



Controllable 5-sulfosalicylic acid assisted solvothermal synthesis of monodispersed superparamagnetic Fe₃O₄ nanoclusters with tunable size



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ABSTRACT

Monodispersed Fe₃O₄ nanoclusters were synthesized in a one-pot solvothermal route with 5-sulfosalicylic acid (SSA) as the functional ligand in a mixed-solvent system of diethylene glycol/ethylene glycol (DEG/EG). Nucleation and aggregation growth model was responsible for the formation of secondary structure of the clusters. In the process, the size of the clusters can be effectively controlled by varying the amounts of SSA and the volume ratio of DEG/EG. The nanoclusters exhibited superparamagnetic properties with high saturation magnetization value of about 68.7 emu g⁻¹ at room temperature. The water-soluble small-molecule SSA grafted on the surface of Fe₃O₄ nanocrystals rendered the superparamagnetic clusters dispersible in water, which is crucial for potential applications in biomedical fields.

1. Introduction

High-quality nanocrystals with well-defined shapes and controllable sizes play an important role in nanotechnology because the unique physicochemical properties of nanomaterials are strongly associated with their shape and size distribution [1,2]. Among these nanomaterials, nanostructured magnetic materials exhibit unique properties for diverse applications in ferrofluids, high-density magnetic recording media, catalysts, medical diagnostics, and electronic devices because of their intrinsic magnetic features combined with their nanosize, surface effects, and electrochemical properties [3–6]. According to the specific requirements from *in vitro* and *in vivo* applications, the current research has focused on the synthesis of monodispersed magnetic nanospheres with high magnetization to achieve fast manipulation and the sensitive magnetic signal [7,8]. In particular, superparamagnetic colloidal nanocrystal clusters comprising multiple single-domain magnetic nanocrystals assembled into submicrometer scale particles are favored because of their highly magnetic field responsiveness, easy separation, and good biocompatibility and stability under physiological conditions.

In the past few years, numerous scientists have extensively studied the preparation of superparamagnetic nanoparticles. Yin and co-workers reported a high-temperature hydrolysis method to grow poly(acrylic acid) (PAA)-modified monodispersed Fe₃O₄ nanoclusters by injecting hot NaOH/DEG stock solution into a high-temperature

mixture of DEG, FeCl₃, and PAA. These as-prepared Fe₃O₄ particles can be assembled to photonic crystals in aqueous solution upon an externally applied magnetic field [9,10]. Leung et al. used a bi-solvent system to synthesize superparamagnetic Fe₃O₄ particles using Na acrylate, PAA, and PVP as the stabilizers [11]. More recently, Su et al. reported a one-step synthesis of highly negatively charged superparamagnetic Fe₃O₄ nanoclusters in a modified solvothermal reaction using poly(4-styrenesulfonic acid-co-maleic acid) sodium as stabilizer [12]. However, all stabilizers mentioned above formed high polymers bonded on the surface of Fe₃O₄ particles.

In this paper, we demonstrate a one-pot solvothermal method for controlled synthesis of monodispersed superparamagnetic Fe₃O₄ nanoclusters using 5-sulfosalicylic acid (SSA) as the functional ligand with a mixed-solvent system of DEG/EG. The Fe₃O₄ nanoclusters are hydrophilic for the water-soluble small-molecule SSA grafted on the surface of Fe₃O₄ nanocrystals. Moreover, the sizes of Fe₃O₄ nanoclusters can be effectively adjusted by varying the amounts of SSA and the volume ratio of DEG/EG in our experiment. Finally, the synthesized Fe₃O₄ nanoclusters exhibited superparamagnetic properties with high saturation magnetization. These properties render them ideal candidates for practical applications, such as magnetic separation, magnetic resonance imaging (MRI), and drug delivery.

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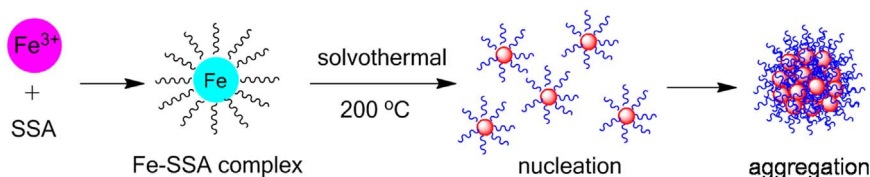


Fig. 1. Schematic illustration showing the formation of Fe₃O₄ nanoclusters.

