



# Superparamagnetic iron oxide nanoparticles prepared by using an improved polyol method

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## ARTICLE INFO

### Article history:

Received 5 June 2012

Received in revised form 3 December 2012

Accepted 5 December 2012

Available online 13 December 2012

### Keywords:

Superparamagnetic iron oxide nanoparticles

Thermal decomposition

PEG

PVP

PEI

Dispersion stability

## ABSTRACT

Superparamagnetic iron oxide nanoparticles were synthesized by thermal decomposition of iron (III) acetylacetonate ( $\text{Fe}(\text{acac})_3$ ) in PEG containing poly(vinyl pyrrolidone) (PVP) or poly(ethylene imine) (PEI). The morphologies and phase compositions of the nanoparticles were determined by transmission electron microscopy and X-ray diffraction, respectively. The surface coating of the nanoparticles was recognized using Fourier transform infrared spectroscopy and the presence of the surface coating was confirmed by Thermogravimetric analyses. Magnetic properties were measured using superconducting quantum interference device. The zeta potentials and hydrodynamic sizes of the nanoparticles were determined using nano-particle and zeta potential analyzer. The superparamagnetic iron oxide nanoparticles with sizes from 4.1 nm to 14.9 nm were prepared in the present work, which could be tuned by varying factors such as the reaction temperature, the reaction time, and the PVP or PEI contents. The superparamagnetic nanoparticles were jointly coated with PEG/PVP or PEG/PEI. With hydrodynamic sizes smaller than 40 nm and neutral or positive zeta potentials these superparamagnetic iron oxide nanoparticles exhibited higher dispersion stability in deionized water and in phosphate buffered saline as compared with the superparamagnetic iron oxide nanoparticles coated with PEG alone. This work demonstrates that superparamagnetic iron oxide nanoparticles with modulated properties can be prepared simply by using the improved polyol method.

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## 1. Introduction

Superparamagnetic iron oxide nanoparticles (SPIONs) have been intensively studied for their biomedical applications, such as drug and gene delivery carriers [1,2], and as  $T_1$  and  $T_2$  contrast agents in magnetic resonance imaging (MRI) [1,3,4]. High crystalline SPIONs are normally produced by the thermal decomposition of  $\text{Fe}(\text{acac})_3$  in non-polar solvents [5–7], but a ligand-exchange process must be used to achieve their water dispersibility [8]. To synthesize water-dispersible SPIONs by the thermal decomposition of  $\text{Fe}(\text{acac})_3$  in a polyol is a simple method to obtain high crystalline SPIONs [9–11]. However, the aggregation of the nanoparticles in aqueous media may take place with time because of the interaction of the nanoparticles, and extra treatments have to be exploited to prevent the aggregation [12]. In this work, we synthesized SPIONs by the thermal decomposition of  $\text{Fe}(\text{acac})_3$  in PEG containing PVP or PEI, the SPIONs showed excel-

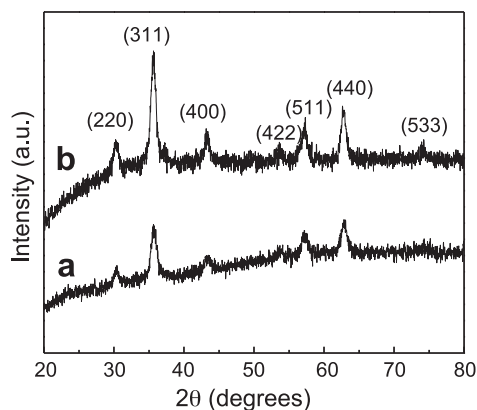
lent colloidal stability in aqueous media and their properties such as sizes and zeta potentials were also modulated by the PVP or PEI.

## 2. Experimental

Raw materials were purchased from Sinopharm Chemical Co. and used without further modification, unless otherwise noted. 0.3–1 g PVP (PVP, Mw = 58,000, 99%) or PEI (PEI 1800, Mw = 1800, 99%) was dissolved in 15 g PEG (PEG 1000, Mw = 1000, 99%, Xilong Chemical) at 90 °C with vigorous magnetically stirring in a three-neck round-bottom flask for 10 min, then 0.7 g of  $\text{Fe}(\text{acac})_3$  (98%, Aladdin Reagent) was added to the flask with stirring for another 10 min. This red solution was heated to 200–300 °C at a heating rate of 15 °C/min under a flow of argon and kept at the temperature for 0.5–8 h. The reaction products were cooled to 60 °C by removing the heat source and then mixed with 60 mL of toluene, after ultrasonic stirring, the particles were collected by a magnet and washed twice with acetone to remove the excess organics. 0.05 M PBS solution was used to test the stability of the nanoparticles. To prepare 1 l 0.05 M PBS, 40.05 g NaCl, 1 g KCl, 7.2 g  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  and 1.2 g  $\text{KH}_2\text{PO}_4$  were dissolved into 800 mL deionized water, then put in more deionized water to make 1 l solution, and adjust the pH level to 7.4 with 0.1 M NaOH [13].

