposites was presented. Firstly, Fe$_3$O$_4$ nanoparticles were prepared by co-precipitation and stabilized with the sodium tartrate. Secondly, Fe$_3$O$_4$/Ag composite nanoparticles were synthesized by a simple reflux method, which using sodium tartrate as a green reducing agent to reduce the AgNO$_3$ to Ag NPs. In addition, the catalytic performance of Fe$_3$O$_4$/Ag NPs for the degradation of methyl orange (MO) in the presence of H$_2$O$_2$ was studied. More importantly, the degradation percentage of Fe$_3$O$_4$/Ag NPs retained more than 90% after 5 cycle times and the composition was unchanged.

2. Experimental section

2.1. Materials and instruments

All of the chemicals, including Ferric chloride (FeCl$_3$·6H$_2$O, 99%), ferrous sulfate (FeSO$_4$·7H$_2$O, 99%), ammonium hydroxide (NH$_3$·H$_2$O,
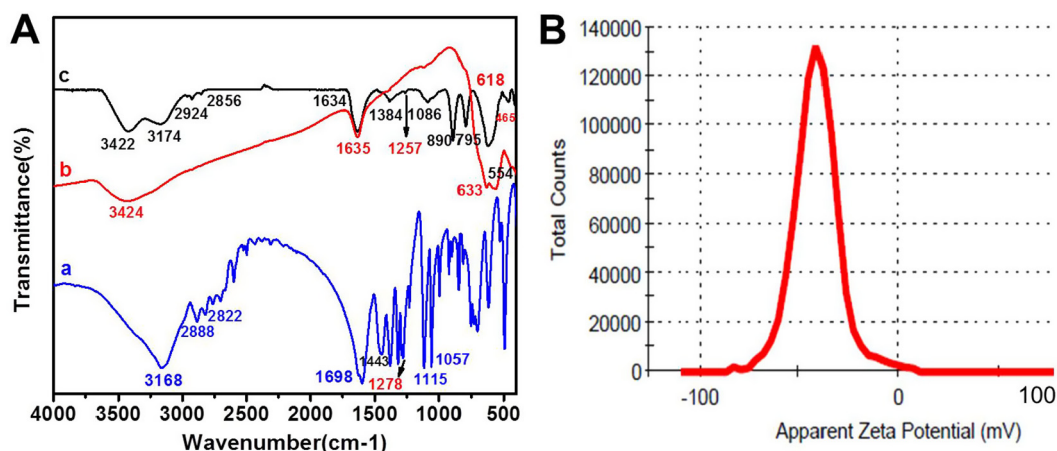
Fig. 1. FT-IR spectra of ST (a) and Fe_3O_4 NPs (b) and Fe_3O_4@ST NPs(c) synthesized at initial m (ST) = 0.5 g and 60 °C for 15 min (A); Zeta -potential of Fe_3O_4@ST NPs (B).

25%–28%), sodium tartrate ($C_4H_4Na_2O_6$, ST), methyl orange (MO) and silver nitrate ($AgNO_3$)were taken from Tianjin No. 1 Reagent Factory, China and used without further purification. The ultrapure water (κ = 18.25 MΩ·cm) was used in our experiments.

Fourier transform infrared (FT-IR) spectra was used to investigate the nature of the chemical bonds formed while synthesized the sodium tartrate stabilized Fe_3O_4 nanoparticles. Optical properties of nanoparticles were investigated by UV-2450 spectrometer in the range of 300–800 nm. The hydrodynamic diameter and zeta-potential was conducted on dynamic light scattering (DLS, Malvern Mastersizer 2000). The structure analysis and morphologies observation of nanoparticles were carried out using a transmission electron microscopy (TEM, H-600) and Scanning Electron Microscopy (SEM). The crystal structure of the nanoparticles were confirmed by an X-ray diffractometer (XRD, DMAX-2400) with Cu Kα radiation. Magnetic properties of the obtained nanoparticles were measured with a vibrating sample magnetometer (VSM, LakeShore 7073). The surface compositions of elements such as Fe and Ag in Fe_3O_4/Ag NPs was analyzed with X-ray photoelectron spectroscopy (XPS, K-Alpha).

