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Ionic liquid-assisted solvothermal synthesis of oriented self-assembled Fe_3O_4 nanoparticles into monodisperse nanoflakes

(Supporting Information)

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Experimental Section

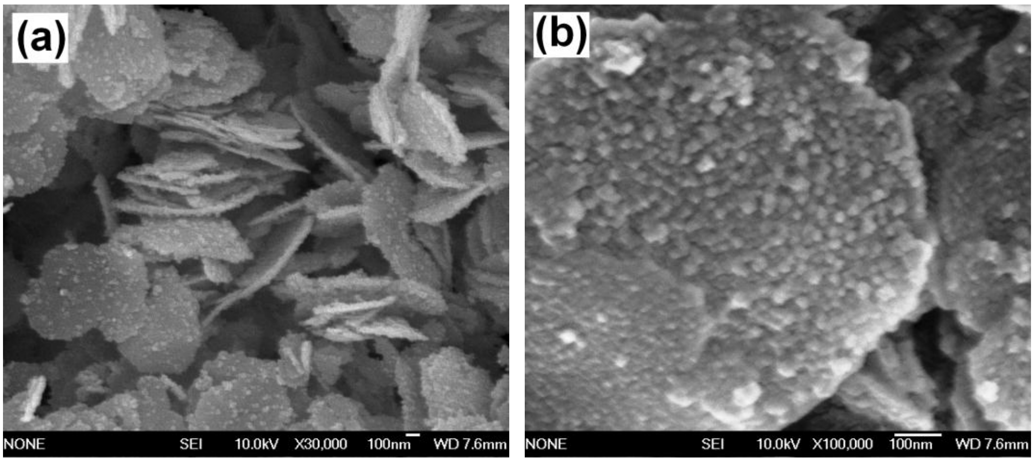
Chemicals: All chemicals were analytical-grade and used without further purification. [C_{16}mim]Cl was prepared according to the literature procedures.[1]

Synthesis of Fe_3O_4 nanoflakes: In a typical synthesis, $FeCl_2 \cdot 4H_2O$ (0.03 g) was dissolved into 7.5 mL glycerol/distilled water mixed-solvent (the volume ratio is 2:1) with continuous magnetic stirring until a clear solution was obtained. Then [C_{16}mim]Cl (0.4 g) and $N_2H_4 \cdot H_2O$ (2.5 ml) were added to the solution. In the end, the solution was transferred into a Teflon-lined stainless steel autoclave (20 mL). The autoclave was sealed and maintained at 180 °C for 24 h, and then it was cooled to room temperature naturally. The products were separated by centrifugation, washed by distilled water and anhydrous ethanol, and then dried in a vacuum at 50 °C for 4 h. Finally black powder was obtained.

Instruments and Characterizations: The phase of the product was examined by X-ray diffraction (XRD) on a Rigaku D/max 2500V/PC X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). The morphology and size of the products were characterized by a JSM 6700F scanning electron microscopy (SEM). The X-ray photoelectron spectra (XPS) were collected on a PHI-1600 ESCA X-ray photoelectron spectroscopy, using Mg Kα as the excitation source. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) micrographs were taken with a Hitachi H-7650 transmission electron microscopy, which were operated at an accelerating voltage of 100 and 200 kV, respectively. Energy-dispersive spectrum (EDS) was obtained with an EDS detector installed on the same HRTEM. The magnetic property of the sample was measured using a superconducting quantum interference device (SQUID, Quantum Design) magnetometer.

