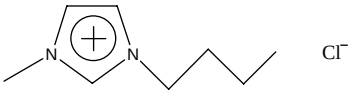
Supporting Information

Detailed Experiments

Preparation of Ionic Liquid [Bmim]Cl: The ionic liquid 1-n-butyl-3-methylimidazolium chloride ([Bmim]Cl) was synthesized according to the reported literature.[1] In a typical synthesis, 1-chlorobutane (144 cm^3, 1.38 mol) was added to a vigorously stirred solution of 1-methylimidazole (1.25 mol) in toluene (125 cm^3) at room temperature. The solution was heated to reflux at 110 ^oC for about 24 hours, after which it was placed in a freezer at –20 ^oC for 12 hours. The toluene was decanted and the remaining viscous oil/semi-solid re-crystallized from acetonitrile and then repeated re-crystallized from ethylacetate to yield a white crystalline solid, which was dried in vacuo to produce [Bmim]Cl. And its general structure is shown:



Synthesis of Fe_3S_4 Nanowalls: *In a typical synthesis, 0.5 mmol of $FeCl_3 \cdot 6H_2O$ was firstly dissolved into 15 mL of distilled water containing 0.55 mmol of ionic liquid [Bmim]Cl under mild stirring. Then, 3 mmol of KSCN and 0.55 mmol of vitamin C were put into the above solution. Finally, the homogeneous solution was transferred into a 20 mL Teflon-lined stainless steel autoclave, sealed, and then heated to 180 ºC. After the autoclaves were maintained at 180 ºC for 24 h, the resulting product was centrifuged, rinsed with distilled water, and finally dried at 60 ºC in a vacuum.*

Synthesis of Triple Hierarchical Microspheres of Fe_3S_4: *For the synthesis of triple hierarchical microspheres of Fe_3S_4, 0.5 mmol of $FeCl_3 \cdot 6H_2O$ was firstly dissolved into 15 mL of the mixed solution of ethylene glycol and distilled water containing 2.2 mmol of ionic liquid [Bmim]Cl with a volume ratio of 1:2 under mild stirring. Then, 3 mmol of KSCN was put into the above solution. Finally, the homogeneous solution was transferred into a 20 mL*

Teflon-lined stainless steel autoclave, sealed, and then heated to 180 ºC. After the autoclaves were maintained at 180 ºC for 24 h, the resulting product was centrifuged, rinsed with distilled water, and finally dried at 60 ºC in a vacuum.

Controlled Experiments: *To elucidate the roles of ionic liquid in synthetic systems, controlled experiments were carried out. Irregular nanosheets and microspheres (Fig. S1 and S2) were produced when the reactions were conducted under the same conditions except without any ionic liquid, respectively. From the analysis of our above experiments, we believe that the introduction of ionic liquid [Bmim]Cl to the reaction systems could lead to the formation of hierarchical structures assembled from hexagonal nanoplates. Therefore, it is reasonable that the ionic liquid [Bmim]Cl plays crucial roles for the formation of hexagonal nanoplates and their assembly into various hierarchical nanostructures.*

Characterization: *The samples of as-prepared* Fe_3S_4 *nanostructures were characterized by X-ray powder diffraction (XRD) with Rigaku D/max Diffraction System using a Cu Kα source (λ = 0.15406 nm). The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV). The high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The magnetic properties of* Fe_3S_4 *samples with various morphologies were measured at 300 K in the applied magnetic field sweeping from –10 to 10 kOe using a vibrating sample magnetometer (VSM, LDJ 9600, U.S.A.).*

Reference

1. L. Cammarata, S. G. Kazarian, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192-5200.

Table S1. Summary of the Experimental Parameters and their corresponding morphologies of Fe_3S_4 Obtained under Various Conditions.

Reactant	Solvent	Ionic liquid(mol/L)	Morphology
$FeCl_3·6H_2O$, KSCN and vitamin C[a]	distilled water	0	irregular platelike particles in Fig. S1
$FeCl_3·6H_2O$, KSCN and vitamin C[a]	distilled water	0.037	nanowalls in Fig. 1
$FeCl_3·6H_2O$, KSCN and vitamin C[a]	distilled water	0.257	microplates in Fig. S2
$FeCl_3·6H_2O$ and KSCN[b]	EG and distilled water[c]	0	irregular microspheres in Fig. S3
$FeCl_3·6H_2O$ and KSCN[b]	EG and distilled water[c]	0.037	microspheres assembled by microplates in Fig. S4
$FeCl_3·6H_2O$ and KSCN[b]	EG and distilled water[c]	0.147	triple microspheres assembled by microplates in Fig. 2

[a] All the reactions were conducted with 0.033 mol/L of $FeCl_3·6H_2O$, 0.2 mol/L of KSCN and 0.037 mol/L of vitamin C at 180 ºC for 24 h. [b] All the reactions were conducted with 0.033 mol/L of $FeCl_3·6H_2O$ and 0.2 mol/L of KSCN at 180 ºC for 24 h. [c] EG and distilled water is set to 1:2 by volume ratio.

