Journal of Magnetism and Magnetic Materials 340 (2013) 57–60

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Preparation and characterization of PVPI-coated Fe_3O_4 nanoparticles as an MRI contrast agent

Guangshuo Wang [a], Ying Chang [b], Ling Wang [c,*], Zhiyong Wei [b,*], Jianyun Kang [d], Lin Sang [a], Xufeng Dong [a], Guangyi Chen [b], Hong Wang [e,*], Min Qi [a,*]

[a] School of Material Science and Engineering, Dalian University of Technology, Dalian 116024,PR China
[b] School of Automotive Engineering, State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, PR China
[c] Department of Oncology, First Affiliated Hospital of Dalian Medical University, Dalian116011, PR China
[d] Department of Radiology, First Affiliated Hospital of Dalian Medical University, Dalian116011, PR China
[e] Department of Orthopedics, First Affiliated Hospital of Dalian Medical University, Dalian 116011, PR China

ARTICLE INFO

Article history:
Received 9 September 2012
Received in revised form
20 November 2012
Available online 26 March 2013

Keywords:
Fe_3O_4 nanoparticle
Polyvinylpyrrolidone-iodine
Superparamagnetism
MRI contrast agent

ABSTRACT

Polyvinylpyrrolidone-iodine (PVPI)-coated Fe_3O_4 nanoparticles were prepared by using inverse chemical co-precipitation method, in which the PVPI serves as a stabilizer and dispersant. The wide angle X-ray diffraction (WAXD) and selected area electron diffraction (SAED) results showed that the inverse spinel structure pure phase polycrystalline Fe_3O_4 was obtained. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results exhibited that the resulted Fe_3O_4 nanoparticles were roughly spherical in shape with narrow size distribution and homogenous shape. Fourier transform infrared spectroscopy (FTIR) results suggested that PVPI interacted with Fe_3O_4 via its carbonyl groups. Results of superconducting quantum interference device (SQUID) indicated prepared Fe_3O_4 nanoparticles exhibited superparamagnetic behavior and high saturation magnetization. T_2-weighted MRI images of PVPI-coated Fe_3O_4 nanoparticles showed that the magnetic resonance signal was enhanced significantly with increasing nanoparticles concentration in water at room temperature. These results indicated that the PVPI-coated Fe_3O_4 nanoparticles had great potential for application in MRI as a T_2 contrast agent.

1. Introduction

In recent years, magnetic nanoparticles with properties of superparamagnetism, low toxicity and biocompatibility, have shown great potential applications in a variety of fields, including catalysis, biomedicine, magnetic date storage and environmental remediation [1–4]. It is well known that Fe_3O_4 is the strongest magnetic nanoparticles of all natural minerals on Earth [5]. During recent years, one of the fast developing applications of Fe_3O_4 nanoparticles is in biomedical areas including magnetic resonance imaging (MRI) contrast enhancement, targeted drug delivery, hyperthermia, biological separation, biosensors and diagnostic medical devices [6–11]. Especially, a number of studies have been reported on the application of Fe_3O_4 nanoparticles as MRI contrast agent for early cancer diagnosis and treatment [12,13]. To achieve this aim, Fe_3O_4 magnetic nanoparticles should have a narrow size distribution and good dispersibility in aqueous media. However, pristine magnetic nanoparticles tend to appear aggregation due to large specific surface area and strong dipole–dipole interaction. Thus, a crucial issue influencing the use of Fe_3O_4 nanoparticles for MRI biological application is the stabilization and functionalization of their surface. To improve their stabilization, Fe_3O_4 nanoparticles have been stabilized with formation of a polymeric layer on the surface of magnetic nanoparticles, using lipids, proteins, dendrimers, gelatin, dextran, chitosan, pullulan, poly(ethyleneglycol) (PEG), poly(ethylene-co-vinyl acetate), poly(vinylpyrrolidone) (PVP), or poly(vinyl alcohol) (PVA), etc. [14–19].

