Supporting Information for

A visible-light-driven solid state photo-Fenton reagent based on magnetite/carboxylate-rich carbon spheres

Zhijun Luo, *[a c] Hongjun Tang,[b] Lingling Qu,[b] Tingting Han, [b] Xiangyang Wu*[a]

[a] *School of The Environment, Jiangsu University, Zhenjiang, 212013 P. R. China;*

[b] *School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, P. R. China;*

[c] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*

Corresponding author. Tel.: +86 511 88790955

E-mail address: lzj@ujs.edu.cn

Experimental Section:

Preparation of magnetite/carboxylate-rich carbon microsphere

The magnetite/carboxylate-rich carbon microspheres (MCRCSs) were synthesized via hydrothermal carbonization (HTC) process. Briefly, $FeCl_3$ (0.5 g) and sodium gluconate (2 g) were dissolved in 60 mL deionized water, and then transferred into a Teflon-lined stainless-steel autoclave with a capacity of 100 mL. The autoclave was sealed and heated at 180 ºC for 48 h. After cooling down to room temperature, the black products were washed several times with deionized water and absolute ethanol. Finally, the washed precipitation was dried in vacuum oven at 60 ºC for 12 h.

Preparation of Fe_3O_4 nanoparticles

$FeCl_3.6H_2O$ (2.43 g) and $FeSO_4.7H_2O$ (1.67 g) were dissolved in 50 mL deionized water under nitrogen gas with vigorous stirring at 80 ^{o}C. Then 2 M NaOH aqueous solutions were rapidly added into the solution until the pH of the solution was adjusted to 10. After heating, the black suspension was cooled to room temperature naturally. The black products were washed several times with deionized water and absolute ethanol. Finally, the washed precipitation was dried in vacuum oven at 60 ºC for 12 h.

Characterization

X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu Kα radiation (λ=1.54 Å). The field-emission scanning electron microscope (FE-SEM) measurements were carried out with a Hitachi S-4800 operating at 15 kV. The samples used for FESEM were prepared by dispersing of some products in ethanol, then placing a drop of the solution onto the surface of Al column and letting the ethanol evaporate slowly in air. Fourier transform infrared (FTIR) spectra of all the samples were measured on a Nicolet Nexus 470. Raman spectra were obtained using a Renishaw Raman system model 2000 spectrometer. Thermogravimetric (TG) analysis was performed on a Integrated thermal analyzer (STA 449C) under a flow of air with a temperature ramp of 5 ºC/min. The magnetic properties were measured using an Superconducting Quantum Interference Device (SQUID) magnetometer (Lake Shore 7307). XPS measurements was performed on an ESCALAB 250 spectrometer (Thermo-VG Scientific) with Al Kα X-ray radiation as the X-ray source for excitation.

Photochemical experiments

The photocatalytic activity was evaluated by the degradation of Methylene Blue (MB) under visible light irradiation (λ>420 nm). The visible light was obtained by a 250 W xenon lamp with a 420 nm cutoff filter to ensure the desired irradiation light. A suspension containing a powdered catalyst (100 mg) and a fresh aqueous solution of MB (100 mL, 10 mg/L) was ultrasonicated for 10 min and magnetically stirred in the dark for about 1 h to establish an adsorption/ desorption equilibrium of the MB species. The suspensions were kept under constant air-equilibrated conditions before and during illumination. At certain time intervals, 3mL aliquots were sampled and remove the particles. The filtrates were analyzed by recording variations of the maximum absorption band (633 nm), using a UV-Vis spectrophotometer (Shimadzu Corporation, UV-2450). The generation of •OH radicals was investigated by the terephthalic acid photoluminescence probing technique (TAPL).

Results and discussion

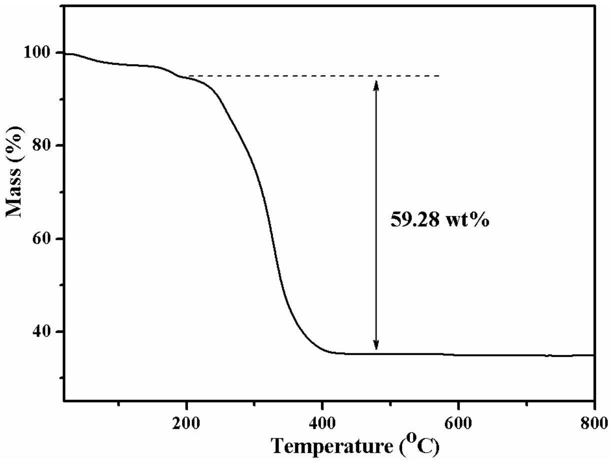


Fig. S1. Thermogravimetric (TG) curve of MCRCSs.

