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Preparation of polylysine-modified superparamagnetic iron oxide nanoparticles

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ABSTRACT

Polylysine (PLL) coated iron oxide nanoparticles (SPIONs) have potential in biomedical application. In the present work PEG coated SPIONs (PEG-SPIONs) with the particle size of 9.4 ± 1.4 nm were synthesized by thermal decomposition of $Fe(acac)_3$ in PEG, and then coated with PLL (PLL/PEG-SPIONs). The PEG-SPIONs and PLL/PEG-SPIONs were superparamagnetic with the saturation magnetization of 53 and 44 emu/g, respectively. The hydrodynamic diameter of PEG-SPIONs in deionized water was 18.8 nm, which increased to 21.3 – 28.2 nm after mixing with different amount of PLL. The zeta potentials of PLL/PEG-SPIONs were −8.9 – −3.4 mV which were changing with time. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses indicated that PLL was attached to the PEG-SPIONs.

1. Introduction

PEG-SPIONs are coated with organic polymers, biomolecules and inorganic materials via the routes such as surface polymerization, surface chemical ligation and adsorption deposition [1]. They are widely used in *in vitro* [2,3] and *in vivo* [4,5] biomedical applications. Lysine is one of the eight essential amino acids [6]. With good biodegradability and biocompatibility, PLL are proved to be excellent polymeric gene carriers [7]. Grafted with copolymers of PLL and PEG, polymer-DNA condensates had been shown to combine low cytotoxicity, stealth properties and high transfection efficiency in COS-7 cells (African green monkey kidney cells), suggesting that they were a promising tool for effective transport and delivery of therapeutic DNA [8]. PLL that was commonly used to enhance cell adhesion to the surface of a culture dish in *in vitro* cell cultivation was investigated as a prospective vehicle for iron oxide nanoparticle transport into cells [9]. PLL had been used to facilitate dendritic cell uptake of SPIONs [10]. PLL modified SPIONs were utilized to label the cancer stem cells derived from U251 glioblastoma multiforme and were further used to treat targeted glioblastoma cells [11]. Therefore, PLL/PEG-SPIONs provide enormous potential for biologists. In the present work, the PEG-SPIONs were synthesized by thermal decomposition of the $Fe(acac)_3$ in PEG, then the PEG-SPIONs were coated with PLL and their properties were investigated for further application.

2. Experimental

2.1. Materials

Iron(III) acetylacetonate ($Fe(acac)_3$, 98%) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Poly(ethylene glycol) (PEG, M_w=1000, 95%), toluene (99%), acetone (99%) were purchased from Xilong Chemistry Co., Ltd. (Shantou, China). Polylysine (PLL, M_w=5000) was provided by Guilin Peptide Technology Co., Ltd. (Guilin, China). All the reagents were used without further purification.

2.2. Preparation of PLL modified PEG-SPIONs

In a typical process, the PEG (15 g) was dissolved in a three-neck round bottom flask with vigorous magnetically stirring at 80 °C for 10 min, then $Fe(acac)_3$ (0.7 g) was added to the flask with stirring for another 10 min. This red solution was heated to 260 °C under a flow of argon and kept at this temperature for 1 h. The reactants were cooled to 60 °C by removing the heat source and then mixed with 60 mL of toluene, the particles were separated by the adsorption of a magnet and washed twice with acetone to remove the excess organics, then dried in air at room temperature and the powder was dispersed in deionized water. 1 mL of PLL water solutions with concentrations of 0.11, 0.22, 0.45, 0.9 and 1.8 mg/ml was mixed with 1 mL of PEG-SPIONs (2 mg/ml) aqueous solution, the solutions were agitated with a shaker for 2 h at 4 °C,

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then solid samples were separated by the midi Magnetic Activated Cell Sorting (midi MACS).

2.3. Materials characterization

The size and morphology of the PEG-SPIONs were determined by transmission electron microscopy (TEM, JEOL 2010). The aqueous dispersion of the nanoparticles was drop-cast onto a copper grid coated with a carbon film, and the grid was air-dried at room temperature before being loaded into the microscope. The phase compositions of the dried samples were analyzed by X-ray powder diffraction (XRD, Xpert Pro PANalytical, Netherlands) using Cu kα radiation (λ= 0.154056 nm). The hydrodynamic size and surface charges of the PEG-SPIONs and PLL/PEG-SPIONs dispersed in water were evaluated using a nanoparticle and zeta potential analyzer (Nano ZS90, Malvern). Magnetic properties of the dried samples were measured at 300 K by the superconducting quantum interference device (SQUID, Quantum Design, MPMS XL). Thermogravimetric analyses (TGA) of the dried samples were performed under nitrogen at a heating rate of 10 °C/min from room temperature up to 800 °C using a TGA Q500 (TA Instruments) analyzer. The surface coating of the nanoparticles was recognized by Fourier transform infrared spectroscopy (FTIR, Varian 3100), the dried samples were milled with KBr and pressed into a pellet for analysis. The X-ray photoelectron spectroscopy (XPS) of the dried sample was performed in vacuum on Thermo ESCALAB 250.

