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Electronic supplementary information for

Ultrathin Nanoporous Fe_3O_4-Carbon Nanosheets with Enhanced Supercapacitor Performance

Dequan Liu,[a,b] Xi Wang,[a,]* Xuebin Wang,[a] Wei Tian,[a] Jiangwei Liu,[a] Chunyi Zhi,[c] Deyan He,[b]

Yoshio Bando,[a] and *Dmitri Golberg* [a,]*

[a]International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan. E-mail: WANG.Xi2@nims.go.jp, GOLBERG.Dmitri@nims.go.jp

[b]School of Physical Science and Technology, Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou, 730000, China

[c]Department of Physics and Materials Science, City University of Hong Kong Tat Chee Avenue, Kowloon, Hong Kong, China.

Experimental

Synthesis of ultrathin nanoporous Fe_3O_4 nanosheets (SNSs): In a typical procedure, $FeCl_3{\cdot}6H_2O$ (1 g) and NH_4HCO_3 (4 g) were added into ethylene glycol (60 ml). After stirring for half an hour in a beaker, the mixture was then transferred into a Teflon-lined autoclave (with a filling volume ratio of 60%), which was sealed and maintained at 185 °C for 10-48 h, and then naturally cooled to room temperature. The resulting products were collected and washed with distilled water and absolute ethanol to remove ions and possible remnants, and dried under vacuum at 60 °C for 6 h. Finally, the as-made products were under heat treatment at 250-400 °C.

Characterizations: Transmission electron microscopy (TEM) images were taken with a JEOL F3000 microscope operated at 300 kV. Samples were first dispersed in ethanol and then collected using carbon-film-covered copper grids for analysis. Scanning electron microscopy (SEM) images were recorded on a S4800 electron microscope operating at 15 kV. XRD patterns were recorded on a Philips X Pert PRO MPD X-ray diffractometer operated at 35 kV and 45 mA with Cu Kα radiation. XPS measurements were carried out with an ESCALab220i-XL spectrometer by using a twin-anode Al Ka (1486.6 eV) X-ray source. All spectra were calibrated to the binding energy of the C 1s peak at 284.6 eV. The base pressure was ~3×10^{-7} Pa. Raman spectra were taken on a Horiba Jobin-Yoon T6400 Raman spectrometer.

Electrochemical Test: Electrochemical performance of the hybrid composite electrode was studied using a Solartron electrochemical workstation. The standard three-electrode cell was composed of Ag/AgCl as a reference electrode, Pt mesh as a counter electrode and the synthesized composite sample as a working electrode, respectively. A 1 M Na_2SO_3 solution served as electrolyte at room temperature. Cyclic voltammetry (CV) was analyzed at various scan rates of 5, 20, 50, and 100 mV/s. Galvanostatic (GV) charge/discharge curves were obtained at various current densities of 1-10 A/g to evaluate the specific capacitance.

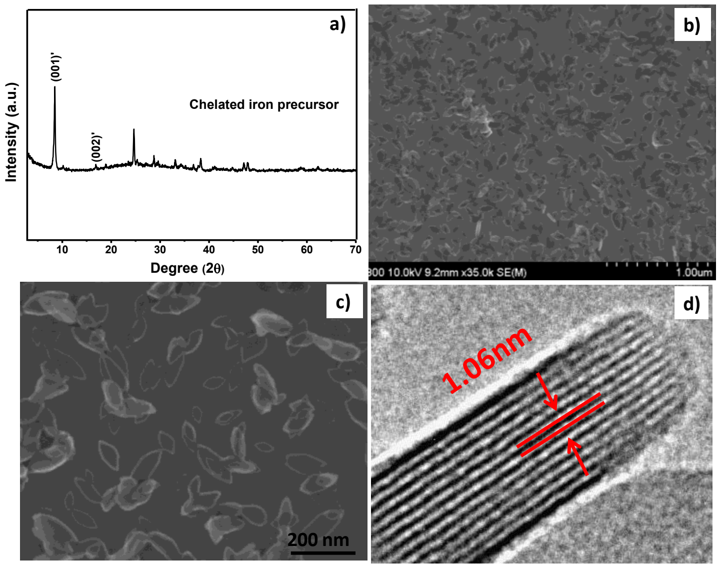

Fig. S1. a) XRD patterns of obtained chelated iron precursors. b-c) Low- and high-magnification SEM images of the obtained chelated iron precursors. d) TEM image of the obtained chelated iron precursors. The inset shows their corresponding HRTEM images, Scale bar: 10 nm.

