

Electronic Supplementary Information
for
3D Graphene/Magnetite composite as the electrode material for symmetric
supercapacitors

Kaliyappan Karthikeyan^a, Dharmalingam Kalpana^{b,*}, Samuthirapandian Amaresh^a, Yun Sung Lee^a

^a Faculty of Applied Chemical Engineering, Chonnam National University, Gwang-ju 500-757, South Korea

^b Central Electrochemical Research Institute, Karaikudi 630006, India

Experimental

Preparation of Graphene

For the synthesis of graphene, initially graphene oxide (GO) was prepared and then graphene was obtained by the reduction of GO using a reduction agent. GO was prepared according to the modified Hummers-Offeman's method.²⁵ Graphite (KS-6) was used as the starting material. In a typical synthesis, 1 g of graphite was added into 23 ml of concentrated sulfuric acid and 3 g of KMnO_4 (Sigma Aldrich, 99.9%) was gradually mixed into the acid bath with continuous stirring for 2h. Then, the bath mixture was heated to 35 °C for 0.5 h and followed by addition of distilled water, which raised the temperature of the bath mixture up to 98 °C and then kept for 1 h to increase the oxidation degree of the graphite oxide. The resultant bright yellow suspension was terminated by continuous addition of distilled water and hydrogen peroxide (30%, Wako, Japan) mixture solution. The final product was obtained by filtering and washing the precipitate with 5 % HCl and distilled water to remove the sulphate ions and then dried at 60 °C for 12 h in air. After sonication for 2 h, the graphite oxide transformed to GO. The reduction of GO to graphene (GE) was performed by adding 1:5 ratio of hydrazine (Sigma Aldrich, 99.9%) and distilled water into GO suspension and then the resultant mixture was continuously stirred for 1 h. The reduced GE in the form of graphene nano sheet (GNS) was collected after washing, filtering and drying at 80 °C for further utilization.

Preparation of Fe_3O_4 and Fe_3O_4 -GNS composite

The synthesis of Fe_3O_4 and Fe_3O_4 -GNS was done by urea assisted microwave irradiation method. Iron nitrate (98% Junsei, Japan) and urea (98% Junsei, Japan) were used as the starting materials. For Fe_3O_4 -GNS preparation, iron nitrate and urea (1:10 molar ratio) were added in 250 ml of GNS suspension (5 mg) and stirred for 15 min. Then the above mixture was heated in house hold microwave oven (Daewoo, 700 W) for 10 min and cooled

down to room temperature. Subsequently, the precipitate was filtered, washed with distilled water followed by absolute ethanol and then dried at 100 °C for 10 h in air. Finally, Fe₃O₄-GNS composite was obtained by calcination of the above powders in a box furnace at 320 °C for 2 h in air atmosphere. The pristine Fe₃O₄ was also prepared by the same method without adding GNS.

Characterization methods

The crystallographic nature of the prepared samples were investigated through X-ray diffractometer (XRD, Rigaku Rint 1000, Japan), with Cu-K α as a radiation source ($\lambda=1.54056\text{\AA}$). The surface morphology of the samples was investigated by scanning electron microscope (SEM, Hitachi S-4700, Japan) and transmission electron microscope TEM, (TecnaiF20, Philips, Holland). X-ray photoelectron spectroscopy (XPS) was performed using Multilab 2000, UK with a monochromater Al K α radiation ($h\nu = 1486.6\text{ eV}$). The amount of carbon content in the composite was determined by thermogravimetric analysis (TGA) from 0 to 500 °C at 5 °C min⁻¹ under oxygen flow using thermal analyzer system (STA 1640, Stanton Redcroft Inc., UK). Fourier transform infrared spectroscopic measurements were carried out on IRPresitge-21 spectrometer (Shimadzu, Japan). The Brunauer-Emmett-Teller (BET) surface was calculated through micromeritics ASAP 2010 surface analyzer (Micromeritics, USA)

The electrochemical behaviors of Fe₃O₄ and Fe₃O₄-GNS composite electrodes were measured in 1 M H₂SO₄ electrolyte solution between -1 and 0 V using three electrode cell configuration. The working electrode for the measurements were prepared by pressing a slurry of 80 wt% of active material, 10 wt% of ketzen black as conducting additive and 10 % of teflonized acetylene black as binder on stainless steel mesh and subsequently dried at 160 °C in a vacuum oven for 1 h. Platinum (Pt) wire and saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. The electrodes for symmetrical

supercapacitors were also prepared by the same method as above. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies were performed using electrochemical analyzer (SP-150, Bio-Logic, France). Galvanostatic charge discharge (C/DC) studies for the cells were conducted at different current densities using Won-A-Tech Battery cycler (WBCS 3000, Korea).

