

Novel complex-coprecipitation route to form high quality triethanolamine-coated Fe₃O₄ nanocrystals: their high saturation magnetizations and excellent water treatment properties

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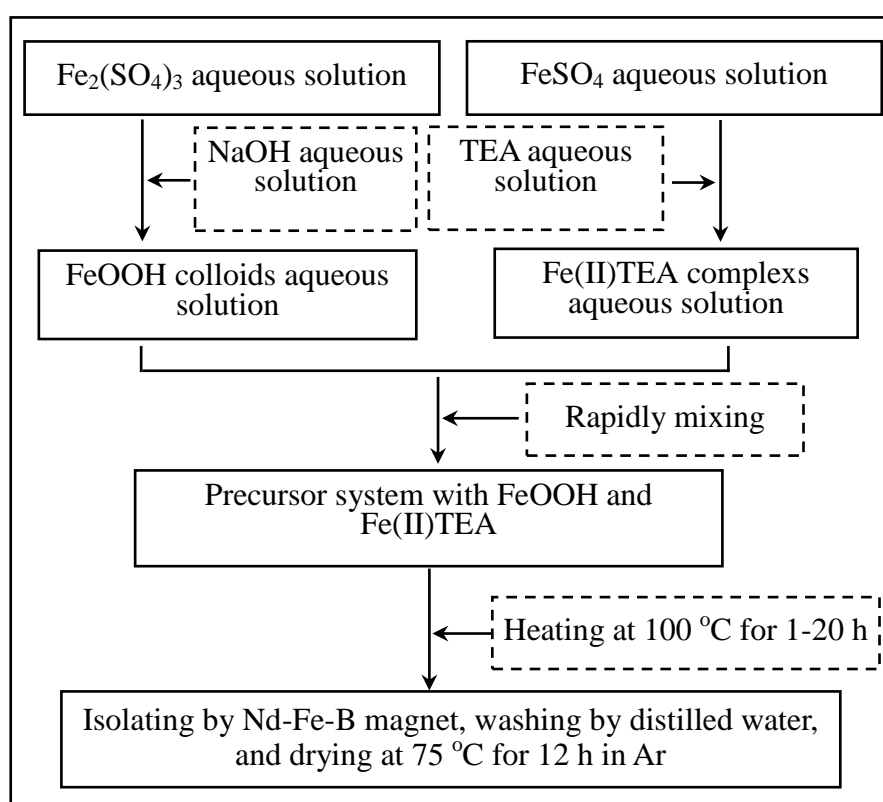
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Experimental

Synthesis

Chemicals: $\text{Fe}_2(\text{SO}_4)_3$ (99.9%), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99%), triethanolamine (TEA, 98%), NaOH (99.9%) and $\text{K}_2\text{Cr}_2\text{O}_7$ (99.5%) were purchased from Beijing Fine Chemical Company, and HCl was commercially available analytical grade. All chemicals were used as received without further purification.



Scheme S1 Experimental flowchart for the synthesis of the Fe_3O_4 NCs by a complex-coprecipitation route.

The overall synthetic procedure is presented in Scheme S1. In a typical synthesis, $\text{Fe}_2(\text{SO}_4)_3$ (0.3599 g, 0.9 mmol), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.3336 g, 1.2 mmol), TEA (0.8951 g,

6 mmol) and NaOH (1.44 g, 36 mmol) were each dissolved into 10 mL, 10 mL, 5 mL and 5 mL distilled water under magnetic stirring. Subsequently, NaOH and TEA solutions were added into the $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 solutions to form the FeOOH colloid and Fe(II)-TEA complex solutions with stirring for 5 min, respectively. The above solutions were rapidly mixed and transferred in a poly(tetrafluoroethylene) (PTFE) beaker (inner volume of 40 ml) covered by the plastic preservative film, followed by heating at 100 °C and holding for various times (1, 4, 7 and 20 h) in an digital oven. Then the solution was naturally cooled down to room temperature. The black powder was obtained and isolated by Nd-Fe-B magnet, and washed several times by distilled water. Finally the as-prepared products were dried at 75 °C for 12 h under Ar atmosphere. The samples prepared at different reaction times were denoted as M-reaction time, M1, M4, M7 and M20.