The layered structure of the obtained chelated iron precursors can be well proofed by XRD, SEM and TEM characterizations. As shown in Fig. S1, one strong peak and another weak peak with corresponding *d* spacings of 10.6 and 5.3 3.5 Å can be indexed to the 00*l* reflection series of a with an interlayer spacing of *ca.* 10.6 Å. In addition, other peaks in a region of 2θ from 10 to 70° are indexed to the iron glycolate phase (Fig. S1a), similar to other metal glycolate compounds.[1] The as-synthesized chelated iron precursors can be produced in large scale as observed in SEM image (Fig. S1b). And the oval shapes of these nanosheets can be clearly seen in Fig. 1c. Their well-defined multilayered structures along the thickness direction can be clearly observed from the high-resolution transmission electron microscopy (HRTEM) images (Fig. S1d), indicating that the nanostructures are formed by stacking of several ultrathin nanosheets. And the interlayer spacing of the nanosheets is estimated to be ~1.06 nm, fitting well its XRD data (Fig. S1a).

1. a) X. Wang, X. -L. Wu, Y. T. Zhong, Y. -G. Guo, Y. Ma, J. N. Yao, *Adv. Funt. Mater*. **2010**, *20*, 1680. b) Y. Wang, X. Jiang, Y. Xia, *J. Am. Chem. Soc.* **2003**, *125*, 16176.

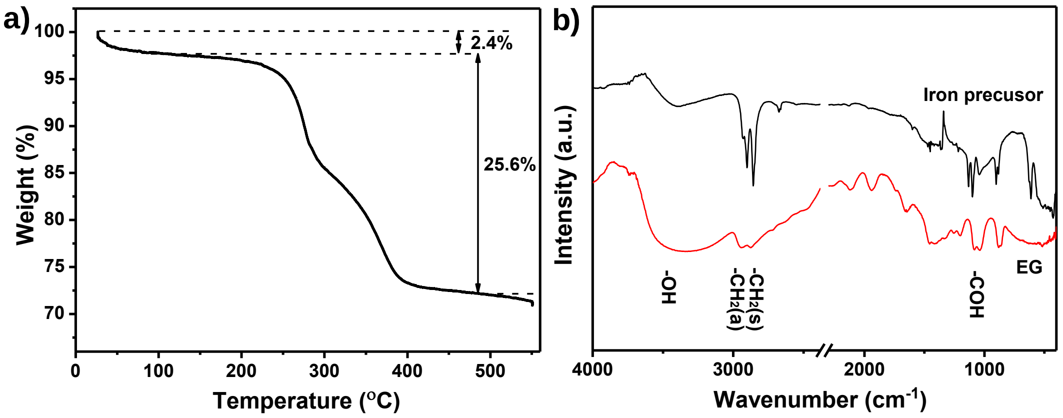

Fig. S2. a) TG curve of the chelated iron precursors. b) FT-IR spectrum of EG (red line), and the chelated iron precursors (black line).

The components of the precursors can also be noticed under both thermogravimetric (TG) analysis (Fig. S2a) and Fourier transform infrared (FT-IR) spectroscopy (Fig. S2b). The TGA curve shows a total weight loss of ~25.4% from 100°C to 500°C, which is attributed to the decomposition of organic components within the composite structure.[1] As shown in FT-IR spectra in Fig. S2b, compared with pure EG, the vibrational bands of CH_2- and C-O of the iron precursors become stronger and sharper. The lower peak frequencies of the methylene C-H stretching mode are due to ordered alkyl chains of intercalated ethylene glycol molecules.[2]

1. a) X. Wang, X. -L. Wu, Y. T. Zhong, Y. -G. Guo, Y. Ma, J. N. Yao, *Adv. Funt. Mater.* **2010**, *20*, 1680. b) Y. Wang, X. Jiang, Y. Xia, *J. Am. Chem. Soc.* **2003**, *125*, 16176.

2. A. N. Parikht, D. L. Auara, I. B. Azouz, F. Rondelez, *J. Phys. Chem.* **1994**, *98*, 7577.

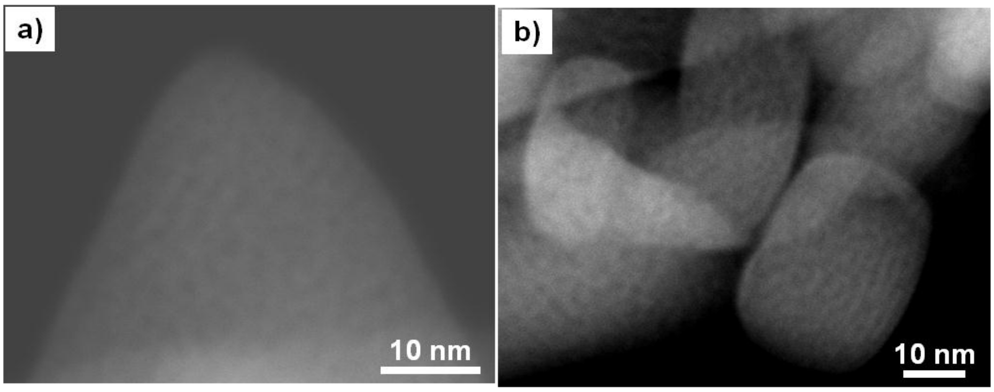

Fig. S3. HAADF-STEM images of SNSs after 5000 cycles viewed from the top (a) and from the side (b).

