Materials Research Bulletin 62 (2015) 217–221

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Short communication

Hydrothermal synthesis of superparamagnetic Fe_3O_4 nanoparticles with ionic liquids as stabilizer

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ARTICLE INFO

Article history:
Received 25 June 2014
Received in revised form 17 October 2014
Accepted 8 November 2014
Available online 11 November 2014

Keywords:
A. Magnetic materials
B. Chemical synthesis
B. Magnetic properties

ABSTRACT

Superparamagnetic Fe_3O_4 nanoparticles have been successfully synthesized under hydrothermal condition with the assistant of ionic liquid 1-hexadecyl-3-methylimidazolium chloride ($[C_{16}mim]Cl$). The structure and morphology of the sample have been investigated by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM), and the results indicate that the as-synthesized inverse spinel Fe_3O_4 nanoparticles have an average diameter of about 10 nm and exhibit relatively good dispersity. More importantly, it is found that $[C_{16}mim]Cl$ acts as stabilizer for the Fe_3O_4 nanoparticles by adsorbing on the particles surfaces to prevent the agglomeration. In addition, the obtained superparamagnetic Fe_3O_4 nanoparticles have a saturation magnetization of 67.69 emu/g at 300 K.

1. Introduction

Fe_3O_4 nanoparticles (NPs), as one kind of the most important magnetic materials, have been widely applied in biomedicine, magnetic storage devices, ferrofluids, and separation processes due to their excellent magnetic properties [1,2]. The magnetic property of Fe_3O_4 NPs strongly depends on their sizes, and Fe_3O_4 NPs with diameters between 3 and 15 nm possess superparamagnetic property [3]. Most recently, superparamagnetic magnetic materials have attracted much attention in the biomedical field such as drug delivery and magnetic resonance imaging (MRI) [4]. To date, several synthesis processes, including hydrothermal/solvothermal technique, sol–gel route, and co-precipitation method, have been developed to synthesize Fe_3O_4 NPs [2,5–7]. In the synthesis, Fe_3O_4 NPs tend to agglomerate for their large surface energy and magnetization, which would seriously affect the applications; therefore, several stabilizers such as surfactants and polymer matrixs have been used to improve the dispersity of Fe_3O_4 NPs [4,8,9]. However, the final products would possess relatively low saturation magnetizations for the nonmagnetic layers [10]. Thus, it is still a challenge to explore novel routes for the fabrication of Fe_3O_4 NPs with both good dispersity and excellent magnetic property.

Ionic liquids (ILs) are organic salts with low melting points and consist of predominantly ionic species [11]. Most recently, ILs possessing 1-alkyl-3methlyimidazolium cation ($[C_nmim]^+$) have gained much attention for their favorable physico-chemical properties, and they have served as reactants, solvents, and templates in the fabrication of nanomaterials [12–14]. ILs can be manufactured to be hydrophobic or hydrophilic by designing their structures; furthermore, the low surface tensions of ILs are beneficial to improve the stability of the as-formed nanomaterials. In these regards, some imidazolium-based ILs have been chosen as stabilizers to prepare dispersible nanomaterials [15–17]. For example, Dupont et al. have synthesized stable transition-metal NPs (2–3 nm in size) by reduction of transition-metal compounds dissolved in $[Bmim]PF_6$. Therefore, it is reasonable to conceive that ILs with special cations and anions can be employed as stabilizers to improve the monodispersity of Fe_3O_4 NPs.

Herein, we have developed a novel and effective hydrothermal method for the fabrication of superparamagnetic Fe_3O_4 NPs. IL 1-hexadecyl-3-methylimidazolium chloride ($[C_{16}mim]Cl$) have been used as stabilizer in the synthetic system. The effect of $[C_{16}mim]Cl$ on the morphology of product have been investigated in details.

2. Material and methods

2.1. Materials

All chemicals were analytical-grade and used without further purification. $[C_{16}mim]Cl$ was prepared according to the literature procedures [18].

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http://dx.doi.org/10.1016/j.materresbull.2014.11.022
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2.2. Synthesis of Fe_3O_4 NPs

In a typical synthesis, $FeCl_2{\cdot}4H_2O$ (0.15 mmol) and $C_6H_5Na_3O_7{\cdot}2H_2O$ (0.30 mmol) were dissolved into deionized water (7.5 mL) with magnetic stirring until a clear solution was obtained. Then, $[C_{16}mim]Cl$ (0.4 g) and $N_2H_4{\cdot}H_2O$ (2.5 mL) were added to the solution. After it was stirred for 5 min, the solution was transferred and sealed in a teflon-lined stainless steel autoclave with a capacity of about 20 mL. The autoclave was sealed and maintained at 150 °C for 12 h. The products were separated by centrifugation, washed by deionized water and anhydrous ethanol, and then dried in a vacuum at 60 °C for 5 h. Finally black powder was obtained.