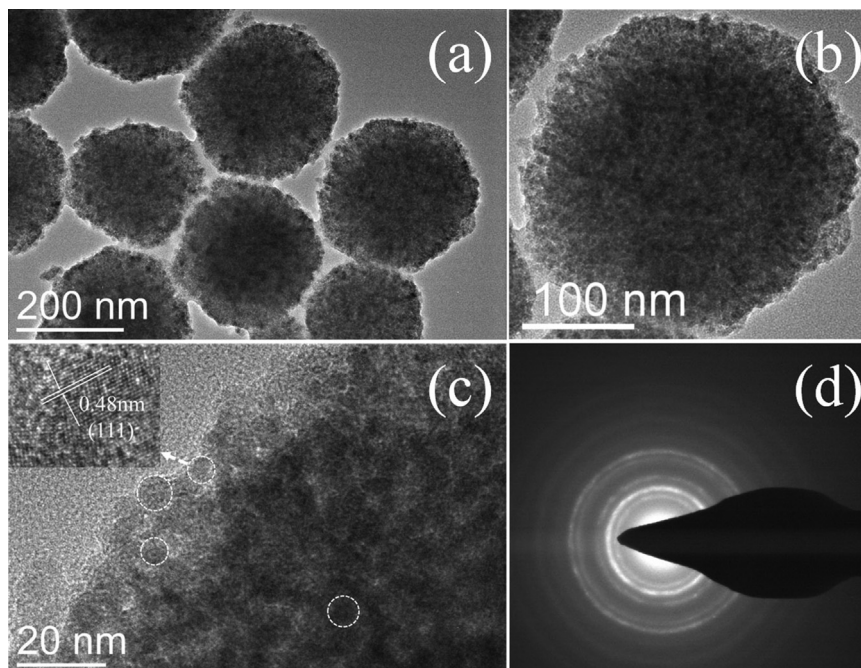


Fig. 2. (a) TEM images of 269 nm Fe₃O₄ particles, (b) TEM image at higher magnification, (c) HRTEM image, and (d) SAED pattern on the edge of the cluster in (c).

2. Experimental

2.1. Materials

Iron (III) chloride anhydrous (FeCl₃) was purchased from Xilong Chemical Co., Ltd., China. Sodium acetate anhydrous (CH₃COONa, NaOAc) was obtained from Bodi Chemical Co., Ltd., China. 5-sulfosalicylic acid dihydrate (C₇H₆O₆S·2H₂O, SSA) was purchased from Dasen Chemical Product Sales Co., Ltd., China. Ethylene glycol (EG) was purchased from Fuyu Fine Chemical Co., China. Diethylene glycol (DEG) was provided by Guangfu Fine Chemical Research Institute, China. All chemicals were of analytical grade and used without further purification.

2.2. Synthesis of Fe₃O₄ nanoclusters with tunable sizes

In a typical synthetic procedure, FeCl₃ (10 mmol) and SSA (1 g) were dissolved in a mixed solvent of DEG (40 mL) and EG (40 mL) to form a clear solution under mechanical stirring at 120 °C. After 0.5 h, NaAc (50 mmol) was added, and vigorous stirring was continued for additional 1 h. The obtained homogeneous solution was transferred to a Teflon-lined stainless steel autoclave (100 mL volume) and then sealed and heated at 200 °C. After a 10 h reaction period, the autoclave was cooled to room temperature. Dark precipitates were isolated by a magnet, washed several times with deionized water, and then dried in vacuum for 12 h.

2.3. Characterization

X-ray powder diffraction patterns (XRD) of the products were obtained on a Japan Rigaku D/Max 2400 automatic X-ray power

diffractometer equipped with graphite monochromatized Cu-Kα radiation (λ=1.54178 Å). Scanning electron microscopy (SEM) images were taken with a FEI Nova NanoSEM 450 apparatus. High-resolution transmission electron microscopy (HRTEM) was conducted on a FEI Tecnai G2 F30 microscope equipped with an energy-dispersive X-ray spectrometer (EDS) working at 300 kV. X-ray photoelectron spectra (XPS) were measured on a ESCALAB250 multifunction surface analysis system using Al-Kα radiation. The ⁵⁷Fe Mössbauer spectrum was measured at room temperature using a Wissel MSS-10 Mössbauer spectrometer with a ⁵⁷Co/Rh source in the transmission mode. The velocity scale was calibrated using an α-Fe metal foil at room temperature. FTIR spectroscopic analyses were conducted in transmission mode using a Thermo Scientific Nicolet 6700 FTIR spectrometer with a KBr wafer. Thermogravimetric analyses (TGA) were conducted with a TA Instruments Universal Analysis 2000. The magnetic properties (M-H and ZFC-FC curves) were measured on a Quantum Design MPMS-XL-7 system.

3. Results and discussion

3.1. Mechanism and structure analysis

Monodispersed Fe₃O₄ nanoclusters were prepared through a modified solvothermal method at 200 °C. FeCl₃ was reduced with SSA as coordinative ligand in the presence of sodium acetate as alkali source. A mixture of EG and DEG was selected as both solvent and reductant. The growth of Fe₃O₄ nanoclusters follows the well-documented two-stage growth model, in which primary nanocrystals nucleate first in a supersaturated solution and then aggregate into larger secondary particles [13]. The mechanism underlying the synthesis of polycrystalline Fe₃O₄ nanoclusters is illustrated in Fig. 1. Fe³⁺ cations first

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