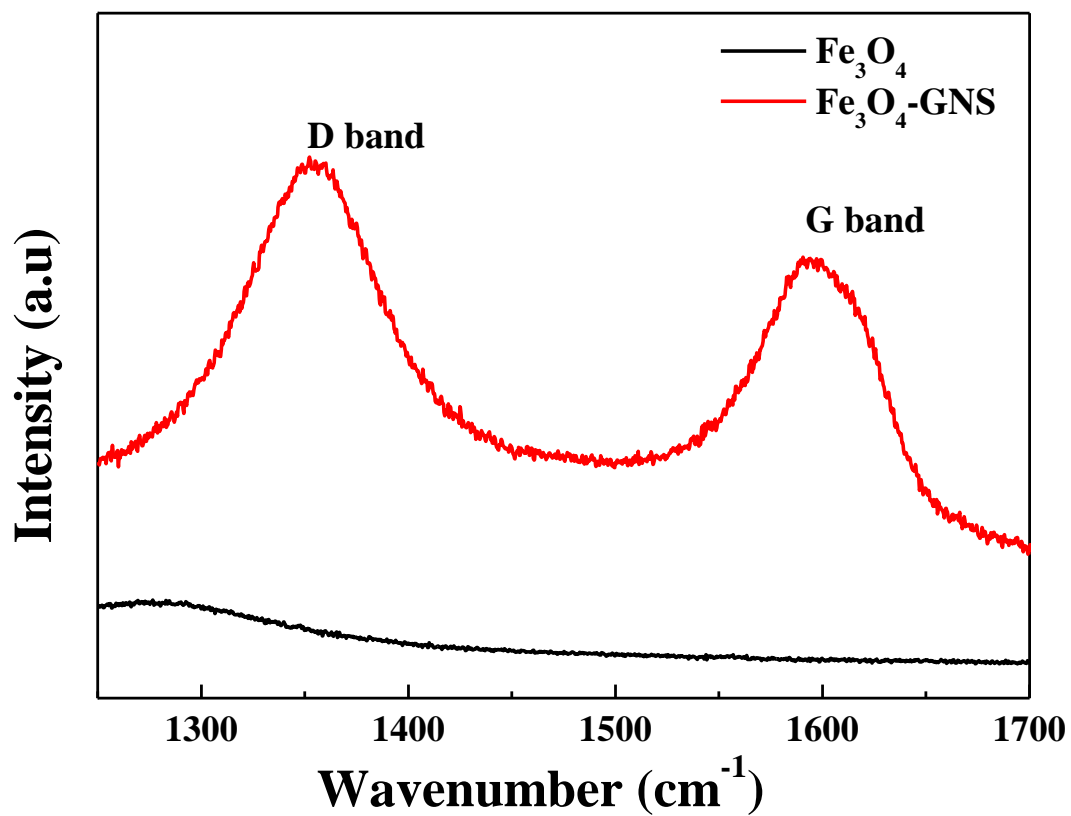


Figure S1. Raman spectrum of Fe₃O₄ and Fe₃O₄-GNS composite material prepared using microwave method

