Electronic Supplementary Information for

Ultrafast microwave-assisted synthesis of MCNCs with high saturation magnetization and sustained aqueous stability

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Experimental

Chemicals

Iron(III) chloride hexahydrate ($FeCl_3.6H_2O$), ammonia acetate (NH_4OAc), ethylene glycol (EG), Trisodium citrate (Na_3Cit), anhydrous ethanol were purchased from Shanghai Chemical Reagents Company, China. Sodium poly(γ-glutamic acid) (PGA) with Mw of 1000 kDa was purchased from Dingshunxin Biotechnology Company, China. Poly (acrylate acid) (PAA) with Mw of 1800 Da was purchased from Sigma Aldrich, USA. All these reagents were received without further purification. Deionized water was used throughout in the experiments.

Microwave synthesis of MCNCs

All syntheses of MCNCs were carried out in a commercial-available single-mode microwave synthesizer CEM Discovery (CEM Inc. NC, USA) continuous power at 2.45 GHz. The microwave synthesizer is attached with an automation system to provide automated reaction handling capabilities. The 35ml quartz molded vessel for microwave reaction was sealed by a crimp cap.

In a typical procedure, 0.54g of $FeCl_3.6H_2O$ and 0.77g of NH_4OAc were dispersed into 20 ml EG to form a homogeneous yellow solution under 10 min ultrasonication. Then the dispersion was decanted into a specialized microwave reaction vessel, sealed by a crimp cap, and transferred into the microwave synthesizer. The maximum power setting was set as 180 watts and the pressure cut-off limit was 200 psi. The desired reaction temperature and time were programmed by the intelligent software and could be facilely altered. The temperature was quickly ramped to 120^{o}C, 130^{o}C, 140^{o}C, 150^{o}C, 160^{o}C, and 200^{o}C, respectively, and maintained for 10min. Besides, at a fixed temperature of 150^{o}C, the reaction time was changed to be 5min, 20min, and 60min, respectively.

Once the reaction was completed, the microwave power was turned off automatically to terminate the reaction and the air flow was increased to rapidly cool the solution, quenching the reaction which minimizes colloidal size distributions resulting from Ostwald ripening. Black precipitates were formed in the bottom of the vessels and showed strong response to the applied magnetic field (Fig. S1). The product was collected by using a magnet and rinsed with absolute ethanol and deionized water, stored in a sealed bottle for further use. For preparation of modified Fe_3O_4 CNCs, 0.3g of various stabilizers, such as Na_3Cit, PAA, or PGA was added to the above precursors, forming homogeneous dispersion under ultra-sonication. Then the dispersion was transferred to the microwave system to undergo microwave irradiation as described above.

Solvothermal synthesis of MCNCs

The Fe_3O_4 CNCs were prepared through a modified solvothermal reaction as reported. Typically, 1.350 g of $FeCl_3·6H_2O$, 1.927g of NH_4OAc were dissolved in 70 mL EG to form a homogeneous dispersion under ultrasonication. Then the yellow mixture was transferred into a 100ml three-necked flask and stirred vigorously at 160^{o}C for 1h. The homogeneous yellow solution changed gradually from light yellow to dark brownish as the reaction proceeded. Then the dispersion was instantly transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity) and held in oven at 200 ^{o}C for 15 h. Then the obtained black precipitates in solution were isolated by magnet and washed several times with ethanol and deionized water for removing the residues from the products. The purified products were kept in ethanol for protection and further use.

Characterization

High-resolution Transmission electron microscopy (HRTEM) images were taken on a JEM-2010 (JEOL, Japan) transmission electron microscope at an accelerating votage of 200 kV. The samples for HRTEM measurements were obtained by dropping a little amount of the sample on copper grids coated with carbon. Scanning electron microscopy (SEM) measurement were performed using a TS-5136MM (TESCAN, Czech) scanning electron microscope at an accelerating voltage of 20 kV. Samples dispersed at an appropriate concentration were cast onto a thin glass sheet at room temperature and sputter-coated with gold nanoparticles. Powder X-ray diffraction (XRD) patterns were collected on a D8 advance (Bruker, Germany) diffraction meter with Cu KR radiation at 0.154 nm, operating at 40 kV and 40 mA. XPS data was obtained by using an RBD upgraded PHI-5000C (Perkin-Elmer, USA) ESCA system with Mg Kα radiation ($h\nu$ = 1253.6 eV) at 250 W and 14.0 kV with a detection angle at 54^o. Magnetic characterization was carried out with a vibrating sample magnetometer on a Model 6000 physical property measurement system (Quantum Design, USA) at 300 K. The size and zeta potential of the particles was determined by DLS-Zeta Potential Analyzer (Malvern Zetasizer Nano). Transmittance of MCNCs dispersion in PBS (pH 7.4, 50mM) at 670 nm was measured on a 721 visible spectrophotometer and monitored as a function of time.