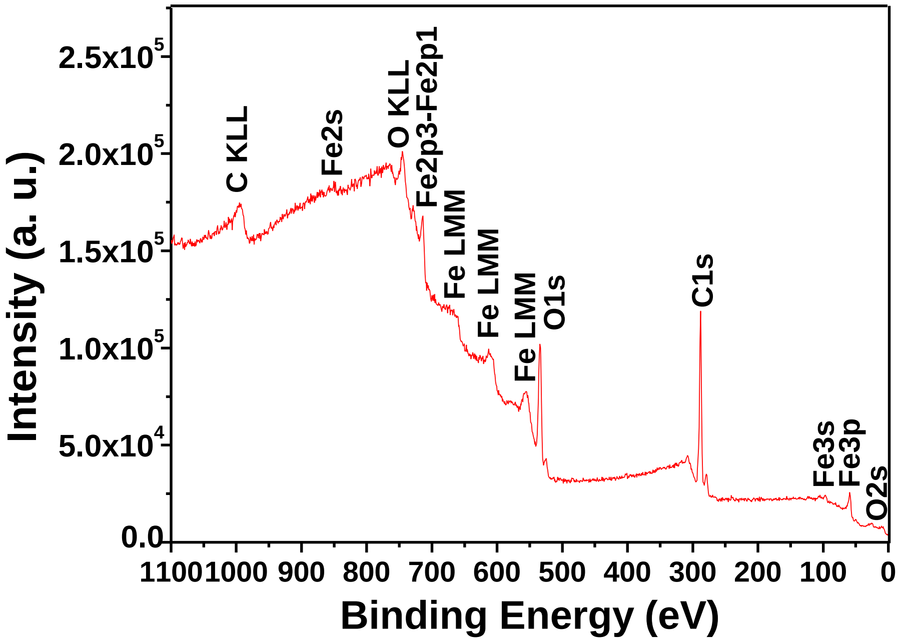
1 Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem*. **2000**, *72*, 2275-2287

Fig. S1 (a) SEM image of large-scale self-assembled Fe_3O_4 nanoflakes; (b) Magnified SEM image of a typical Fe_3O_4 nanoflake.



As shown in Fig. S1a, the products are almost entirely quasi-round nanoflakes with good monodispersity; moreover, these nanoflakes have an average diameter of 500 nm and a mean thickness of 15 nm. At a higher magnification (Fig. S1b), the apparently rough surfaces of the Fe_3O_4 nanoflakes can be observed.

Fig. S2 XPS survey spectrum of the obtained Fe_3O_4 nanoflakes.



The XPS survey spectrum shows typical peaks corresponding to the binding energies of C1s, O1s, and Fe2p. The binding energies are corrected for specimen charging by referencing the C 1s to 284.60 eV. No peaks of elements other than Fe, O, and C are observed in the survey spectrum, which confirms that the Fe_3O_4 have high purity and no $[C_{16}mim]Cl$ resides in the product.

Fig. S3 SEM and TEM images of Fe_3O_4 formed at different reaction times with the other reaction parameters uncharged: (a) 4 h; (b) 8 h; (c) and (d) 12 h.