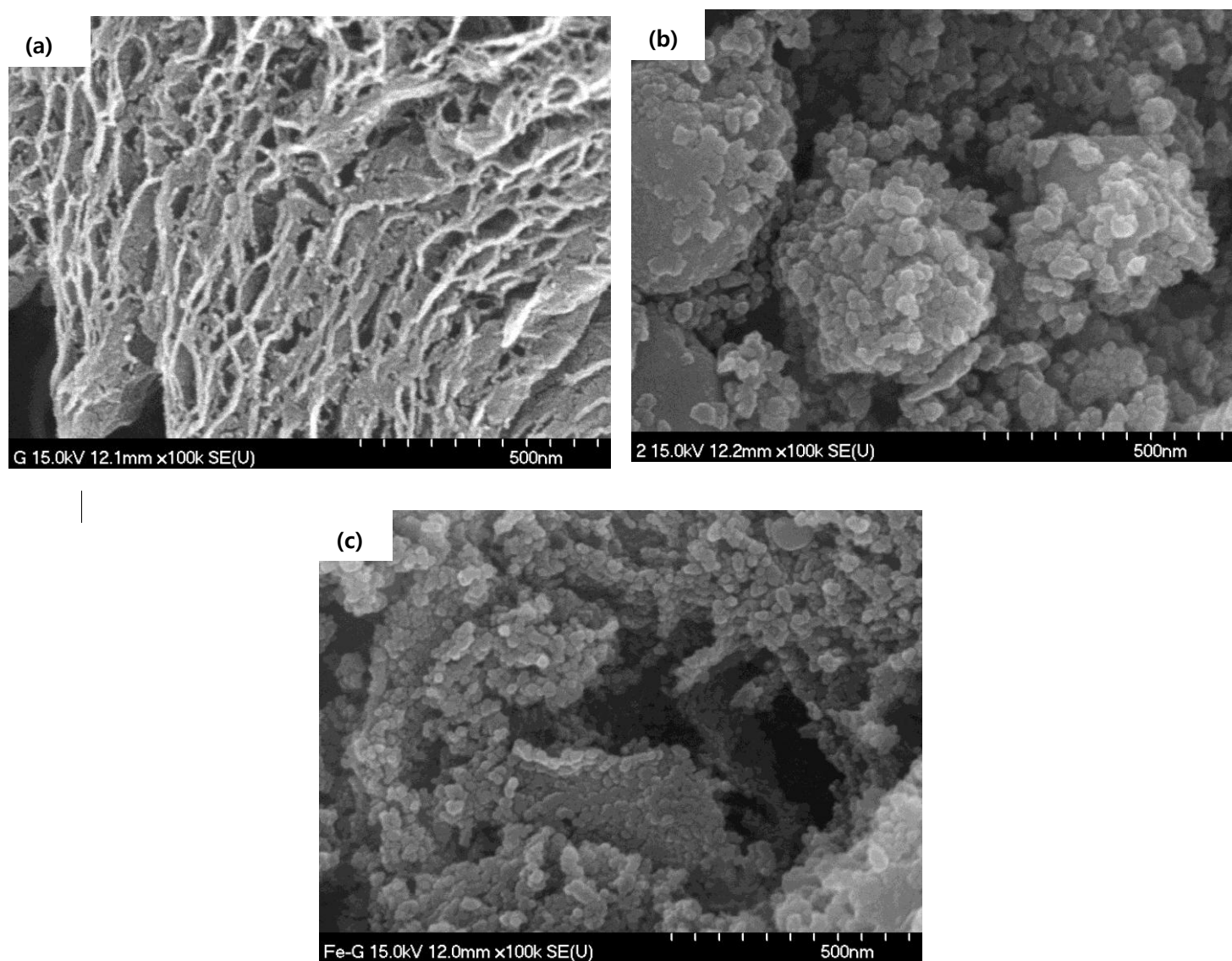


Figure S2. SEM images (a) GNS (b) Fe₃O₄ and (c) Fe₃O₄-GNS composite material prepared using microwave method