Results

Fig. S1 showed the solution state of the sample before and after microwave irradiation, as well as applied with a magnetic field. The precursors were yellow homogeneous dispersion of $FeCl_3$ and NH_4OAc mixture in EG, as shown in Fig. S1. Upon microwave irradiation of 10 min at 150^oC, black precipitates formed at the bottom of the vessel, leaving the supernatant brownish and transparent, which resembled the phenomenon occurring after traditional solvothermal process. Under an applied magnetic field, the precipitates exhibited strong response and moved close to the magnet rapidly, indicating the high saturation magnetization of the obtained products.

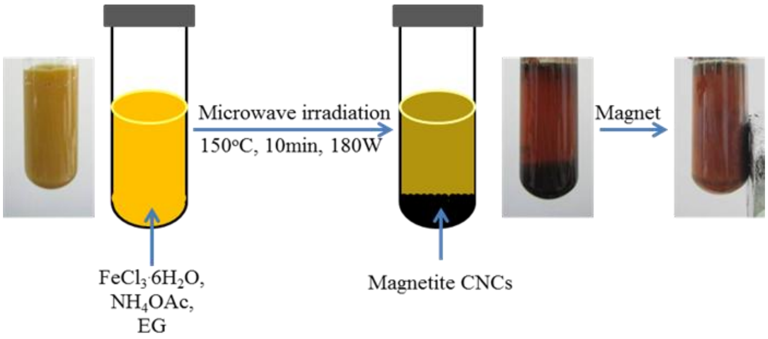

Fig. S1 Schematic diagram to illustrate the microwave-assisted preparation of MCNCs.

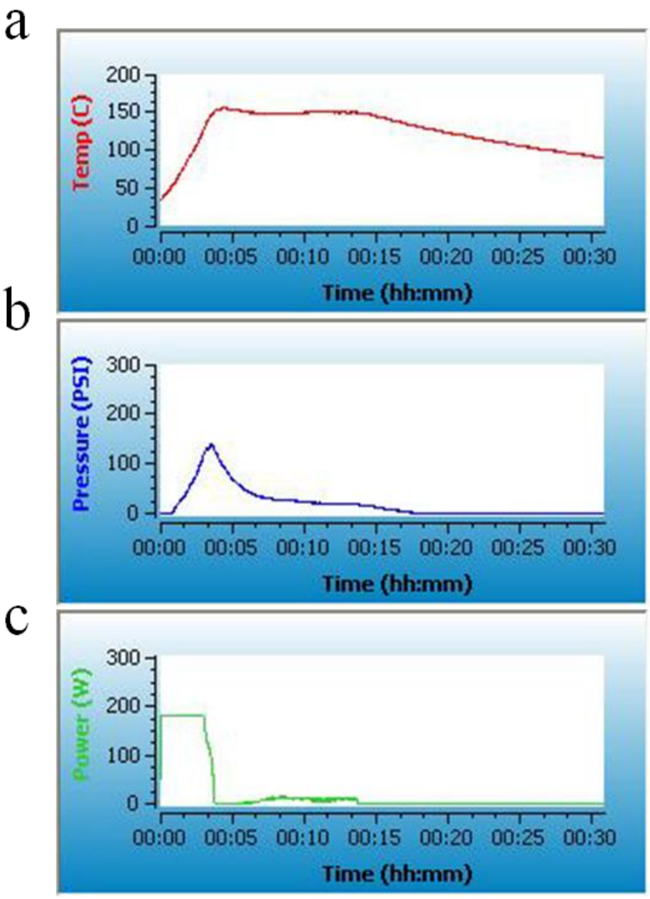

Fig. S2 Typical profile of (a) temperature, (b) pressure, (c) power for the preparation of MCNCs under microwave irradiation.