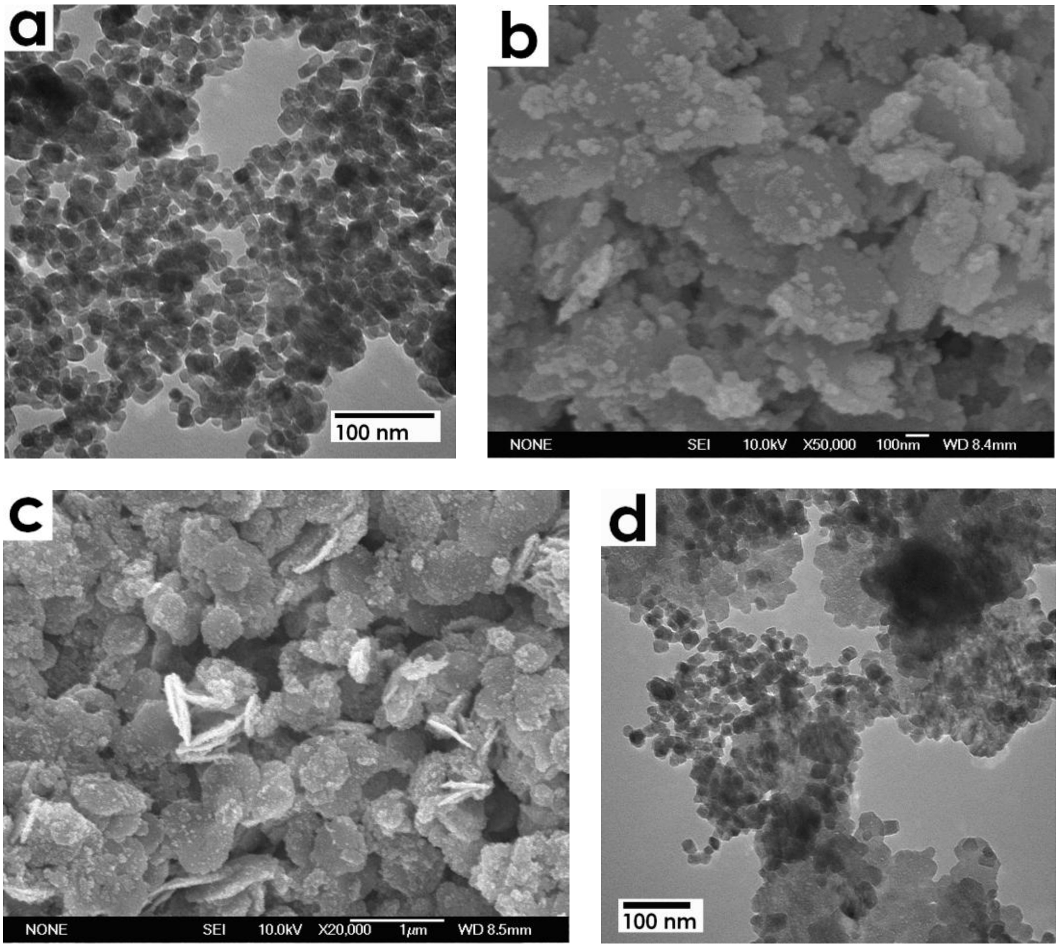


Fig. S4 XRD pattern of Fe_3O_4 nanoparticles formed at 4 h with the other reaction parameters uncharged.

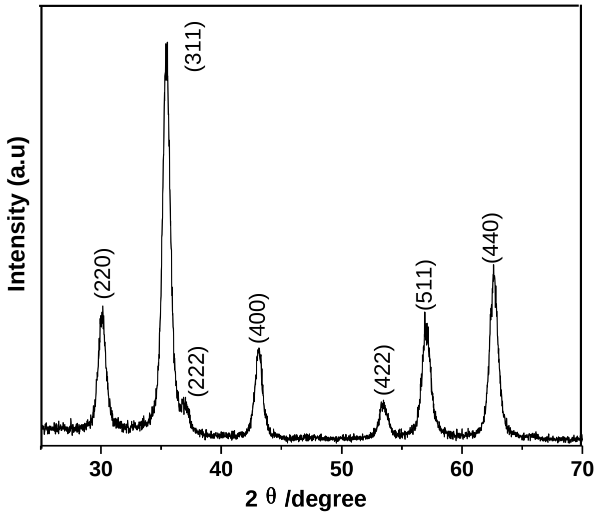
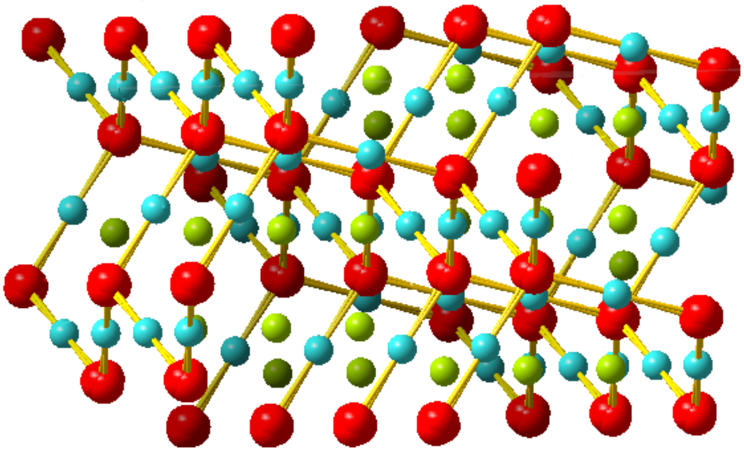


