

Supporting information

***In situ* preparation of 3D graphene aerogels@ hierarchical Fe₃O₄ nanoclusters as high rate and long cycle anode materials for lithium ion batteries**

Lishuang Fan, Bingjiang Li, David W. Rooney, Naiqing Zhang and Kening Sun

Dr. L.S. Fan, B.J. Li

Department of Chemistry, Harbin Institute of Technology,

Prof. N.Q. Zhang, K.N. Sun

State Key Laboratory of Urban Water Resource and Environment,

Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology,

92 Xidazhi Street, Harbin 150001 (China)

E-mail: keningsunhit@126.com, znqmww@163.com,

Prof. David W. Rooney

School of Chemistry and Chemical Engineering/QUILL Research Centre, Queen's University,

Belfast, BT9 5AG, Northern Ireland, U.K.

Experimental Section

Materials:

Graphite powder was purchased from Shanghai Chemicals, China. Ferric trichloride(FeCl_3) was purchased from Fluka. Ethylene glycol (EG), Sodium citrate (Na_3Cit) and Sodium acetate (NaAc) were obtained from Tianjin kermelchemical reagent co., LTD (Tianjin, China). All other chemicals used were of analytical reagent grade.

Characterization

The morphologies of samples were observed by scanning electron microscopy (SEM) using a Hitachi S-4300 (Hitachi, Tokyo, Japan). High-resolution transmission electron microscopy (HRTEM) images, and selected area electron diffraction (SAED) patterns were performed using a field emission transmission electron microscope (Tecnai G²F30, FEI, US). The X-ray diffraction (XRD) patterns were obtained on a PANalytical X'pert PRO X-ray diffractometer with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). Specific surface area measurements were made using the Brunauer–Emmett–Teller (BET) method (ASAP 2020). Pore volume was calculated from adsorption-desorption data using the Barrett-Joyner-Halenda (BJH) model. Thermogravimetry analyses (TG, NETZSCH, STA 449F3) were performed in the range of 30-800 °C at a heating rate of 5 °C min⁻¹ in air gas. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha XPS (Fisher Scientific Ltd, Nepean, ON).

Synthesis of Fe_3O_4 NCs/GAs Composites:

GO was synthesized from natural graphite flakes by a modified Hummers methods.^[1] Fe_3O_4 NCs were prepared by ethylene glycol reduction of ferric chloride via solvothermal process.^[2] Fe_3O_4 NCs/GAs were prepared by solvothermal assembly of GO, iron chloride and Na_3Cit , subsequently combining with freeze drying. In a typical experiment, 325 mg iron chloride was added to GO solution (45 mg GO was dispersion in the 20 ml EG solution) to achieve the electrostatic adsorption of Fe^{3+} ions on GO under mechanical stirring, and then 100 mg Na_3Cit and 600 mg NaAc was slowly added to form a stable complex solution by stirring for 30 min. Subsequently, the stable suspension was sealed in a Telfon-lined autoclave and solvothermally treated at 200 °C for 10 h. The autoclave was naturally cooled to room

temperature. The obtained GAs supported with Fe₃O₄ NCs was washed and freeze dried. The Fe₃O₄ NCs were obtained using with the same condition without GO.

Electrochemical Measurements:

The GAs@Fe₃O₄ were mixed with polyvinylidene fluoride (PVDF) binder in a weight ratio of 9:1 in N-methyl-2-pyrrolidinone (NMP) solvent and then spreading onto Cu foil to obtain electrodes. The Fe₃O₄ electrode was fabricated with PVDF and carbon black with a weight ratio of 9:1, and then coated onto Cu foil. The electrodes were dried in a vacuum oven at 120 for 12 h and then pressed at a uniaxial pressure of 10 MPa to enhance the contact between the active material and Cu foil. **The mass loading is about 1.5mg/cm². For comparison, Fe₃O₄ mixed with GAs was noted as Fe₃O₄+GAs.**