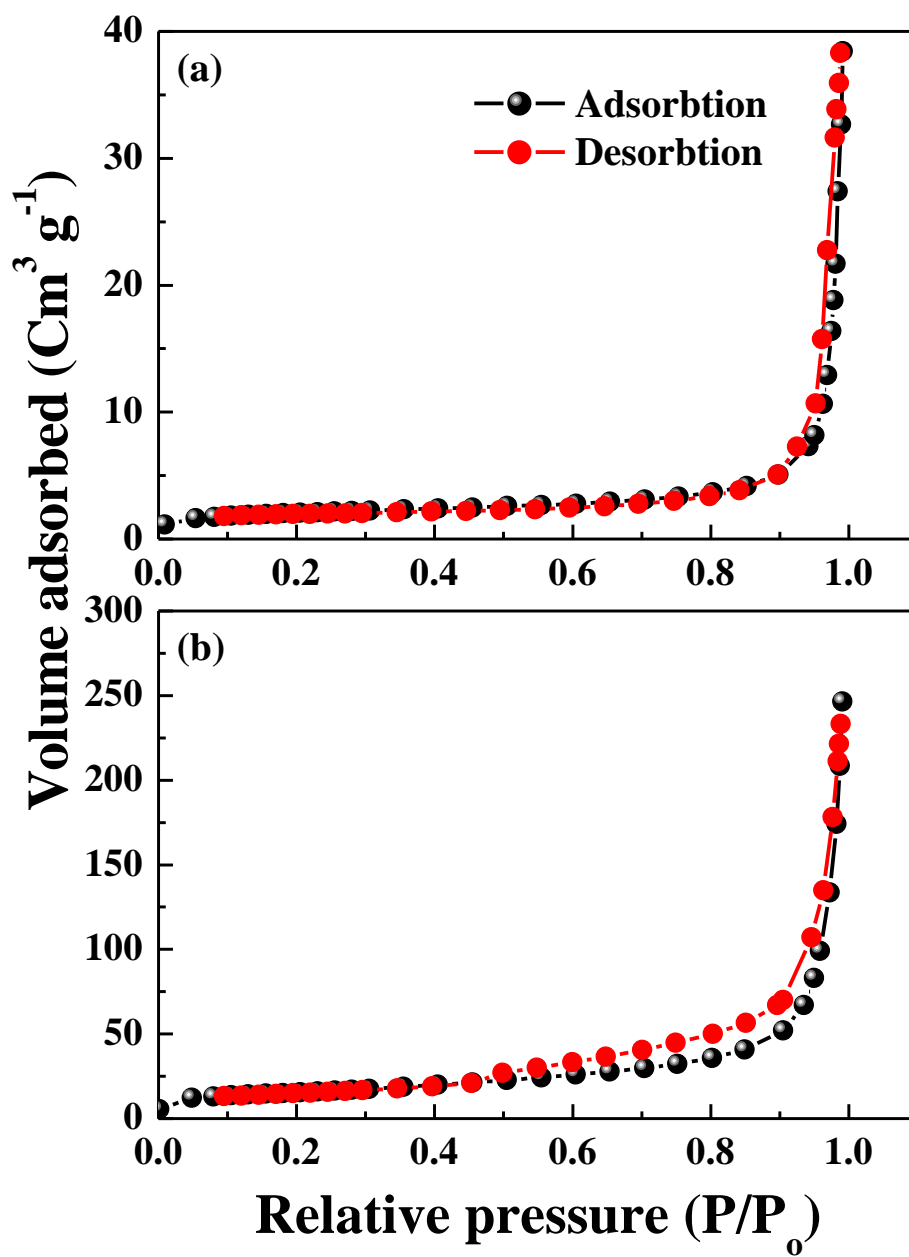


Figure S3. Adsorption/desorption isotherms of N₂ at 77 K on (a) Fe₃O₄ (b) Fe₃O₄-GNS hybrid composite.