Characterization

The powder X-ray diffraction (XRD) pattern of the products was performed on a Rigaku D/MAX-2500 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM), high-resolution transmission electron microscopic (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained on a FEI TF30 microscope operated at 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a high performance AXIS 165 X-ray photoelectron spectrometer (UK, KRATOS). Fourier transform infrared spectra (FTIR) were measured on a Bruker EQUINOX55 FTIR spectrometer using

KBr pressed pellet technique.

The magnetic measurements were carried out on a superconducting quantum interference device (SQUID) magnetometer (LakeShore 7303) at 300 K and 2 K. For the water treatment experiments, $K_2Cr_2O_7$ was used as the source of Cr (VI). The concentration of Cr (VI) ions was 8 mg L^{-1} , and the pH value of the aqueous solution was adjusted to 3 using HCl. Then, 0.01 g of the absorbent sample was added to 8 mL of the above solution under stirring at room temperature (300 K). After a specified time, the solid absorbent and liquid were separated and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) (Thermal Electron, XSeries II) was used to measure the chromium concentration in the remaining solution.

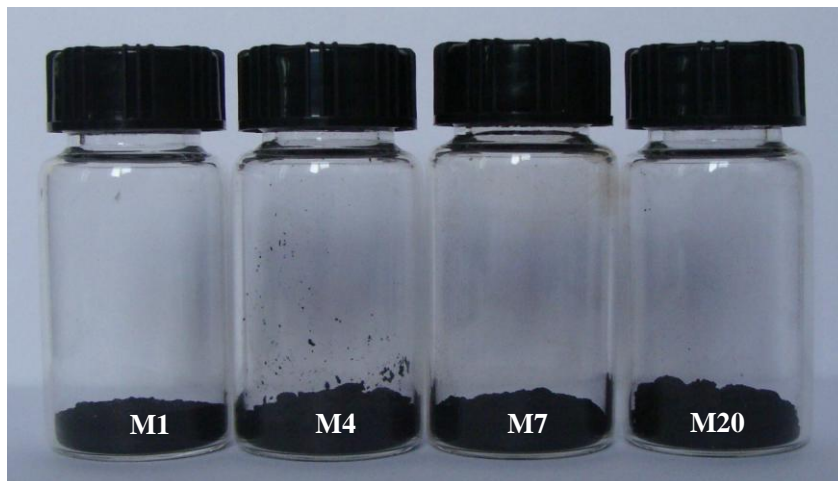


Fig. S1 Photographs of as-prepared Fe₃O₄ NCs with different reaction times (M1, M4, M7 and M20).

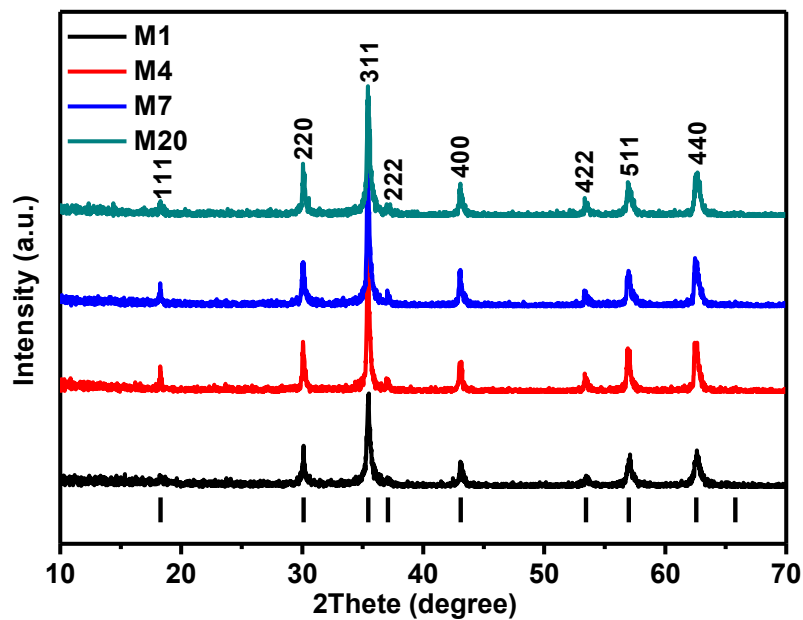


Fig. S2 XRD patterns of M1, M4, M7 and M20. The vertical bars at the bottom indicate the JCPDS data (JCPDS card no. 19-0629) for magnetite.