The electrochemical properties of the Fe₃O₄ NCs/GAs was measured by the galvanostatic charge/discharge technique as anode materials in LIBs.^[3] The coin type (CR-2025) test cells were assembled in an argon-filled glove box (Mbraun, H₂O<0.1ppm O₂<1ppm) using 1 M LiPF₆ in diethylcarbonate, ethylenecarbonate and ethylmethylcarbonate (EC/EMC/DMC, 1:1:1 by vol) as an electrolyte, two pieces of porous polypropylenelms (Celgard2400) as the separator, and metallic lithium as the counter/reference electrode. Over a voltage range of 0.01-3.0 V (vs Li /Li), the discharge/charge measurements were carried out by using a Neware (Shenzhen Neware Electronic Co.,China) battery test system at various current rates (1C is equivalent to 865 mAhg⁻¹). The theoretical capacity of the Fe₃O₄ NCs/GAs was calculated as follows:

$C_{\text{theoretical}} = C_{\text{Fe}_3\text{O}_4} * \text{mass percentage of Fe}_3\text{O}_4 + C_{\text{graphene}} * \text{mass of percentage of graphene} = 926 * 67\% + 744 * 33\% = 865 \text{mAhg}^{-1}$. Electrical impedance spectroscopy (EIS) measurements were carried out using an electrochemical work station (Princeton Applied Research PAR-STAT2273 advanced electrochemical system) over the frequency range between 1 MHz and 10 mHz with the amplitude of an ac signal of 5 mV.

Reference

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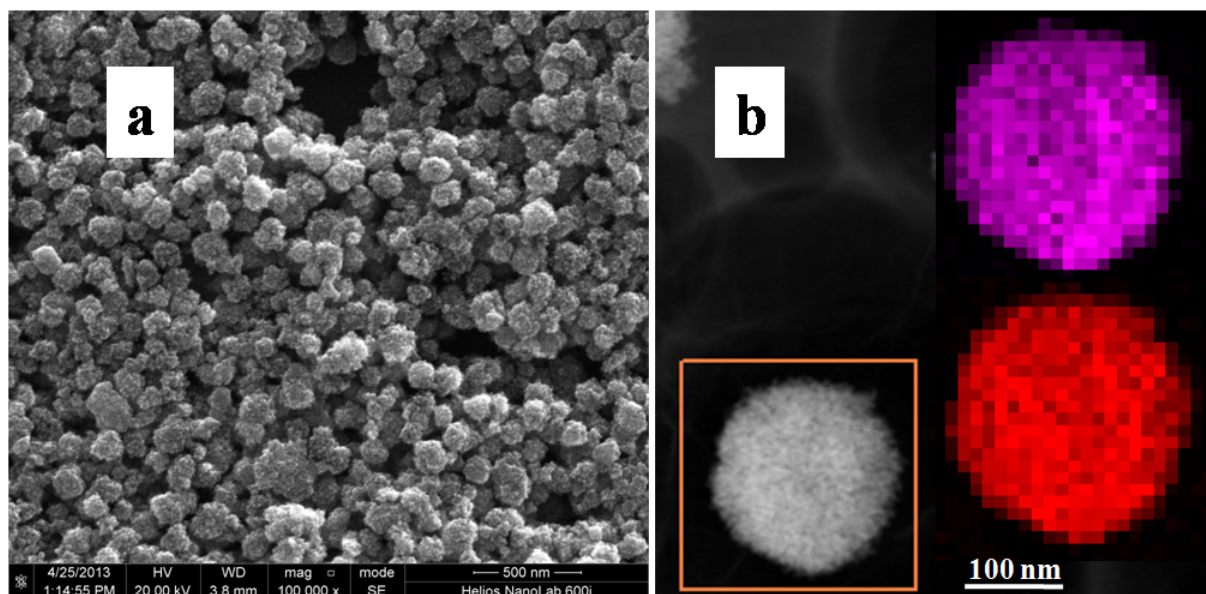


Figure S1. SEM and mapping image of Fe_3O_4 NCs.