Fig. S3 shows the XRD pattern of the as-prepared Fe_3O_4 nanoparticles formed at 4 h with the other reaction parameters uncharged; all the diffraction peaks can be indexed as cubic Fe_3O_4, which is consistent with the reported data (JCPDS No. 88-0866). Based on Scherrer formula, the average crystallite size of Fe_3O_4 is calculated to be 14.5 nm by using the full width at half maximum (FWHM) intensity of (311) peak of Fe_3O_4

Fig. S5 Crystal structure of cubic inverse spinel Fe_3O_4 (●Fe^{3+} ●Fe^{2+} ●O)



In the cubic cell, the O atoms form a fcc closed packing and the Fe atoms occupy interstitial tetrahedral sites and octahedral sites, symbolized as $[Fe^{3+}]_A$-$[Fe^{2+}Fe^{3+}]_BO_4$, in which *A* (tetrahedral sites) are occupied by Fe^{3+} ions and *B* (octahedral sites) are occupied by equal numbers of Fe^{2+} and Fe^{3+} ions.

Fig. S6 SEM images of Fe_3O_4 synthesized with different contents of [C_{16}mim]Cl and keeping other reaction parameters uncharged: (a) 0 g; (b) 0.1 g; (c) 0.2 g; (d) 0.4 g.