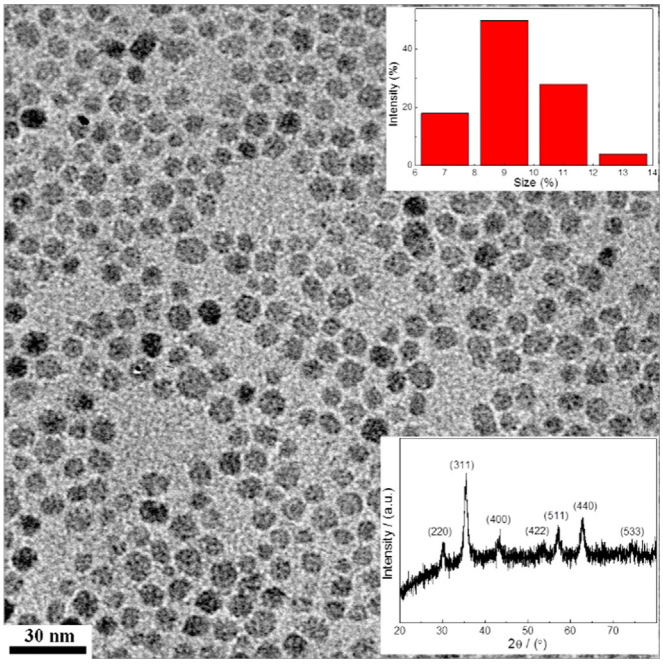

Fig. 1. The TEM image and XRD pattern of PEG-SPIONs.

3. Results and discussion

Fig. 1 shows the TEM image with size distribution of PEG-SPIONs synthesized by thermal decomposition of $Fe(acac)_3$ in PEG at 260 °C, the average size of SPIONs are 9.4 ± 1.4 nm, which was measured and calculated using the software "Image J". The XRD pattern of the sample inserted in Fig. 1 is matching well with the standard XRD pattern for magnetite (JCPDS File no. 01-088-0315). The peaks with 2θ 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 magnetite, respectively. The spinel crystal structure of magnetite is very similar to that of maghemite and the iron oxide nanoparticles are often a mixture of magnetite and maghemite [12,13].

The hydrodynamic diameter and zeta potential of PEG-SPIONs were 18.8 nm and −2.1 mV, respectively. With increasing concentration of PLL from 0.11 to 1.8 mg/ml, the zeta potential of PLL/PEG-SPIONs changed from 11.5 to −6.1 mV (Table 1), this might be caused by the formation of hydrogen bonds between different groups. When the concentration of PLL was 0.11 mg/ml, the hydrogen bonds might be formed by hydroxyl groups of PEG-SPIONs and carboxyl groups of PLL, and the zeta potential of PLL/PEG-SPIONs was positive because the amine groups of PLL protrude outside. On the contrary, the hydrogen bonds might be formed by hydroxyl groups of PEG-SPIONs and amine groups of PLL when the concentration of PLL increased, and the zeta potential of PLL/PEG-SPIONs become negative because the carboxyl groups of PLL protrude outside. The hydroxyl groups connect with the amine groups more stably than with the carboxyl groups,

Table 1
The hydrodynamic diameters and zeta potentials of PEG-SPIONs coated with PLL with different concentrations at pH=7.4.

PLL concentration	Hydrodynamic diameter of PLL coated PEG-SPIONs (nm)	Zeta potential of PLL coated PEG-SPIONs (mV)	Zeta potential of PLL coated PEG-SPIONs after six days (mV)
0	18.8	−2.1	−2.0
0.11	21.3	11.5	−8.4
0.22	23.8	4.5	−8.9
0.45	25.5	−1.7	−7.1
0.9	26.1	−4.3	−3.8
1.8	28.2	−6.1	−3.4

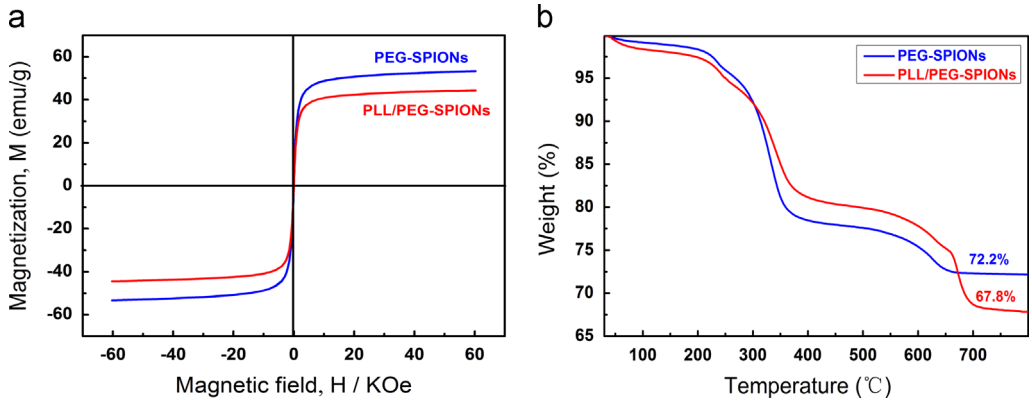

Fig. 2. Hysteresis loops of PEG-SPIONs and PLL/PEG-SPIONs at 300 K (a) and their TGA curves from 0 to 800 °C (b).