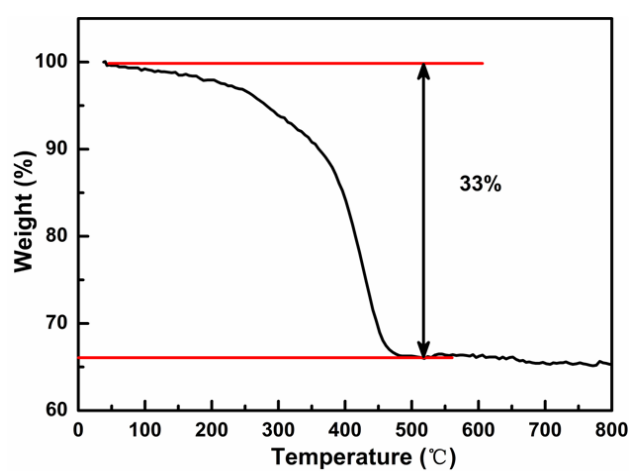


Figure S2. TGA curves of Fe_3O_4 NCs/GAs nanocomposites.

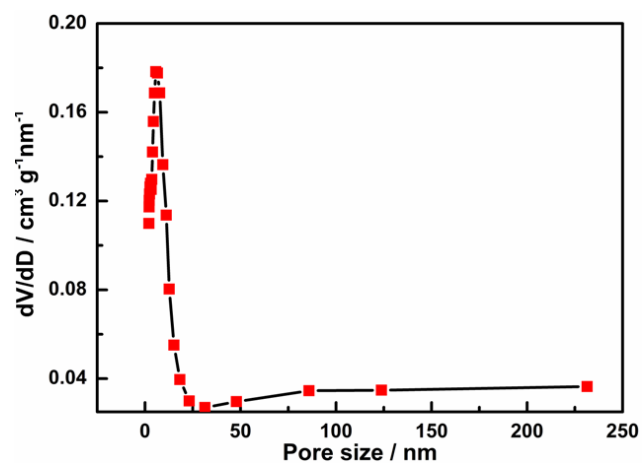


Figure S3. The pore size distribution of Fe_3O_4 NCs/GAs.

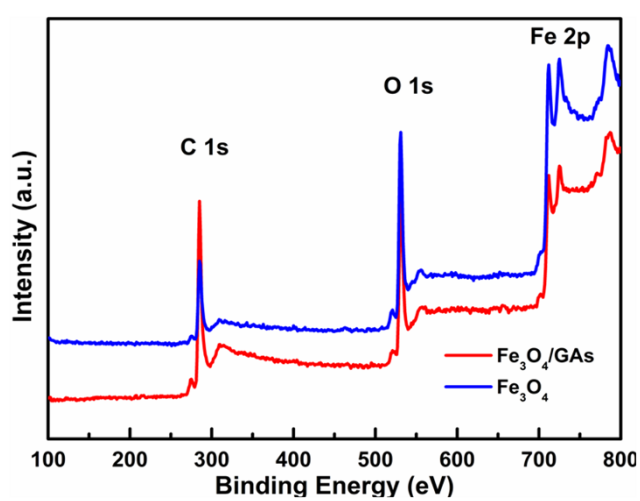


Figure S4. XPS spectra of Fe_3O_4 NCs and Fe_3O_4 NCs/GAs.

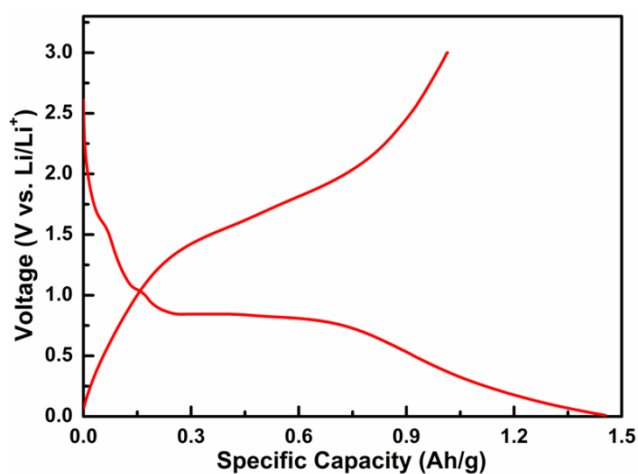


Figure S5. Galvanostatic discharge-charge profiles of Fe_3O_4 NCs/GAs at a current density of 0.1C.