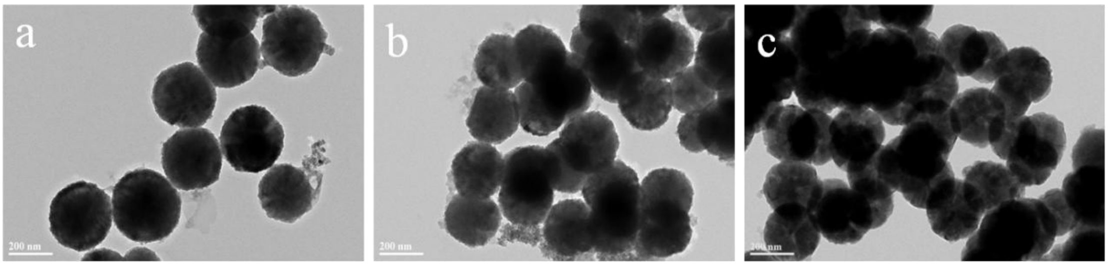

Fig. S3 TEM images of MCNCs synthesized for (a) 5min, (b) 20min, (c) 60min at 150°C. All scale bars are 200nm.

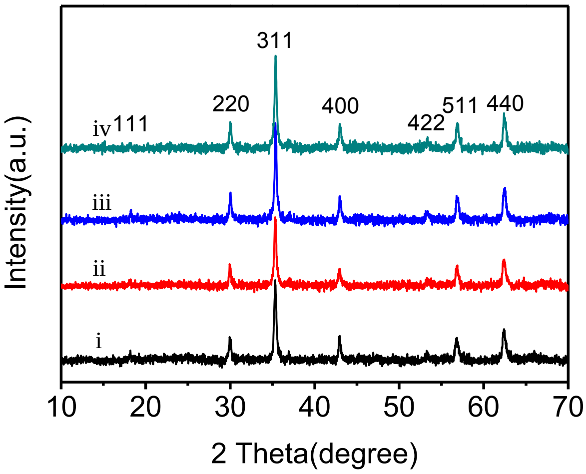

Fig. S4 Power XRD patterns of MCNCs synthesized for (i) 5min, (ii) 10min, (iii) 20min, and (iv) 60min at 150°C.

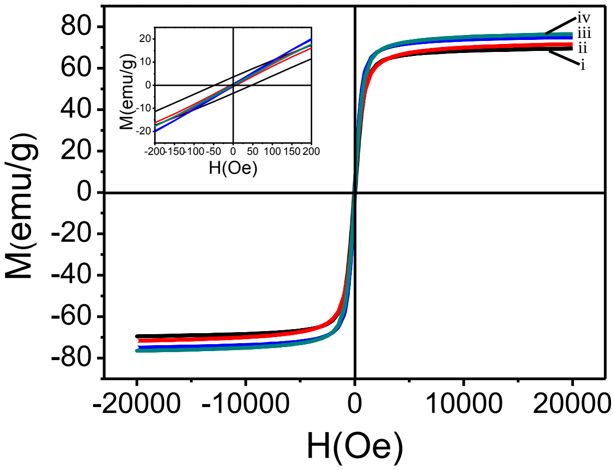

Fig. S5 Magnetization curves of MCNCs synthesized for (i) 5min, (ii) 10min, (iii) 20min, and (iv) 60min at 150°C

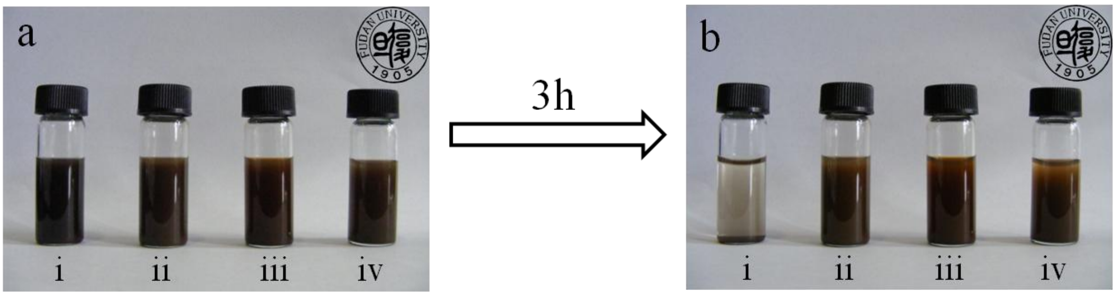

Fig. S6 Photographs of the (i) Fe_3O_4 CNCs and Fe_3O_4 CNCs stabilized by (ii) citrate acid, (iii) poly(acrylate acid), and (iv) poly(γ-glutamic acid) dispersed in the phosphate buffered saline(PBS, pH=7.4, 0.05M) (a) before and (b) after 3 hrs of setting.

Table S1. Size and PDI results of CA, PAA, and PGA stabilized MCNCs after setting.

Stabilizer	0 h		3 h	
	Size(nm)	PDI	Size(nm)	PDI
CA	321.9	0.254	383.3	0.314
PAA	354.8	0.297	374.1	0.266
PGA	314.7	0.218	398.8	0.335