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**Fig. 1.** XRD patterns of the nanoparticles synthesized by thermal decomposition of  $\text{Fe}(\text{acac})_3$  in 15 g PEG containing 0.3 g PVP at 260 °C for 1 h (a) and in 15 g PEG containing 0.5 g PEI at 260 °C for 0.5 h (b).

The phase compositions were analyzed by X-ray powder diffraction (XRD, Xpert Pro PANalytical, Netherlands). The measurements were done under 37 kV voltage and 45 mA current using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154056$  nm). The size and morphology of the SPIONs were determined using transmission electron microscopy (TEM, JEOL2010). The aqueous dispersions of the nanoparticles were drop-cast onto copper grids, and the grids were air-dried at room temperature before being loaded into the microscope. The surface coating of the nanoparticles was recognized by Fourier transform infrared spectroscopy (FTIR, Varian 3100). The hydrodynamic sizes and zeta potentials of SPIONs in aqueous media were evaluated using a nanoparticle zeta potential analyzer (Nano ZS90, Malvern). Magnetic properties of the nanoparticles were measured by the superconducting quantum interference device (SQUID, Quantum Design, MPMS XL). Thermogravimetric analyses (TGA) were performed under nitrogen at a heating rate of 10 °C/min from room temperature up to 700 °C using a TGA Q500 (TA Instruments) analyzer.

### 3. Results and discussion

The XRD patterns of the nanoparticles synthesized by the thermal decomposition of  $\text{Fe}(\text{acac})_3$  in 15 g PEG containing 0.3 g PVP at 260 °C for 1 h (Fig. 1a) and in 15 g PEG containing 0.5 g PEI at 260 °C for 0.5 h (Fig. 1b) are matching with the standard XRD patterns for bulk magnetite (JCPDS File no. 00-019-0629) or maghemite (JCPDS File no. 00-039-1346). The peaks with  $2\theta$  values of 30.09°, 35.44°, 43.07°, 53.43°, 56.96°, 62.55° and 74.00° correspond to the crystal planes (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) of crystalline  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$ , respectively [14]. The TEM images of the SPIONs are shown in Fig. 2. The selected area electron diffraction (SAED) patterns and the high-resolution TEM (HRTEM) image of the SPIONs synthesized in PEG containing PVP reveal the highly crystalline nature of the nanoparticles (Fig. 2a). Analysis of the  $d$ -spacing of the SAED rings suggests that the rings correspond to the Bragg reflections of [2 2 0], [3 1 1], [4 2 2], [5 1 1], and [4 4 0] crystal planes of bulk magnetite (JCPDS File no. 00-019-0629). The interplanar distances measured from the HRTEM image are 4.83 Å and 2.96 Å, which are consistent with known values for the {1 1 1} and {2 2 0} planes of magnetite [15], respectively. The sizes of SPIONs synthesized by thermal decomposition of 0.7 g  $\text{Fe}(\text{acac})_3$  in 15 g PEG containing 0.3 g PVP or PEI at different temperatures are listed in Table 1. The mean particle size and distribution were evaluated by measuring the diameters of 100 particles. The sizes of nanoparticles synthesized by thermal decomposition of  $\text{Fe}(\text{acac})_3$  in PEG containing PVP at 200 °C for 8 h and in PEG containing PEI at 200 °C for 1 h are  $4.1 \pm 0.9$  nm (Fig. 2c) and  $5.4 \pm 1.1$  nm (Fig. 2d),

**Table 1**

The sizes of the nanoparticles synthesized by thermal decomposition of 0.7 g  $\text{Fe}(\text{acac})_3$  in 15 g PEG containing 0.3 g PVP or PEI at different temperatures.

Polymers	200 °C	240 °C	260 °C	300 °C
PEG/PVP	$4.1 \pm 0.9$ nm <sup>a</sup>	$6.2 \pm 1.2$ nm	$8.8 \pm 1.8$ nm	$10.2 \pm 1.6$ nm
PEG/PEI	$5.4 \pm 1.1$ nm	$9.4 \pm 1.9$ nm	$10.0 \pm 1.7$ nm	$13.8 \pm 2.3$ nm

<sup>a</sup> Heating for 8 h; other samples were heated for 1 h.

