

Supporting Information

Magnetic Response Photonic Crystals Based on Nucleating Agents of Binuclear Complexes

*Mengdong Tu, Mengying Xu, Xi Wei, Depeng Gong, Jun Chen, Chaocan Zhang**

School of Materials Science and Engineering, Wuhan University of Technology, Wuhan,
430070, China

E-mail: polymers@whut.edu.cn

Experiments Section

Materials. Ethylene glycol (EG, $\geq 99.5\%$), Ethanol ($\geq 99.7\%$), anhydrous ferric chloride (FeCl_3 , $\geq 97.0\%$; FeCl_2 , $\leq 1.0\%$), anhydrous sodium acetate (NaAc, $\geq 99.0\%$), sodium hydroxide (NaOH, $\geq 96.0\%$), were purchased from Sinopharm Chemical Reagent Co.,Ltd. Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA, $M_w \approx 20000$, SS: MA=1:1), anhydrous ferric chloride (FeCl_2 $\geq 99.5\%$) were purchased from Shanghai Aladdin Biochemical Technology Co.,Ltd. Ethylene glycol was predried by enough molecular sieve (type 3A) while other chemicals were used as received.

Synthesis of Monodispersed Fe₃O₄ Nanoparticles. In a typical experiment, 0.65 g anhydrous FeCl₃ was dissolved in ethylene glycol (40 mL) under the magnetic stirring, then a certain volume of hydrogen peroxide, 1.0 g PSSMA, and 3.0 g anhydrous NaAc were added to form a mixed solution. The mixing process was conducted in a 50 °C water bath. Subsequently, a specific amount of FeCl₂ was added to the mixed solution under a nitrogen atmosphere. Afterward, 0.6 g of NaOH was added to form an even solution. The as-received solution was transferred to a Teflon-lined stainless-steel autoclave and heated at 190 °C for 9 h. After the reaction, when cooled to room temperature, the dark precipitates were isolated by a magnet and washed three times with a 30 mL mixture ($V_{\text{Ethanol}}: V_{\text{Distilled water}}=1:1$) and 30 mL Distilled water.

Configuration of the instrument. Transmission electron microscope(TEM) images were taken on JEOL JEM-2100F, Test conditions: accelerating voltage: 80kV~200 kV, maximum resolution: 0.1nm. X-ray diffraction(XRD) analysis was carried out on a D8 Advance X-ray diffractometer ($\lambda=1.5418 \text{ \AA}$) in the 2θ range of 10-80° using Cu-K α radiation. Operating voltage 40kV, operating scanning speed 5°/min. X-ray photoelectron spectrometry(XPS) analysis was performed using a Thermo ESCALAB 250Xi multifunctional imaging electron spectrometer manufactured by Thermo Fisher Scientific. The X-ray source was a monochromatic K α -rays of Al ($h\nu=1486.6 \text{ eV}$) with an operating voltage of 15 kV, a power of 150 W, and a beam spot of 500 μm . Fourier transform infrared spectrum(FTIR) was obtained using a Thermo Fisher Nicolet 6700 FTIR spectrometer in the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1} . Ultraviolet-Visible absorption spectrum(UV) was collected using a Macylab Instruments UV-1500PC spectrometer. The wavelength range is 200 nm to 800 nm. Magnetic properties were tested using a LakeShore 7404 Vibrating Sample Magnetometer(VSM) at room temperature with an applied magnetic field from -6k Oe to 6k Oe. Reflectance spectroscopy tests were performed using an American Ocean

Optics spectrometer USB2000+ with a wavelength range of 300-1000 nm and a resolution of 0.30 nm, and the spectrometer was calibrated with a standard white board before use. Particle size was analyzed using a Zetasizer Nano Series Dynamic Light Scattering (DLS) instrument from Malvern instruments Co.