2.2. Synthesis of sodium tartrate stabilized Fe_3O_4 nanoparticles

The synthesis of the sodium tartrate stabilized Fe_3O_4 NPs (Fe_3O_4@ ST) through co-precipitation of Fe^{3+} and Fe^{2+} with ammonium hydroxide with slight modification [13,31]. Firstly, $FeCl_3 \cdot 6H_2O$ (2.0 g, 7.4 mmol) and $FeSO_4 \cdot 7H_2O$ (1.88 g, 6.8 mmol) were dissolved in 100 mL ultrapure water with constant mechanical stirring. After the reagents had completely dissolved, 5 mL of ammonia solution (25%–28%) was rapidly added to the mixed system. This system maintained at 75 °C in a N_2 stream with continuous stirring for 15 min. A black precipitate was obtained by cooling the reaction mixture to room temperature. The precipitate was then thoroughly rinsed three times with ultrapure water. Secondly, 0.5 g of sodium tartrate as a mild stabilizer was added to this mixture which re-dispersed in 100 mL ultrapure water, while maintained at 60 °C in a N_2 atmosphere for 15 min. Finally, sodium tartrate stabilized Fe_3O_4 nanoparticles were decanted with a permanent magnet and cleaned by ultrapure water several times.

2.3. Synthesis of Fe_3O_4/Ag NPs

Fe_3O_4/Ag NPs were synthesized by a simple reflux method, which using sodium tartrate as a green reducing agent. At first, PVP (0.4 g) was added to 0.01 mol/L silver nitrate solution (100 mL). When the mixture was heated to boiling, quickly added 25 mg Fe_3O_4@ST to the obtained solution and after the solution was boiling again, 1% tartaric acid (1 mL) was also rapidly added to the system. The reaction was kept

at boiling temperature for 1 h and then the nanoparticles were separated out by external magnetic field and washed with ultrapure water to remove the impurities. Finally, the synthesized Fe_3O_4/Ag composite nanoparticles were re-dispersed in ultrapure water and stored at 4 °C. During the preparation process, the content of PVP, reaction time and reaction temperature were optimized, respectively.

2.4. Catalytic activity

In order to evaluate the catalytic activity of the synthesized Fe_3O_4/Ag NPs, the degradation of MO was employed. Typically, MO solution (20 mL, 8 mg/L) was mixed with Fe_3O_4/Ag NPs (4 mL, 1 mg/mL). Then the H_2O_2 (1 mL, 30%) was added to the mixture to investigate their catalytic activity. The reaction was performed at room temperature with continuous stirring. The color of the MO solutions changed gradually from yellow to colorless with the reaction proceeding. Finally, the degradation of MO was monitored by measuring the absorbance peak of the –N = N- at 464 nm.

3. Results and discussion

3.1. Characterization of Fe_3O_4@ST NPs

To confirm the successful modification of the Fe_3O_4 nanoparticles with the ST, FT-IR spectra of pure ST, pure Fe_3O_4 NPs and the Fe_3O_4@ ST NPs were analyzed as shown in Fig. 1A. The prominent peak appeared (curve a) at 1698 cm^{-1} was attributed to asymmetric stretching vibrations of COO^- from the ST shifted to 1634 cm^{-1} for Fe_3O_4@ST NPs (curve c), indicating the binding of a tartrate radical to the surface of Fe_3O_4 NPs by chemisorption of carboxylate ions [32]. Carboxylate groups of tartrate form complexes with the Fe atoms on the surface of Fe_3O_4, resulting in particles single bond character to the C=O bond and this led to the weakening of the C=O bond and shifted the stretching frequency to a lower value. Furthermore, the bands around1384, 1257 and 1086 cm^{-1} were originated from the symmetric stretching of COO^-, symmetric stretching of C−O, and OH groups of tartrate, respectively. The strong IR band observed at around 618 and 554 cm^{-1} in Fe_3O_4@ST and Fe_3O_4 NPs absorbance spectrum can be ascribed to the iron oxide skeleton (Fe−O) of Fe_3O_4 [33]. From zeta-potential measurements (Fig. 1B), it had been observed that absorption of tartrate onto the surface of Fe_3O_4 NPs results in highly negative surface charge that the valve was −41.4 mV. These high negative values of Fe_3O_4@ST NPs confirmed the presence of negatively charged carboxylate groups on the surface of the nanoparticles.

Fig. 2A showed the photo of the unstabilized and sodium tartrate stabilized Fe_3O_4 NPs that dispersed in water. The unstabilized Fe_3O_4