Journal of Alloys and Compounds 511 (2012) 163–168

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Preparation of $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites and their adsorption of bovine serum albumin

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ARTICLE INFO

Article history:
Received 12 July 2011
Received in revised form 7 September 2011
Accepted 10 September 2011
Available online 16 September 2011

Keywords:
Ni–Zn ferrite
Citrate-gel
Porous silica layer
Grain size
Specific surface area
Adsorption
Bovine serum albumin
Protein

ABSTRACT

The magnetic nanocomposites of $(1-x)Ni_{0.5}Zn_{0.5}Fe_2O_4/xSiO_2$ ($x = 0$–0.2) were synthesized by the citrate-gel process and their absorption behavior of bovine serum albumin (BSA) was investigated by UV spectroscopy at room temperature. The gel precursor and resultant nanocomposites were characterized by FTIR, XRD, TEM and BET techniques. The results show that the single ferrite phase of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ is formed at 400 °C, with high saturation magnetization and small coercivity. A porous, amorphous silica layer is located at the ferrite nanograin boundaries, with the silica content increasing from 0 to 0.20, the average grain size of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ calcined at 400 °C reduced from about 18–8 nm. Consequently, the specific surface area of the nanocomposites ascends clearly with the increase of silica content, which is largely contributed by the increase in the thickness of the porous silica layer. The $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites demonstrate a better adsorption capability than the bare $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles for BSA. With the increase of the silica content from 0 to 0.05 and the specific surface area from about 49–57 m^2/g, the BSA adsorption capability of the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites calcined at 400 °C improve dramatically from 22 to 49 mg/g. However, with a further increase of the silica content from 0.05 to 0.2, the specific surface area increase from about 57–120 m^2/g, the BSA adsorption for the nanocomposites remains around 49 mg/g, owing to the pores in the porous silica layer which are too small to let the BSA protein molecules in.

1. Introduction

Magnetic nanoparticles (MNPs) have attracted interests based on their fascinating superparamagnetic behavior, high saturation magnetization and relaxation [1,2]. Now, the MNPs have been widely applied to biological and medical areas [3–5], such as drug and gene delivery [6,7], the control of cells and cellular function [8,9], therapeutic hyperthermia [10,11], bioseparation [12,13], magnetic resonance imaging [14–17], and quantitative immunoassay [18,19]. Beyond the biomedical area, interesting studies have been reported on the use of MNPs for ferrofluids, data storage, and catalysis [20]. Recently, some magnetic nanoparticles, such as CoPt $Co_{1-x}Zn_xFe_2O_4/SiO_2$ $MnFe_2O_4$, CoCrMo [21–24], etc., have been reported for biomedical applications.

Ni–Zn ferrites are one of the most versatile magnetic materials as they have high saturation magnetization, high Curie temperature, chemical stability, low coercivity and biodegradability [25]. Many researchers have studied the synthesis of Ni–Zn ferrites [1,26–29]. However, for bio-related applications, pure Ni–Zn ferrite nanoparticles usually lead to problems associated with the formation of large aggregates, the alteration of magnetic properties, and their toxicity in the biological systems. The layer of protective coating offers magnetic particles an opportunity both to maintain their chemical stability and to reduce the potential toxicity without making an obvious impact on their magnetic properties.

Silica has been considered to be one of the most ideal coating layers of coating for MNPs due to its characteristic including high chemical stability, biocompatibility, and easy functionalization, which make it suitable for conjugation with proteins and *in vivo* applications [13,30–32].

Many efforts have been made on the design and synthesis of silica-coated magnetic nanoparticles (SMNPs) over the past few decades [33,34]. As we know, size and composition may influence the property and application of magnetic nanoparticles in biology and medicine, thus the controllable synthesis of well-defined silica-coated magnetic nanoparticles is crucial to the investigation of their magnetic properties and potential applications in biomedical sciences.

Bovine serum albumin (BSA) is the first biomolecule that has been used in biomedical applications, because it is a relatively large biomolecule and usually has a tendency to accumulate at the interface of solid surfaces [23,35,36], and its adsorption on

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doi:10.1016/j.jallcom.2011.09.020