Figure section

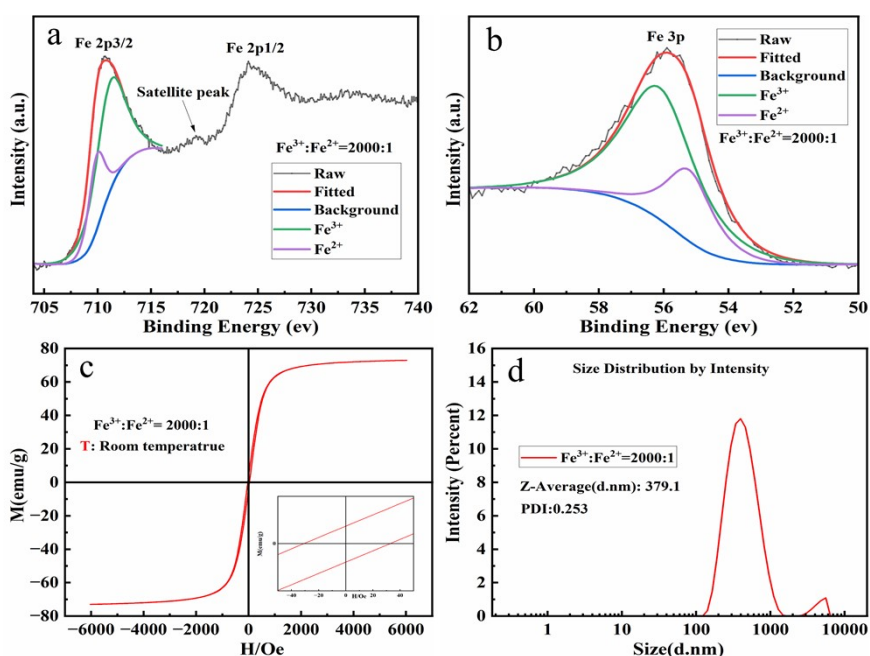


Fig. S1 XPS patterns of Sample 2 (Fe³⁺:Fe²⁺ = 2000:1). (a) Fe 2p, (b) Fe 3p. (c) Room temperature magnetization curve of Sample 2. (d) Particle size distribution curve of Sample 2. The XPS Fe 2p spectrum showed that Sample 2 exhibited a satellite peak of γ -Fe₂O₃, and The relative areas of the resulting deconvoluted peaks assigned to Fe³⁺ and Fe²⁺ were calculated to be nearly 2.8:1 in Fe 2p and 3p spectrum (Fig. S1a, S1b). The sample also contained a small amount of micron-sized agglomerates, showing some soft magnetic properties with coercivity and remanent magnetization value of 32.1 Oe and 3.6 emu/g (Fig. S1c, S1d).

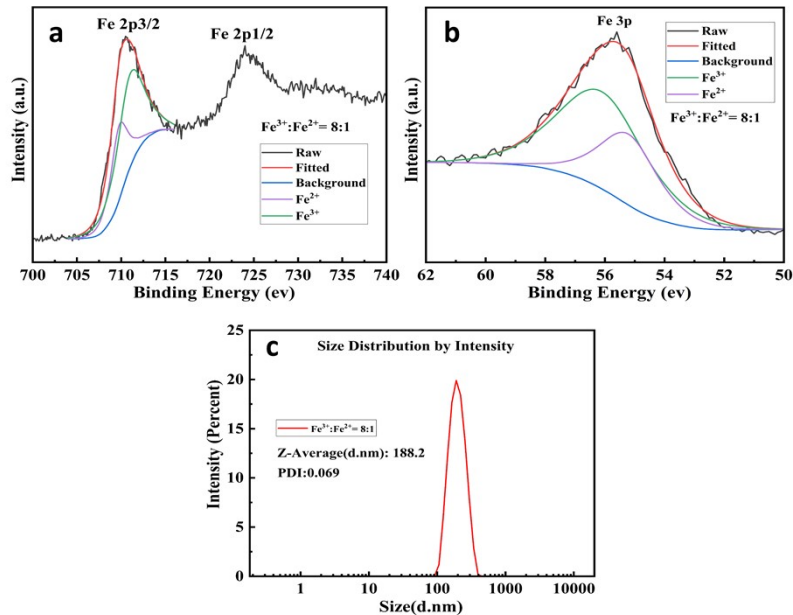


Fig. S2 XPS patterns of Sample 7 ($\text{Fe}^{3+}:\text{Fe}^{2+} = 8:1$). (a) Fe 2p, (b) Fe 3p. (c) Particle size distribution curve of sample 7. The XPS Fe 2p spectrum showed that Sample 7 did not present a satellite peak of $\gamma\text{-Fe}_2\text{O}_3$, and the ratio of peak area corresponding to Fe^{3+} to Fe^{2+} was calculated to be 2:1 in Fe 2p and 3p spectrum (Fig. S2a, S2b), and the sample demonstrated the superparamagnetic behavior (Fig. S2c).