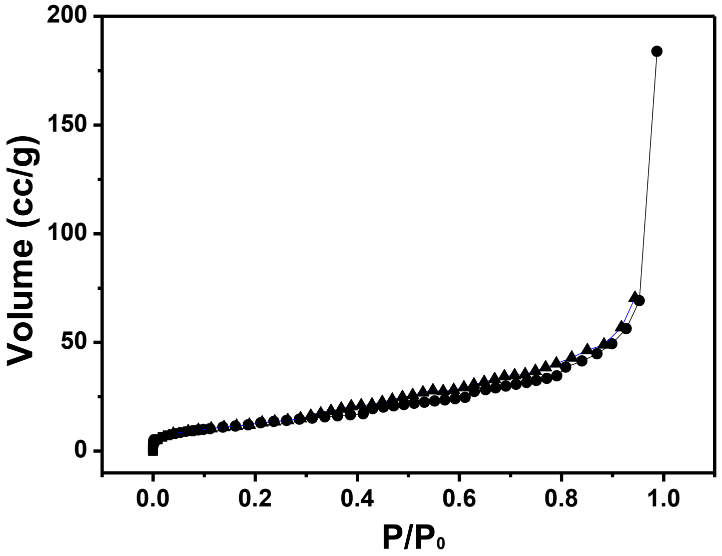

Fig. S4. The nitrogen sorption isotherms at 77 K for Fe_3O_4 nanoparticles.

Table S1. Comparison of the electrochemical performance of SNSs fabricated in this work with previous works.

Samples	Electrolyte	Current density (mA/g	Potential range (V)	Capacitance (F/g)	Capacitance retention (%)	Rate capacity	Ref.
Fe_3O_4 nanocrystals@graphene	KCl	-	0-0.5	88	>90% after 1000 cycles	-	1a
Fe_3O_4 nanosheets	Na_2SO_3	420	(-0.9)-(-0.1)	83	36% after 1000 cycles	-	1b
Fe_3O_4 nanosheets-carbon nanofibers	Na_2SO_3	420	(-0.9)-(-0.1)	135	91% after 1000 cycles	-	1b
Fe_3O_4@SnO_2 nanorod film	Na_2SO_3	0.2 $mAcm^{-2}$	(-0.8)-(-0.2)	7.013 mF cm^{-2}	82.8% after 2000 cycles	2.26 mF cm^{-2} at 1.66 mA cm^{-2}	1c
Fe_3O_4 nanorod film	Na_2SO_3	0.2 $mAcm^{-2}$	(-0.8)-(-0.2)	5.156 mF cm^{-2}	> 70% after 2000 cycles	2.26 mF cm^{-2} at 1.66 mA cm^{-2}	1c
Fe_3O_4 nanoparticle /activated carbon	KOH	0.5 $mAcm^{-2}$	0-1.2	37.9	82% after 500 cycles	36 F/g at 2 $mAcm^{-2}$	1h
Octadecahedron Fe_3O_4 thin film	Na_2SO_3	6	(-1)-0.1	118.2	88.75% after 500 cycles	-	1f
SNSs	Na_2SO_3	1000	(-0.8)-(-0.2)	163.4	93% after 5000 cycles	112 mAh/g at 10 A/g	This work

1. a) B. Li, H. Cao, J. Shao, M. Qu, J. H. Warner, *J. Mater. Chem.* **2011**, *21*, 5069. b) J. B. Mu, B. Chen, Z. C. Guo, M. Y. Zhang, Z. Y. Zhang, P. Zhang, C. L. Shao and Y. C. Liu, *Nanoscale*, **2011**, *3*, 5034. c) R. Li, X. Ren, F. Zhang, C. Du, J. Liu, *Chem. Commun.* **2012**, *48*, 5010. d) K. Y. Xie, J. Li, Y. Q. Lai, W. Lu, Z. A. Zhang, Y. X. Liu, L. M. Zhou, H. T. Huang, *Electrochem. Commun.* **2011**, *13*, 657. e) M. S. Wu, R. H. Lee, *J. Electrochem. Soc.* **2009**, *156*, A737. f) J. Chen, K. L. Huang, S. Q. Liu, *Electrochim. Acta* **2009**, *55*, 1. g) K. W. Chung, K. B. Kim, S. H. Han, H. Lee, *Electrochem. Solid-State Lett.* **2005**, *8*, A259. h) X. Du, C. Y. Wang, M. M. Chen, Y. Jiao, J. Wang, *J. Phys.Chem. C* **2009**, *113*, 2643.