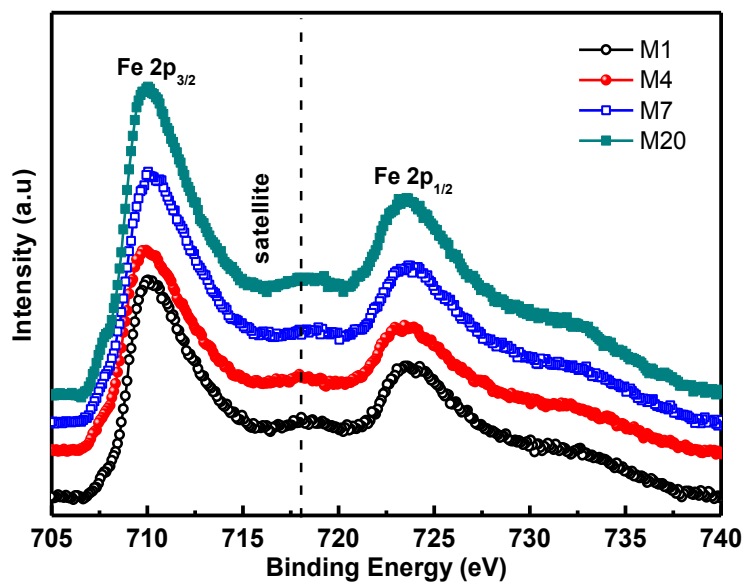


Fig. S3 XPS spectra of M1, M4, M7 and M20.

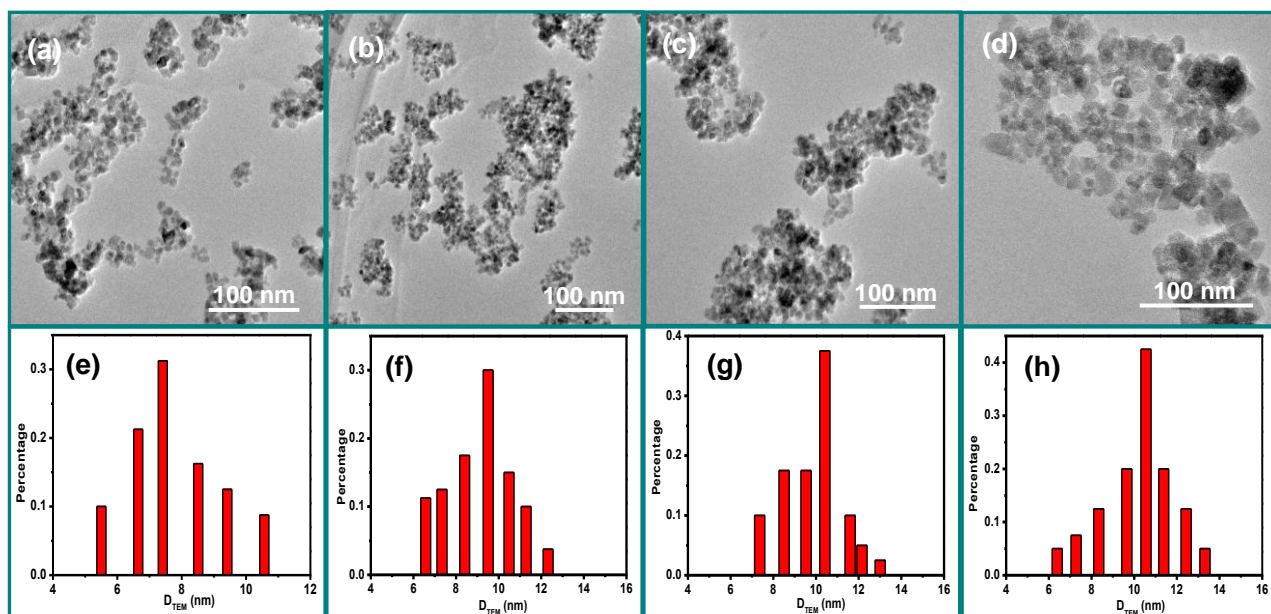


Fig. S4 TEM micrographs (a-d) of the Fe₃O₄ NCs and their corresponding particle size distribution histograms (e-h): (a) 7.8 ± 1.4 nm for M1, (b) 9.1 ± 1.6 nm for M4, (c) 9.9 ± 1.4 nm for M7, (d) 10.2 ± 1.7 nm for M20.