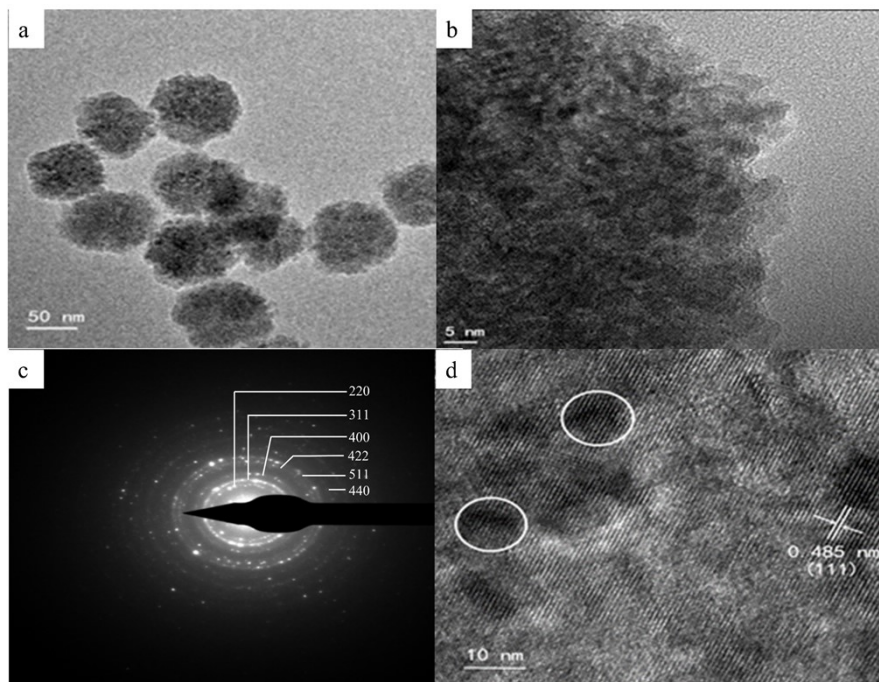


Fig. S3 (a) TEM image of the product nano Fe_3O_4 with $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of 2:1 in the precursor, (b) TEM image at higher magnification, (c) Selected-area electron diffraction (SAED) pattern, (d) HRTEM image. As can be seen in Figure Above, the product Fe_3O_4 was nearly spherical and uniform in size with an average particle size of 75 nm (Fig. S3a). A TEM image at higher magnification revealed that the nanoparticles were composed of nanocrystals with a smaller size (Fig. S3b). The SAED pattern showed their electron diffraction pattern as a series of concentric diffraction rings, indicating that the products were polycrystalline in structure (Fig. S3c). The HRTEM image exhibited that the lattice stripe spacing in d was 0.485 nm, which was consistent with the peak 111 crystal plane spacing (Fig. S3d).

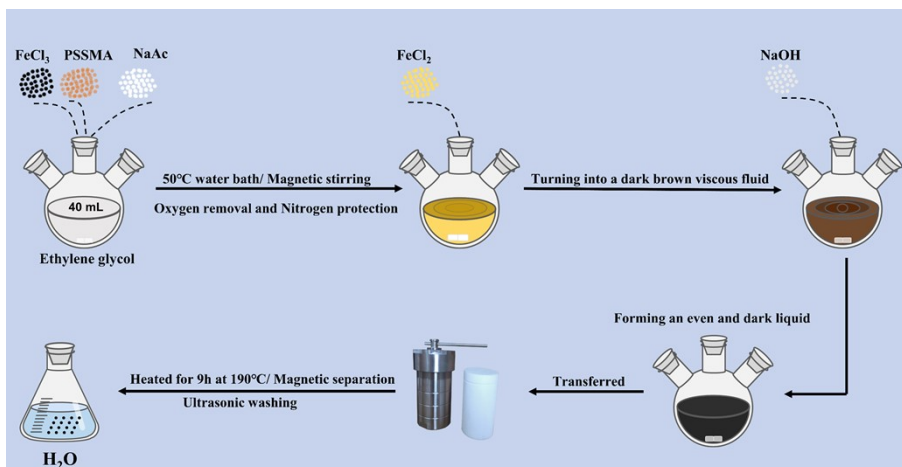


Fig. S4 Flowchart of the experimental preparation.

Videos section

Video S1: No Fe^{2+} in the precursor, and the product is not magnetochromic.

Video S2: Magnetochromic product, the precursor contains a certain amount of Fe^{2+} .