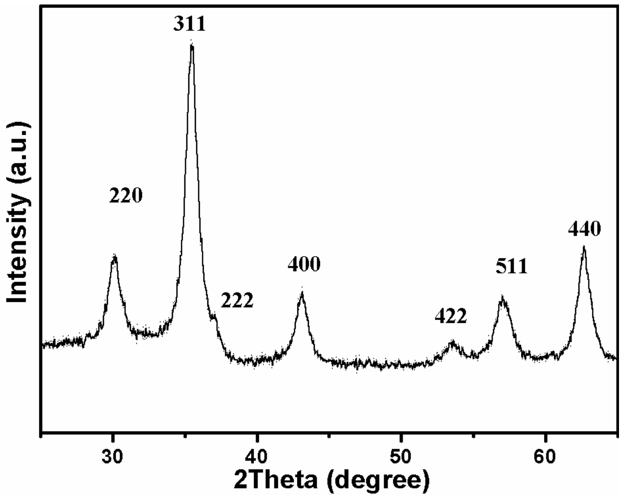


Fig. S2.The XRD pattern of the Fe_3O_4 nanoparticles

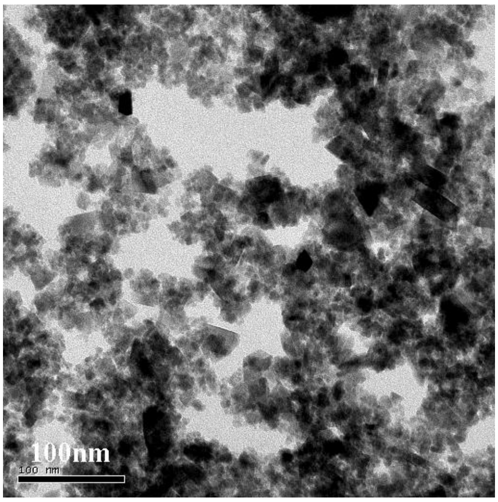


Fig. S3. the TEM image of the Fe_3O_4 nanoparticles

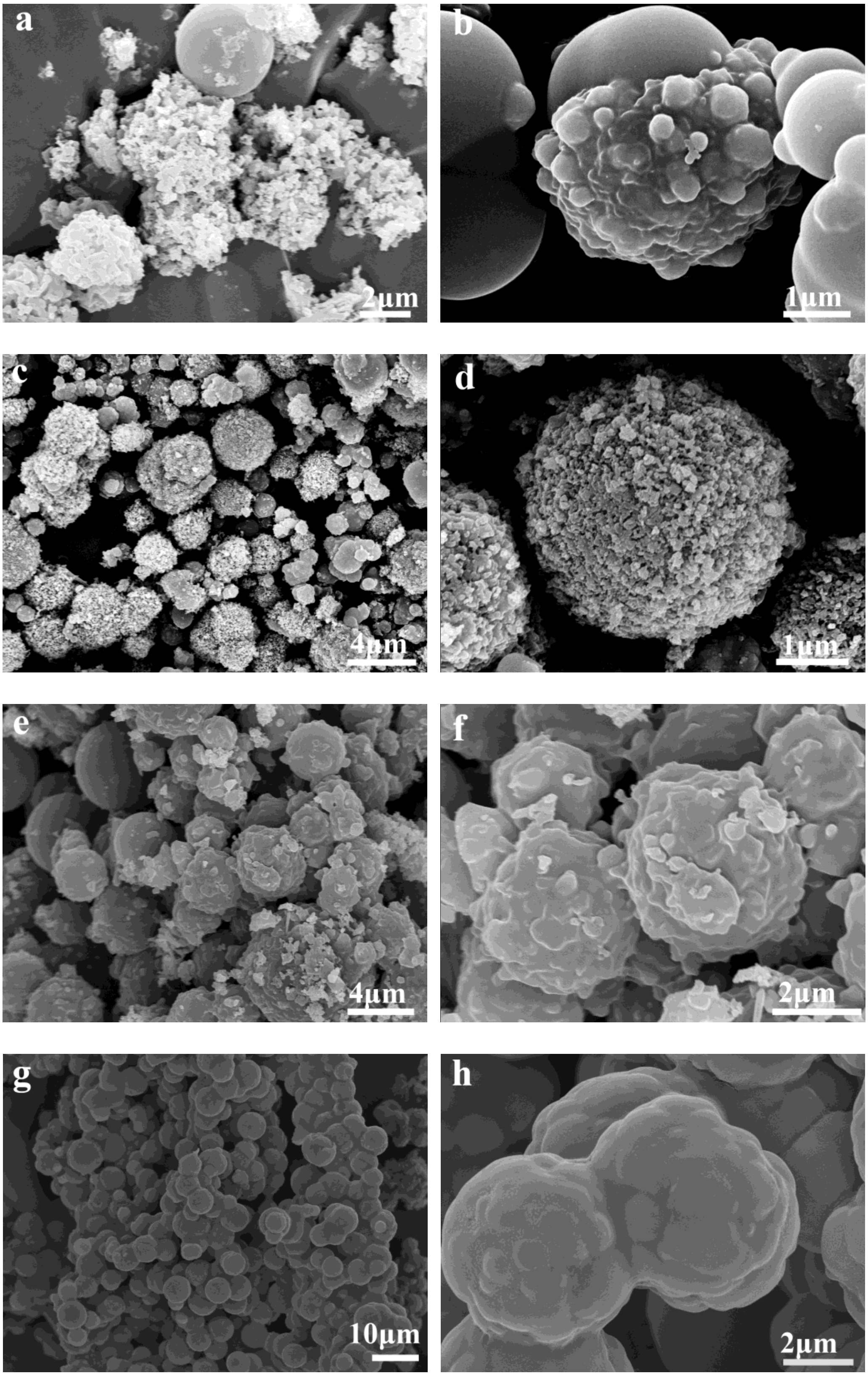


Fig. S4. SEM images of the products obtained at (a, b) 3 h, (c, d) 6 h, (e, f) 12 h and (g, h) 48 h