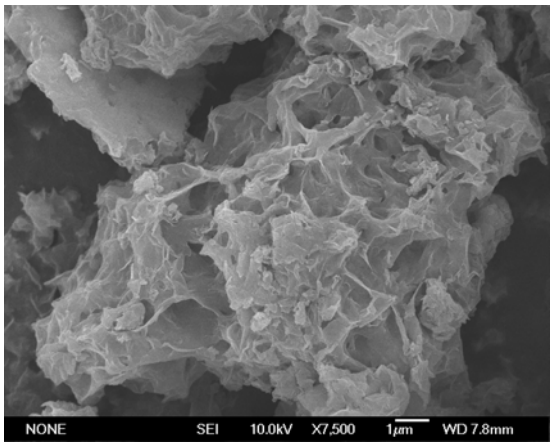


Fig. S1. SEM image of as-prepared sample synthesized under the same condition as that of nanowalls except without adding any ionic liquid.

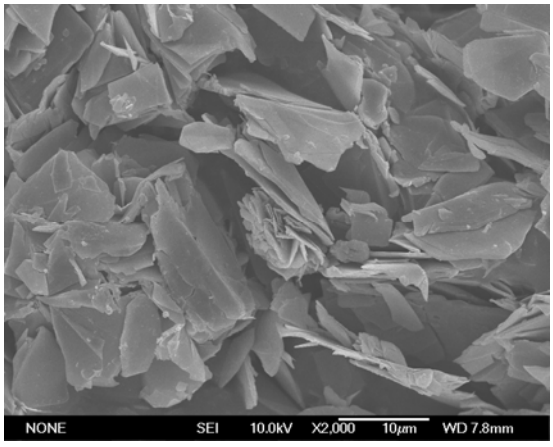


Fig. S2. SEM image of as-prepared sample synthesized under the same condition as that of nanowalls except adding 3.85 mmol of ionic liquid.

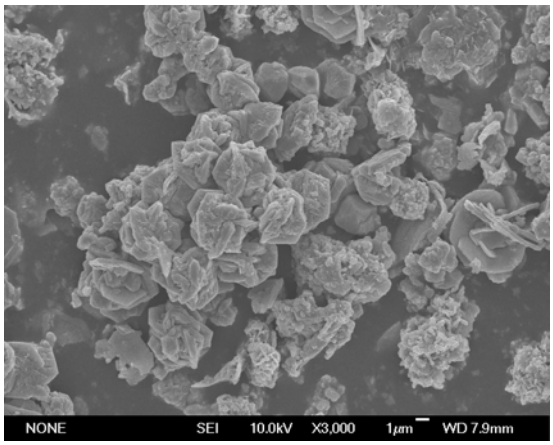


Fig. S3. SEM image of as-prepared sample synthesized under the same condition as that of hierarchical microspheres except without any ionic liquid.

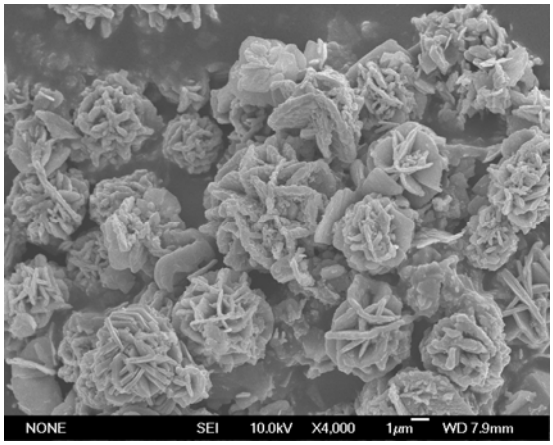


Fig. S4. SEM image of as-prepared sample synthesized under the same condition as that of hierarchical microspheres except adding 0.55 mmol of ionic liquid.