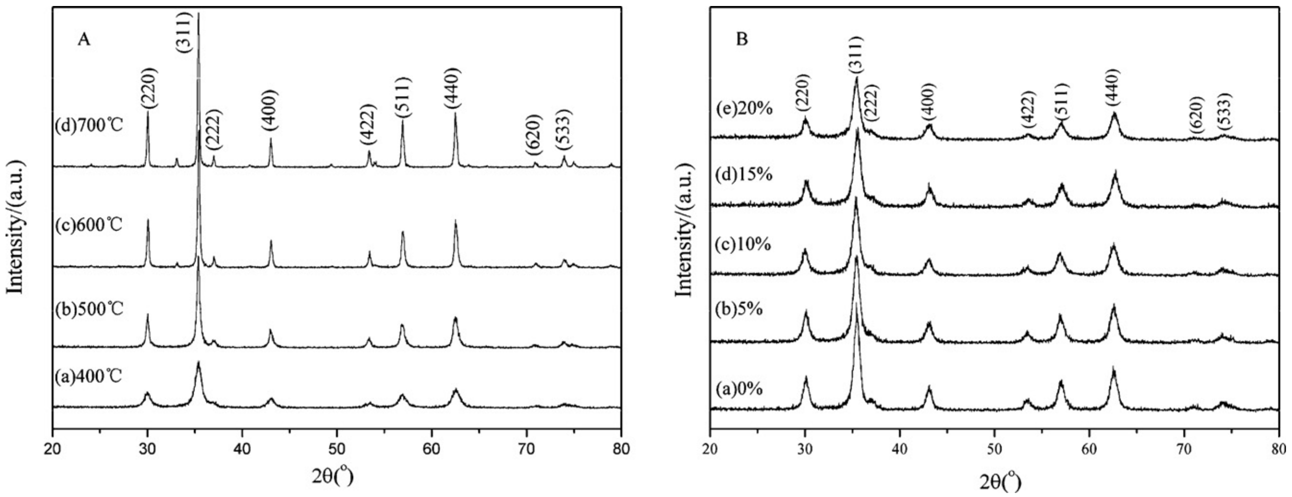

Fig. 1. XRD patterns of $(1-x)Ni_{0.5}Zn_{0.5}Fe_2O_4/xSiO_2$ nanocomposites with (A) silica content (x) of 0.10 calcined at various temperatures; (B) silica content (x) from 0 to 0.20 calcined at 400 °C.

surface of the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ composite nanoparticles can act as adsorption models for other biomacromolecules. In this work, the magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites were synthesized via the citrate-gel process, and effects of silica content on the grain size, specific surface area and adsorption performance of bovine serum albumin on the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites were investigated.

2. Experimental

The $(1-x)$ $Ni_{0.5}Zn_{0.5}Fe_2O_4/xSiO_2$ ($x=0$–0.2, in weight ratio) nanocomposites were prepared via the citrate-gel process, which was described in detail for the mono-dispersed Ni–Zn ferrite nanoparticles in our previous paper [37]. With reagent grade $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$, one mole of citric acid for one mole of metal and tetraethyl orthosilicate (TEOS) according to the various weight ratios of silica in $(1-x)Ni_{0.5}Zn_{0.5}Fe_2O_4/xSiO_2$ from $x=0$ to 0.20 were mixed together in a beaker, and were dissolved in 100 ml distilled water. The mixed solution was magnetically stirred for 20–24 h at room temperature and the surplus water was removed in a vacuum rotary evaporator at 60–80 °C until a viscous liquid was obtained. Then, the viscous liquid was dried at 80 °C in an oven to obtain the dried gel precursor, which was calcined at various temperatures from 400 to 700 °C for 2 h in air to form loose nanocomposites.

The structures, compositions and morphologies of the gel precursors and the nanocomposites obtained were investigated by Fourier transform infrared spectroscopy (FTIR, Nexu670 spectrometer), X-ray diffraction (XRD, RIGAKU), transmission electron microscopy (TEM, JEM2100). The specific surface area and the pore size were measured by the Brunauere–Emmette–Teller (BET) method with the instrument of NOVA 2000e. The adsorption of BSA on the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites was measured with a UV spectrophotometer (UV2550) at room temperature [37]. The adsorption capacity of BSA for the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites can be calculated by the following equation [38]:

$$I = \frac{m_{BSA}(A_{BSA} - A_{mag})}{m_{mag}A_{BSA}}$$

where I refers to the adsorbed BSA amount of the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites (mg/g), m_{BSA} is the total weight of BSA (mg), m_{mag} is the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites weight (g), A_{BSA} is the UV absorbance value of blank BSA solution, and A_{mag} is the UV absorbance value of BSA solution after adsorption.

3. Results and discussion

3.1. Structural characterization of $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites

The X-ray diffraction (XRD) patterns of the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites with silica weight content of 0.10 calcined at various temperatures for 2 h are shown in Fig. 1A. All the as-prepared nanocomposites show characteristic lines of Ni–Zn ferrite with a spinel structure, which indicates that single phase Ni–Zn ferrites are formed even at 400 °C (Fig. 1A(a)). It is well known that narrow lines width for XRD patterns indicate a high crystallinity and a larger grain size. Fig. 1A(a–d) shows that with an increase in the temperature, XRD peaks become sharper, suggesting that the crystallinity is higher and the particles size is larger at a higher temperature.

Fig. 1B shows the XRD patterns for the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites with silica weight content from 0 to 0.20 calcined at 400 °C for 2 h. With the increase of silica weight content (Fig. 1B(a–d)), because of the non-crystalline nature of silica, the corresponding peaks become weaker and broader, which implies the crystallinity is lower and the particles size is smaller at a high silica content.

The average crystallite sizes of Ni–Zn ferrites can be calculated from the value of full-width (FWHM) at half-maximum of (3 1 1) plane using Scherrer's formula [39]:

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

where D is the crystallite size in nanometers, λ is the radiation wavelength (0.154056 nm for Cu Kα), β represents the bandwidth at half-intensity width of the relevant diffraction peak and θ is the corresponding diffraction peak angle. The results show that the grain sizes of nanocrystallites increase with the calcination temperature, while they descend from about 18 nm to 8 nm at 400 °C with the silica content increasing from 0 to 0.20. The reasons for this are that high temperature favors the atomic mobility and causes the grain growth, on the contrary, silica prevents the atomic mobility and causes the decrease of the grain size. The crystallite sizes show that the synthesized $Ni_{0.5}Zn_{0.5}Fe_2O_4$ is nano-crystallites. Therefore, the calcination temperature and the silica content are two important factors in controlling the synthesis of ferrite nanocrystallites.

Fig. 2 shows the TEM observations of the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ composite nanoparticles with silica content of 0.20 calcined at 600 °C for 2 h. It can be estimated from Fig. 2 that the grain size of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ in nanocomposites is about 10–20 nm. These ferrite nanoparticles are well dispersed and the porous amorphous silica layer is located on the nanograin boundaries. The porous layer has very fine pores about 0.5–1.0 nm and is mesoporous [40]. This mesoporous amorphous silica layer will become thick with the silica content in the $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites, leading to a high specific surface area.