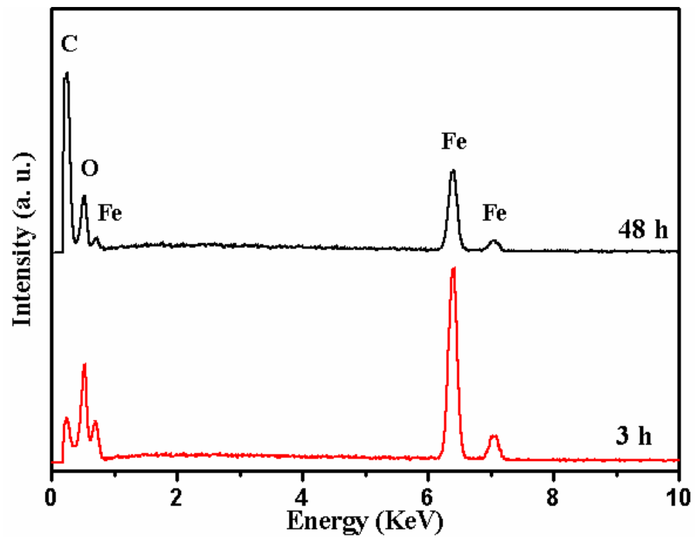
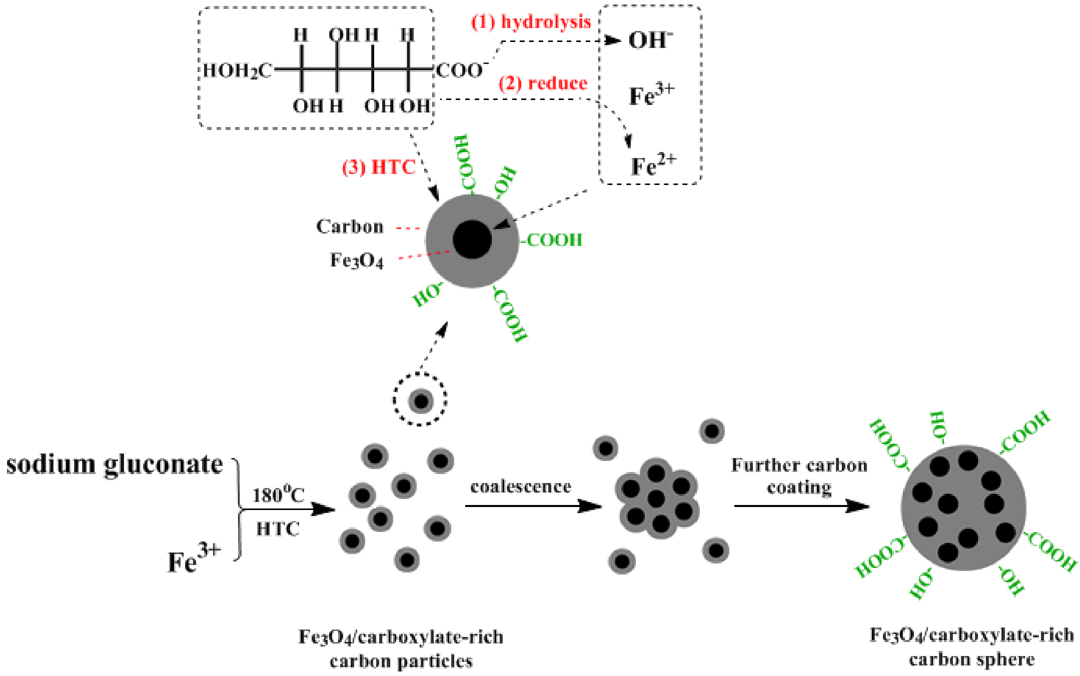


Fig. S5. EDS Spectrum of Fe_3O_4/carboxylate-rich carbon microspheres obtained at different reaction time.



Scheme S1 Schematic illustration of the formation process of MCRCS.