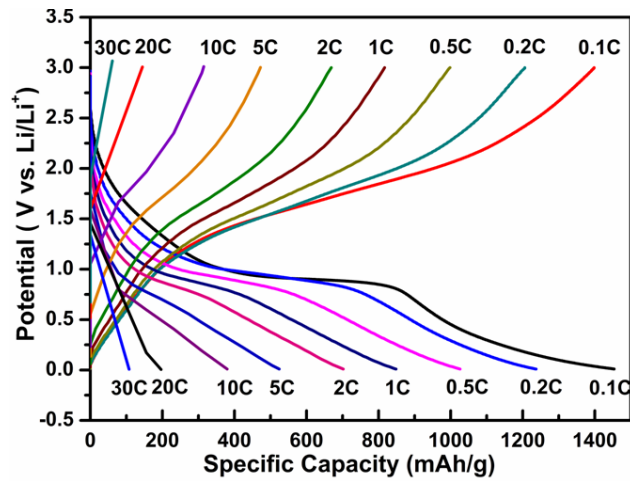


Figure S6. Galvanostatic discharge-charge performance of the Fe_3O_4 NCs/GAs nanocomposites at different current densities.

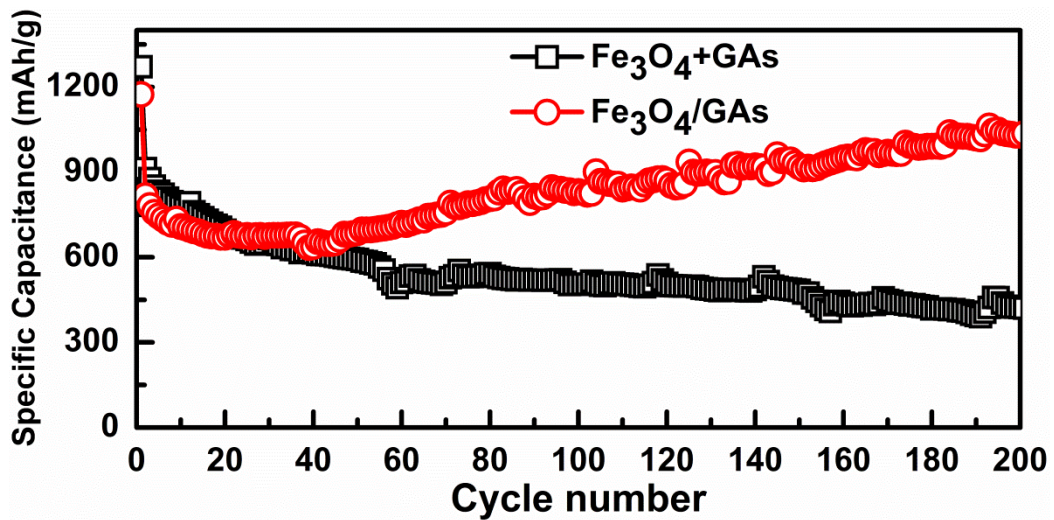


Figure S7. Cycle performance of Fe_3O_4 +GAs and Fe_3O_4 NCs/GAs at a current rate of 1 C.

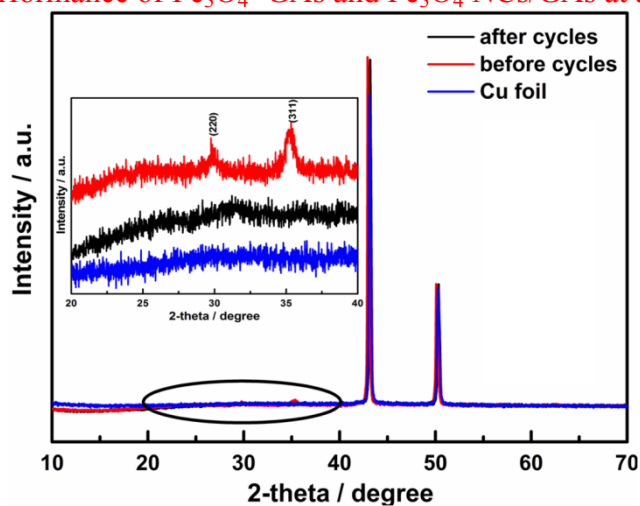


Figure S8. XRD profiles of the composite electrode after and before cycling.