2.3. Instruments and characterizations

The phase compositions of the product were characterized by X-ray diffraction (XRD) on a Rigaku D/max 2500V/PC X-ray diffractometer (Cu Kα, $\lambda = 1.54056$ Å) with a 2θ range between 20° and 80°. The generator voltage was 40 kV, the current was 40 mA and the step velocity was 8°/min. The X-ray photoelectron spectra (XPS) data was characterized using PHI-1600 ESCA X-ray photoelectron spectroscopy with Mg Kα as radiation. The sizes and structures of the products were performed by a Hitachi H-7650 transmission electron microscopy, which were operated at an accelerating voltage of 100 kV and 200 kV, respectively. The magnetic studies were performed on a Quantum Design MPMS-XL-7 SQUID susceptometer and a vibrating sample magnetometer (VSM, LDJ-9600, USA).

3. Results and discussions

3.1. Characterization results of the Fe_3O_4 NPs

Fig. 1a depicts the XRD pattern of Fe_3O_4 NPs. All of the diffraction peaks are indexed as face-centered cubic Fe_3O_4 with the lattice parameters of $a = 8.381$ Å, which matches well with the reported values (JCPDS No. 75-0033). No peaks corresponding to impurities are detected, showing the high purity of the sample. The mean crystallize size of Fe_3O_4 NPs is calculated to be about 10.5 nm based on Scherrer formula. Fe_3O_4 has an inverse spinel structure similar to that of γ-Fe_2O_3; therefore, XRD result cannot provide enough evidence to confirm the formation of Fe_3O_4 [19]. Thus, we employ XPS, which is sensitive to the iron valence state, to distinguish these two different phases [20]. As shown in the XPS spectra of Fe2p in Fe_3O_4 (Fig. 1b), the peaks at 724.1 and 710.5 eV, assigned to Fe2p1/2 and Fe2p3/2, are consistent with the values reported for Fe_3O_4 in the literature; furthermore, no satellite peak around 719.0 eV is identified, indicating the absence of γ-Fe_2O_3 in the sample [21].

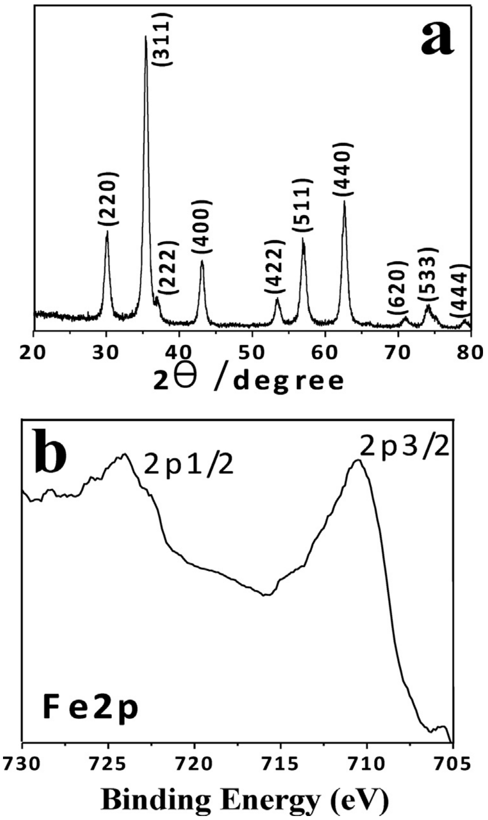

Fig. 1. (a) XRD pattern of the obtained Fe_3O_4 NPs; (b) Fe2p peaks in the XPS spectrum of the Fe_3O_4 NPs.

TEM image (Fig. 2a) gives a general view of the as-synthesized Fe_3O_4 NPs. It can be clearly seen that the sample is quasi-round NPs and has a mean diameter of about 10 nm, consisting with the XRD result. In the HRTEM image taken at a typical particle (Fig. 2b), the Fe_3O_4 nanoparticle has a d-spacing of about 0.255 nm, corresponding to the lattice spacing of the (3 1 1) plane in cubic Fe_3O_4; moreover, its corresponding fast Fourier transform (FFT) pattern

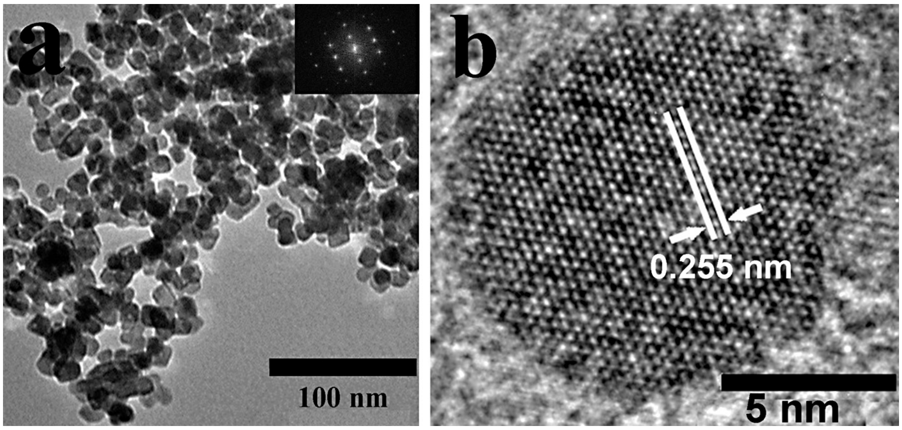

Fig. 2. (a) TEM image of the as-synthesized Fe_3O_4 NPs; (b) HRTEM image of a typical Fe_3O_4 NPs with the electron beam incident along the [0 0 1] direction, and the inset of (a) is its FFT pattern.