It has been known that polyvinylpyrrolidone-iodine (PVPI) complex, commercially named "povidone iodine", is water-soluble, non-toxic and antibacterial, which is often employed in various medical applications [20,21]. Of particular interest for the present work is incorporate PVPI into Fe_3O_4 nanoparticles, which could be a promising dual-modality for MRI and X-ray imaging due to the existence of magnetic Fe_3O_4 and complexed iodine. In this study, for the first time, PVPI-functionalized Fe_3O_4 nanoparticles were synthesized and characterized using inverse chemical co-precipitation method. Then, the structure, morphology and magnetic properties of PVPI-coated Fe_3O_4 nanoparticles were investigated by the wide angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and

* Corresponding authors. Tel./fax: +86 411 84706475.
E-mail addresses: whwl2003@tom.com (L. Wang), zywei@dlut.edu.cn (Z. Wei), whwl@hotmail.com (H. Wang), minqi@dlut.edu.cn (M. Qi).

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.03.023

superconducting quantum interference device (SQUID). Furthermore, T_2-weighted MRI images of PVPI-coated Fe_3O_4 nanoparticles were obtained and the results indicated that such surface functionalized Fe_3O_4 nanoparticles have great potential for application in MRI as T_2 contrast agent.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, 98%), ethanol and ammonium hydroxide (NH_4OH, 30%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone-iodine (PVPI) was obtained from Shanghai WellTone Material Technology Co., Ltd (China). All chemicals were used directly without further purification.

2.2. Synthesis of PVPI-coated Fe_3O_4 nanoparticles

The PVPI-coated Fe_3O_4 nanoparticles were synthesized by the inverse chemical co-precipitation method according to the following procedure. In a typical experiment, 25 mL 30% ammonia solution was added to 250 mL three-necked flask. And then 2.352 g of PVPI was dissolved in 100 mL of distilled water containing 2.352 g $FeCl_3 \cdot 6H_2O$ and 0.86 g $FeCl_2 \cdot 4H_2O$. The mixture was stirred for 30 min to obtain a homogeneous solution. The mixture solution was added dropwise into the flask under vigorous mechanical stirring for 30 min at 25 °C. To prevent oxidative reaction, the system was kept under nitrogen atmosphere. The resulting solution was maintained at 80 °C for 1 h and then the solution was cooled to room temperature. The resulting black precipitate was separated by a permanent magnet and washed three times with deionized water and three times with ethanol. The collected magnetic nanoparticles were dried at 50 °C in vacuum. The prepared Fe_3O_4 nanoparticles with PVPI/$FeCl_3 \cdot 6H_2O$ weight ratio of 1/10, 1/1 and 2/1 were designated as PVPI-Fe_3O_4-1/10, PVPI-Fe_3O_4-1/1 and PVPI-Fe_3O_4-2/1, respectively.

2.3. Characterization

The wide-angle X-ray diffraction (WAXD) patterns of Fe_3O_4 nanoparticles were performed on a Dmax-Ultima+X-ray diffractometer (Rigaku, Japan) with Ni-filtered Cu/K-α radiation (λ=0.15418 nm). The operating target voltage and tube current was 40 kV and 100 mA, respectively. The Fourier transform infrared spectroscopy (FTIR) analysis was performed at room temperature using a Magna 750 spectrometer (Nicolet, USA). The specimen of Fe_3O_4 nanoparticles was mixed with KBr pellet and then pressed into flakes for FTIR measurements. Transmission electron microscope (TEM), selected area electron diffraction (SAED) pattern and high-resolution TEM (HRTEM) were taken on a FEI Tecnai G2 F20 electron microscope. Scanning electron microscopy (SEM) analysis was obtained on a field emission SEM microscope (FEI Nanosem 430). The magnetic properties of Fe_3O_4 nanoparticles were investigated in a MPMS-XL-7 superconducting quantum interference device (SQUID) magnetometer (Quantum Design, USA).