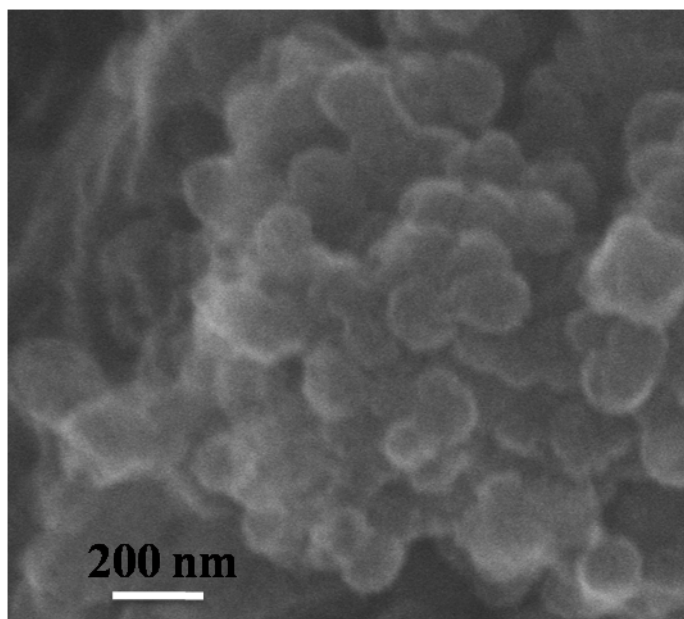


Figure S9. SEM of the composite electrode after 300 cycling.

To further verify the high durability of the nanoclusters structure, the microstructure of the electrode after long-time cycling is examined by both XRD and SEM. As shown in Figure S8, The diffraction peak disappeared after 300 cycles of charge/discharge, which may be due to repeated insertion/extraction causing the amorphous phase transition. One can see that the morphology of the nanoclusters is well preserved after 300 cycles of charge/discharge and the clear spheres structure can be still retained (Figure S9). The robustness of the spherical structure can be ascribed to SEI formation surrounded by polymer/gel-like coating, which retained the structure integrity. This result suggests that the as-formed architecture is highly robust during cycling, ensuring their excellent electrochemical performance.^[1-6]

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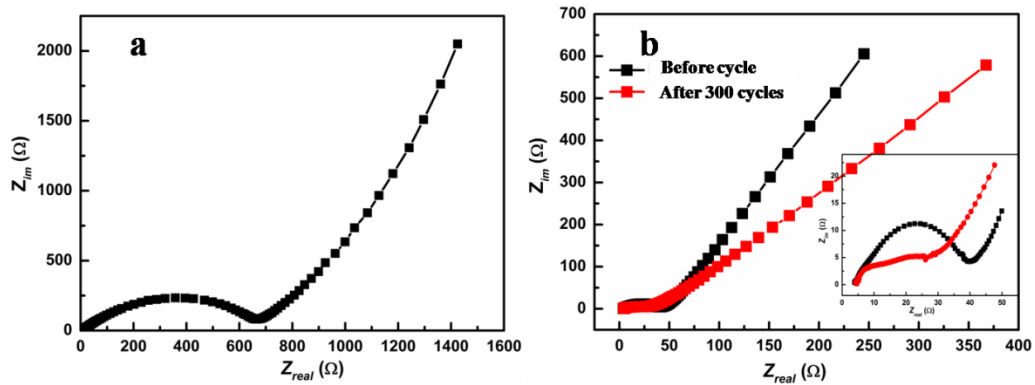


Figure S10. Impedance plots for electrodes containing a) bare Fe_3O_4 and b) Fe_3O_4 NCs/GAs composite (before cycle and after 300 cycles) Frequency range applied was 100 kHz to 0.01 Hz.