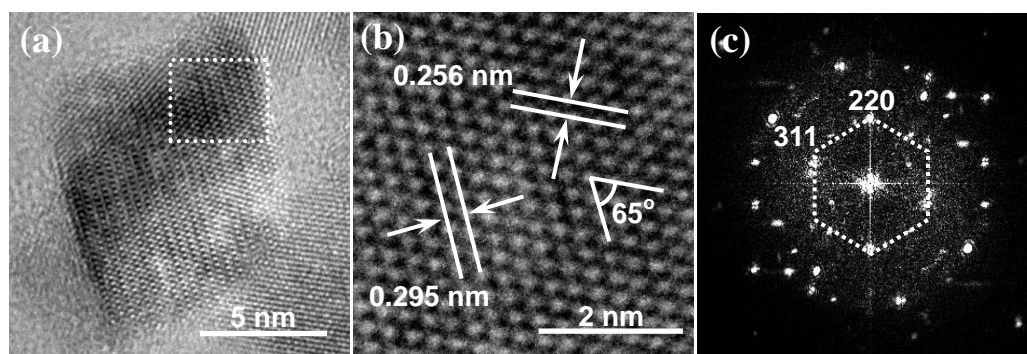


Fig. S5 (a) High-magnification TEM image of an individual Fe₃O₄ octahedron. (b) HRTEM image recorded from the rectangular part of nano-octahedron in (a) and (c) its corresponding FFT pattern.

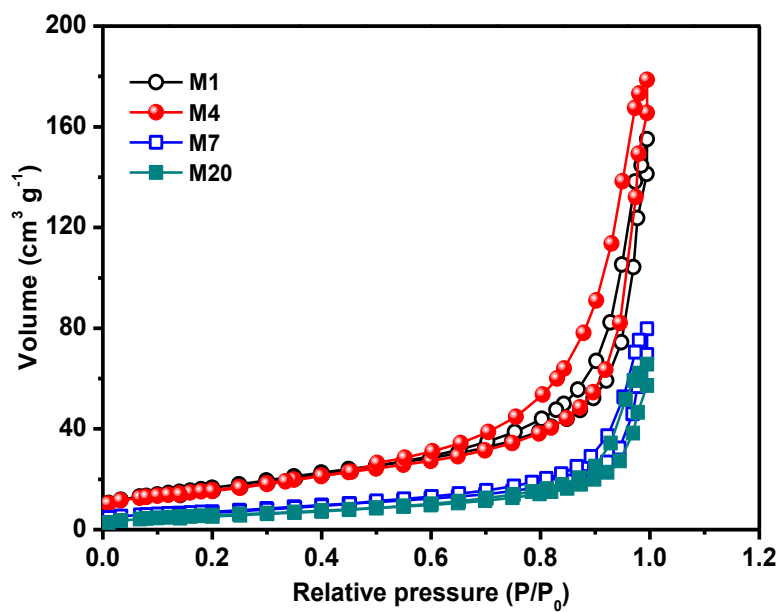


Fig. S6 Nitrogen adsorption and desorption isotherms of the Fe₃O₄ NCs: M1 (60.3 m² g⁻¹), M4 (56.1 m² g⁻¹), M7 (25.6 m² g⁻¹) and M20 (20.9 m² g⁻¹).

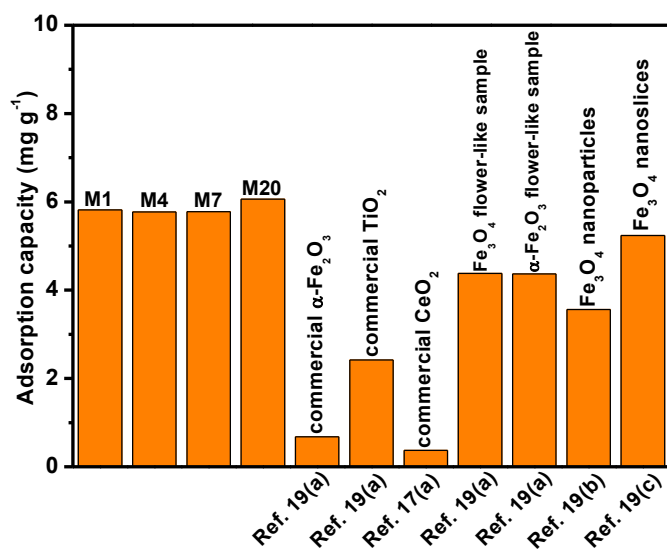


Fig. S7 Comparison of Cr (VI) adsorption capacity for the Fe₃O₄ NCs prepared in this work and some oxide adsorbents taken from the references.

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