2.4. MR imaging

Magnetic resonance imaging (MRI) tests were performed on a 3.0 T magnetic resonance (MR) scanner (Siemens Magnetom Trio). PVPI-coated Fe_3O_4 nanoparticles were dispersed in a 1.5% aqueous solution of agar with various concentrations and then poured into tubes (2 mL). Fe_3O_4 nanoparticles and agar were mixed thoroughly while they were warm by turning the tubes upside down repeatedly. The mixture was allowed to cool to room temperature. The T_2-weighted images were acquired using spin-echo imaging sequencing with the following parameters: matrix size=320 × 320, field of view=200 mm × 200 mm, slice thickness=2 mm, echo time-=30 ms, repetition time=2000 ms, number of acquisitions=1.

3. Results and discussion

The crystalline structure of the Fe_3O_4 nanoparticles functionalized with PVPI molecules was characterized by WAXD. As shown in Fig. 1, it is found that the *d*-spacing values of significant peaks match well with data from the JCPDS card (19-0629) for Fe_3O_4. The diffraction peaks at 2θ=30.4°, 35.7°, 43.4°, 53.8°, 57.2° and 62.9° can be assigned to the (220), (311), (400), (422), (511) and (440) planes, respectively, which indicates the cubic spinal crystal structure of pure Fe_3O_4. Moreover, it can be clearly seen from Fig. 1 that the diffraction peaks are weaker in intensity and broader for the Fe_3O_4 nanoparticles obtained at higher addition of PVPI. It indicates that the crystallinity decreases for the modified nanoparticles. The average crystallite size can be estimated by WAXD pattern, using the Scherrer Equation [22]:

$$\beta = \frac{k\lambda}{d\cos\theta} \quad (1)$$

where, β is the peak-width at half of maximum intensity, k is the shape factor, λ is the X-ray diffraction wavelength (λ=0.154 nm), d is the

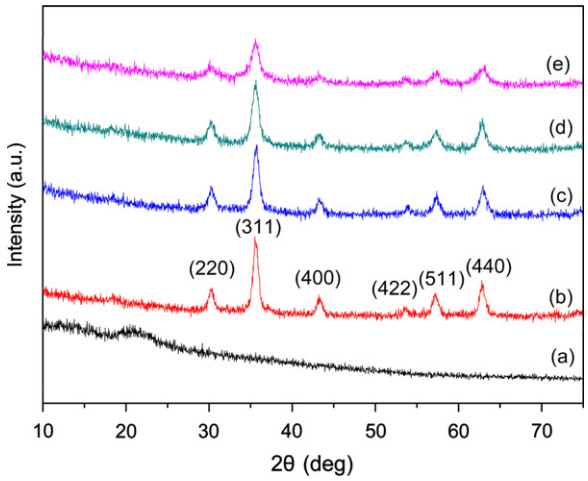

Fig. 1. WAXD patterns of PVPI (a), Fe_3O_4 (b), PVPI-Fe_3O_4-1/10 (c), PVPI-Fe_3O_4-1/1 (d) and PVPI-Fe_3O_4-2/1 (e).

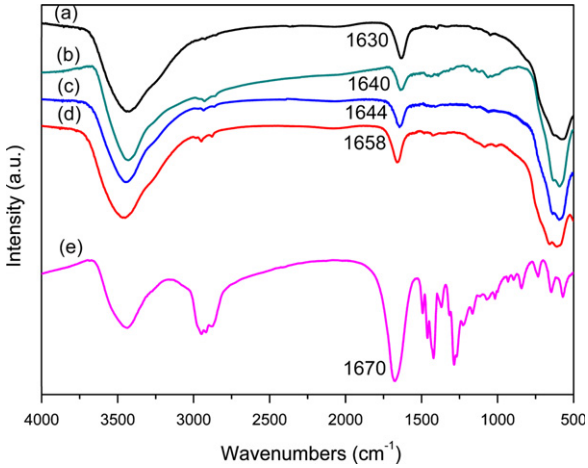

Fig. 2. FTIR spectra of Fe_3O_4 (a), PVPI-Fe_3O_4-1/10 (b), PVPI-Fe_3O_4-1/1 (c), PVPI-Fe_3O_4-2/1 (d) and PVPI (e).