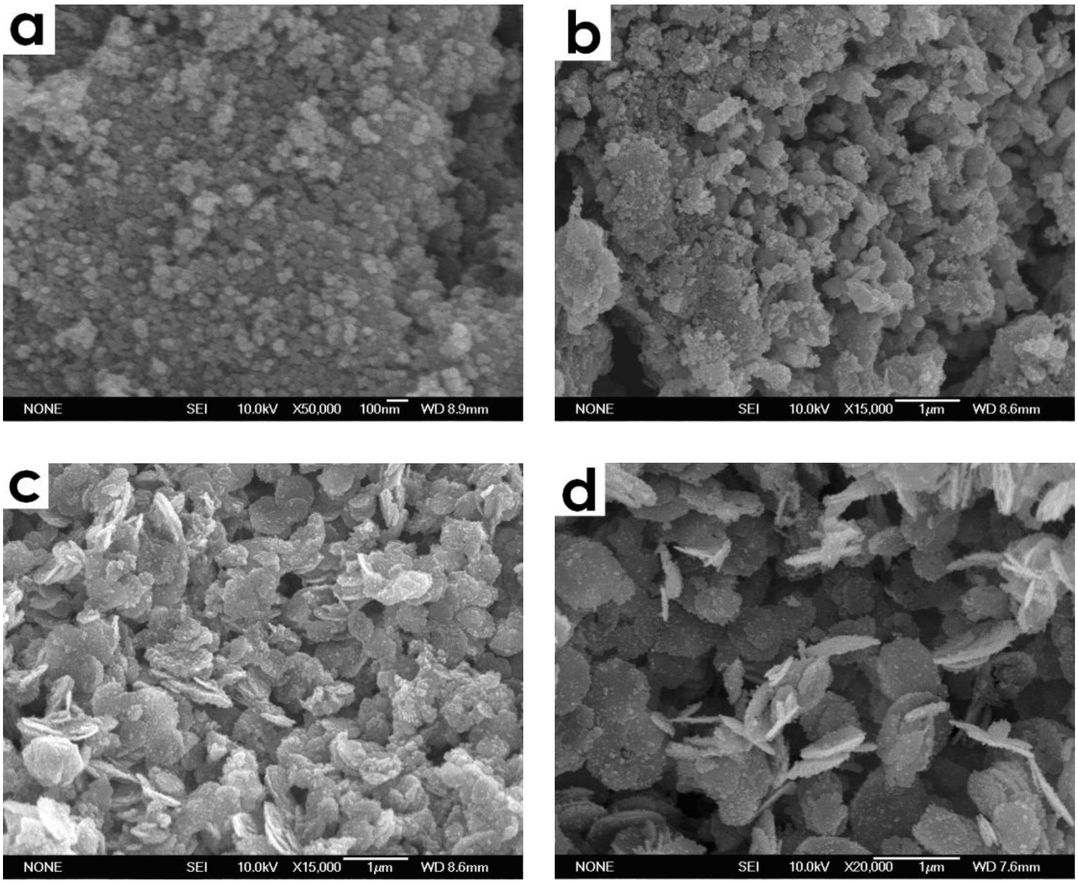


Fig. S7 SEM image of Fe_3O_4 synthesized in aqueous solution and other reaction parameters are uncharged.

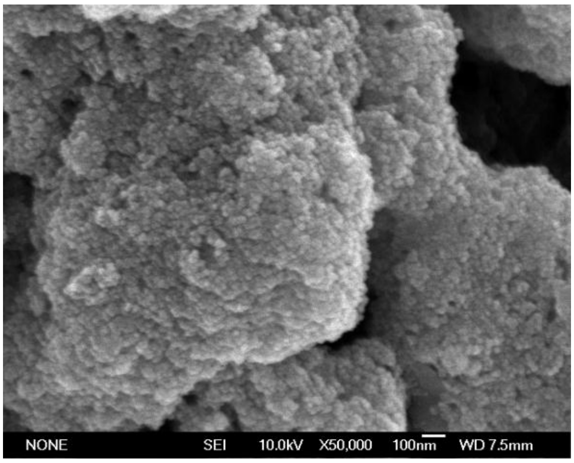
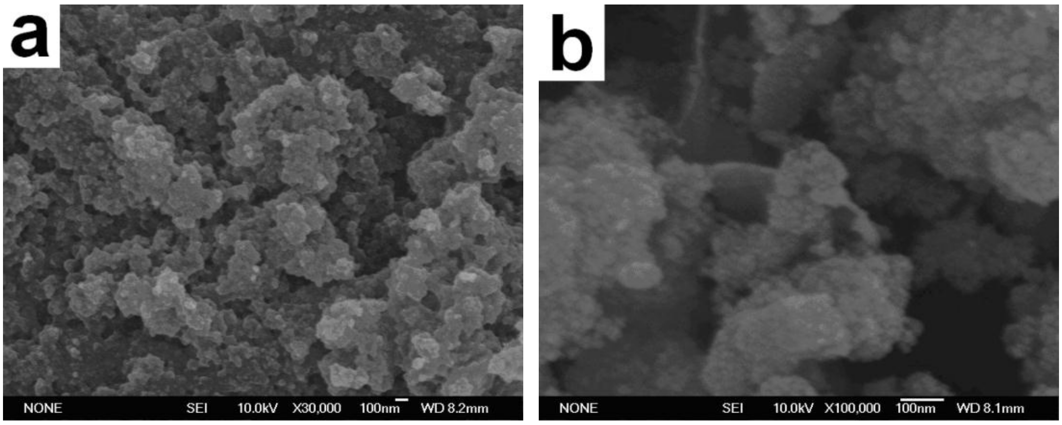


Fig. S8 SEM images of Fe_3O_4 synthesized under different reaction temperatures: (a) 120 °C; (b) 150 °C.



When the reaction temperature is 120 °C, no nanoflakes can be formed. Nanoparticles with minor amount of nanoflakes can be formed with the increase of temperature (150 °C).