Supporting Information for

Rhombic dodecahedral Fe₃O₄: ionic liquid-modulated and microwave-assisted synthesis and their magnetic properties

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Experimental Details

Synthesis of RD nanostructures.

All syntheses were performed using a commercial single-mode microwave synthesizer coupled with an automation system (StartSYNTH, Milestone). The system was equipped with in situ magnetic stirring. The microwave power output was set at 400 W under fixed-power mode conditions and the preset profile (desired time and temperature) was followed automatically by continuously adjusting the applied microwave power. The reactions were conducted in 35 mL quartz vessels. In a typical synthesis, 0.2 g of ILs [C_{12}Py]^+ClO_4^−, 0.6 mmol of phenol and 0.3 mmol of hexamethylenetetramine (HMT) were dissolved in 18 mL of water. Then, 0.1 mmol of FeSO₄(NH₄)₂SO₄·6H₂O was added. After stirring mildly for about 15 min, the solution was transferred into quartz vessels and it was then transferred into the microwave cavity. The temperature was raised up to 90 °C at a rate of 5 °C min⁻¹ and was kept at 90 °C for 15 min, and then the reaction vessel was cooled to room
temperature by a forced-air flow. The as-synthesized black sample was purified by washing with ethanol to remove excess reagents.

**Characterization.** The X-ray diffraction pattern of the products was collected on a Rigaku-D/max 2500 V X-ray diffractometer with Cu-K$_\alpha$ radiation (\(\lambda = 1.5418 \text{ Å}\)), with an operation voltage and current maintained at 40 kV and 40 mA. Field-emission scanning electron microscopy (FESEM) images were obtained with a Hitachi S4800 microscope. Transmission electron microscopic (TEM) images, high-resolution transmission electron microscopic (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. XPS measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K$_\alpha$ X-ray radiation as the X-ray source for excitation. Magnetic properties of the samples were carried out using a Quantum Design superconducting quantum interference device (SQUID). The measurements for all samples were done on pure and dried powders.
**Fig. S1** (a) XPS spectrum of the as-prepared product; (b) the expanded spectrum of Fe 2p.

**Fig. S2** XRD patterns of the products prepared without adding ILs (black line) and with adding ILs of 0.1 g (red line). Other reaction conditions were kept constant.