respectively. The detailed studies to prepare ultra-fine nanoparticles (<4 nm) by lowering the temperature further and to explore their potential as  $T_1$  contrast agent [3] are underway. The sizes of SPIONs increased with increasing the reaction temperature (Table 1 and Fig. 2a and b). We found that with increasing the amount of PEI the nanoparticles grew abnormally, and the particle size distribution became broad. This effect can be alleviated by reducing the reaction time. For example, the size of nanoparticles synthesized by thermal decomposition of  $\text{Fe}(\text{acac})_3$  in 15 g PEG containing 0.5 g PEI at 260 °C for 0.5 h were  $14.9 \pm 3.0$  nm (Fig. 2e). For comparison, Fig. 2f shows the nanoparticles with the size of  $10.1 \pm 2.0$  nm synthesized by thermal decomposition of  $\text{Fe}(\text{acac})_3$  in PEG-1000 alone at 260 °C for 1 h. These results show that the sizes of the SPIONs can be tuned by varying the reaction temperature, the reaction time, and the additive contents.

Fig. 3 shows the FTIR spectra of SPIONs synthesized by the thermal decomposition of  $\text{Fe}(\text{acac})_3$  in 15 g PEG containing 0.3 g PVP at 260 °C for 1 h (Fig. 3a) or in 15 g PEG containing 0.5 g PEI at 260 °C for 0.5 h (Fig. 3b). As can be seen from Fig. 3a, the band at  $1632$   $\text{cm}^{-1}$  can be ascribed to the asymmetric  $\text{COO}^-$  and  $\text{C}=\text{O}$  stretching mode [16], the characteristic peak at  $1280$   $\text{cm}^{-1}$  is due to  $\text{C}-\text{N}$  stretching mode of PVP [17]. As can be seen from Fig. 3b, the band at  $1613$   $\text{cm}^{-1}$  can be ascribed to the asymmetric  $\text{COO}^-$  and the  $-\text{NH}_2$  bending mode [18], the characteristic peak at  $1288$   $\text{cm}^{-1}$  is due to  $\text{C}-\text{N}$  stretching mode of PEI [8,19]. The presence of the  $-\text{COO}^-$  group could be resulted from the partial oxidation of the terminal  $-\text{CH}_2-\text{OH}$  group of the PEG during the high temperature synthesis of SPIONs [11]. The peaks at  $3400$ ,  $2922$ ,  $2853$ ,  $1382$ ,  $1100$  and  $580$   $\text{cm}^{-1}$  appear both in Fig. 3a and b, the broad band at  $3400$   $\text{cm}^{-1}$  is due to the  $\text{O}-\text{H}$  stretching vibration of PEG, the absorption peaks at about  $2922$  and  $2853$   $\text{cm}^{-1}$  represent  $\text{CH}_2$  groups of PEG, PVP and PEI [8,19], the band at  $1382$   $\text{cm}^{-1}$  can be ascribed to the symmetric  $\text{COO}^-$  stretching mode [12]. The characteristic peak at  $1100$   $\text{cm}^{-1}$  is due to the  $\text{C}-\text{O}-\text{C}$  bending vibration of PEG [11], the strong absorption band at about  $580$   $\text{cm}^{-1}$  is due to  $\text{Fe}-\text{O}$  stretching vibration for the SPIONs [19]. FTIR spectroscopic results reveal that PEG/PVP or PEG/PEI are jointly attached to the surface of the SPIONs. PVP or PEI may bond to PEG or to iron oxide directly. Scheme 1 shows the proposed surface coating of PEG/PVP-coated SPIONs.

The SPIONs can be suspended in deionized water without any filtration or dialysis separation process. The zeta potentials were around 0 mV and +38 mV for PEG/PVP (0.3 g PVP, 260 °C, 1 h) and PEG/PEI (0.5 g PEI, 260 °C, 0.5 h)-coated SPIONs, respectively (Fig. 4), demonstrating that the zeta potentials of SPIONs have been modulated by PVP or PEI. The nearly zero zeta potential of PEG/PVP-coated SPIONs may come from the equalized combination effect of the positive zeta potential of PVP-coated SPIONs [19] and the negative zeta potential of PEG-coated SPIONs [11]. The positive zeta potentials PEG/PEI-coated SPIONs are due to the ionized  $-\text{NH}_3^+$  groups stemming from PEI in water [8,21,22].

Fig. 5 shows the hydrodynamic sizes of the PEG/PVP (0.3 g PVP, 260 °C, 1 h) or PEG/PEI (0.5 g PEI, 260 °C, 0.5 h)-coated SPIONs in deionized water as-prepared, in deionized water for 40 days, and in 0.05 M PBS for 7 days. The hydrodynamic sizes almost did not change, demonstrating the high dispersion stabilities of the SPIONs. High stability of PVP-coated SPIONs in water and in PBS has been reported [23]. Our data showed that the average

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