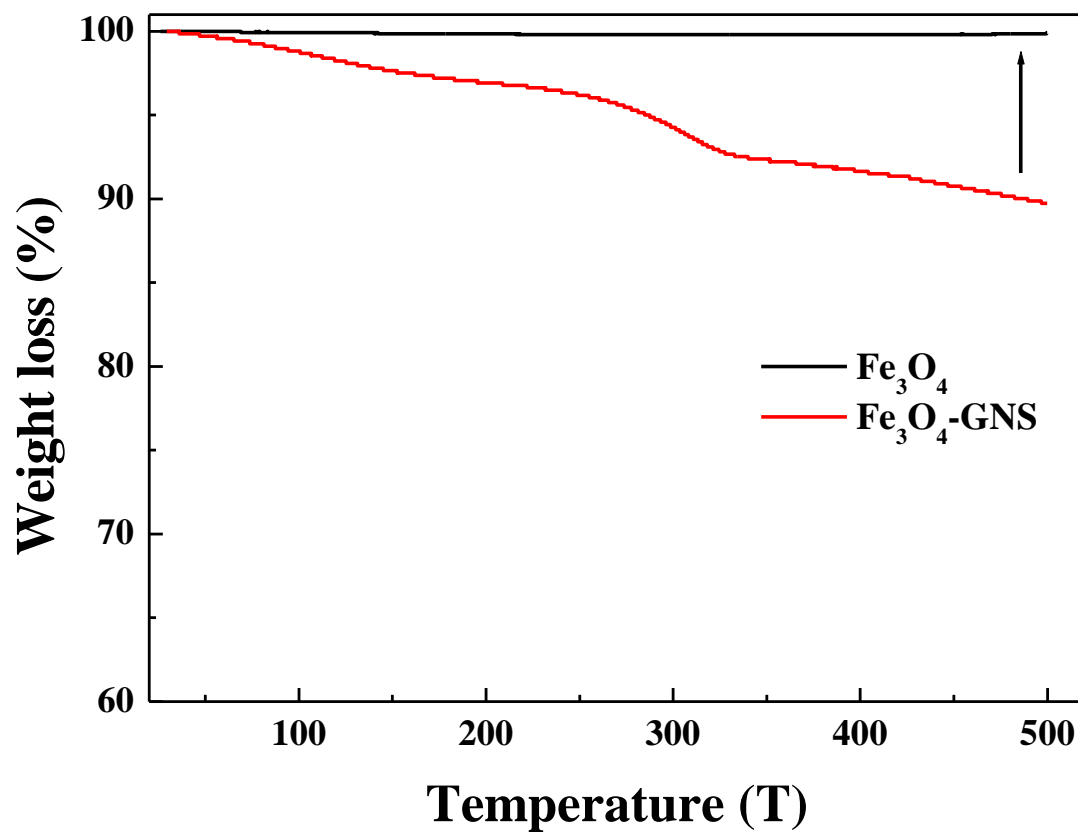


Figure S4. TGA analysis of pristine Fe₃O₄ and Fe₃O₄-GNS composite material prepared using urea assisted microwave irradiation method

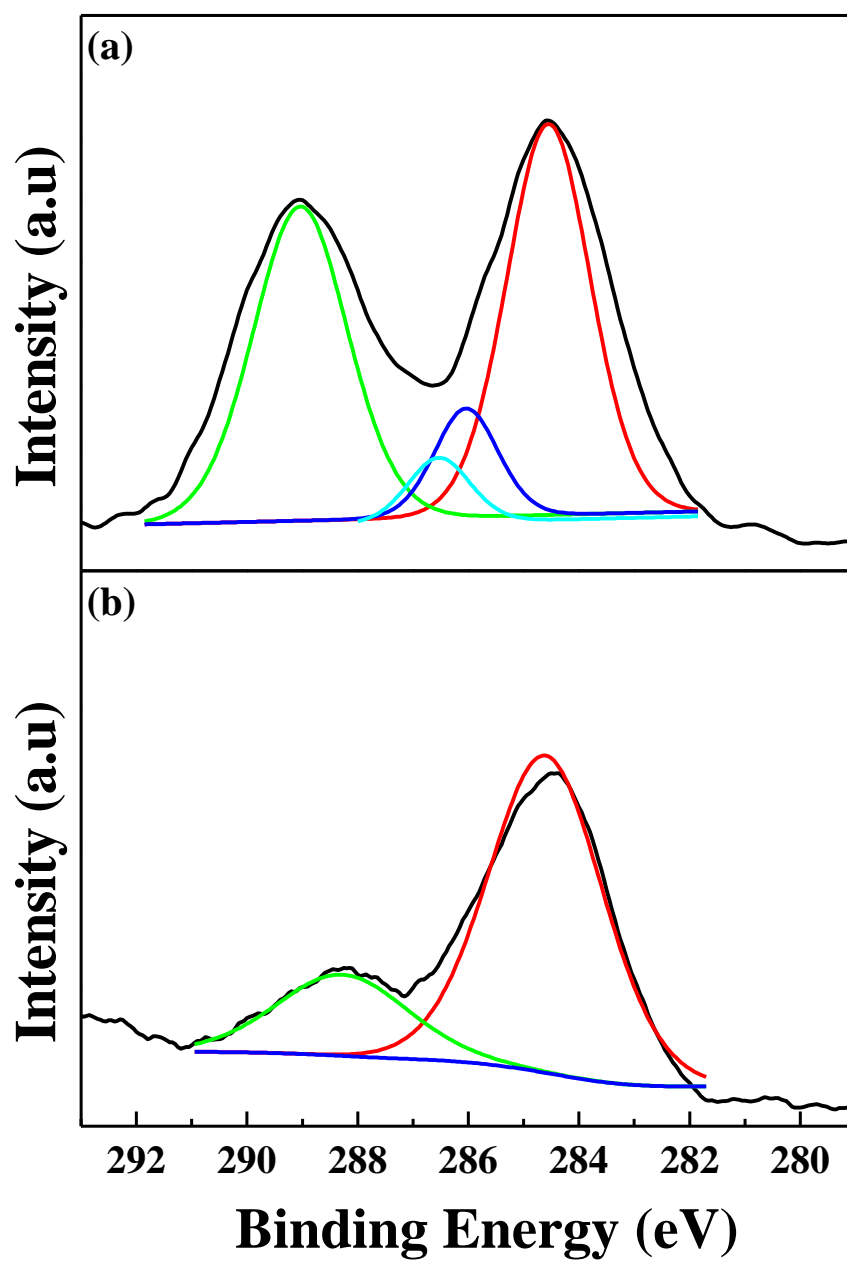


Figure S5 C 1s XPS spectra of (a) GO and (b) graphene in Fe₂O₃-GNS composite reduced by hydrazine vapor

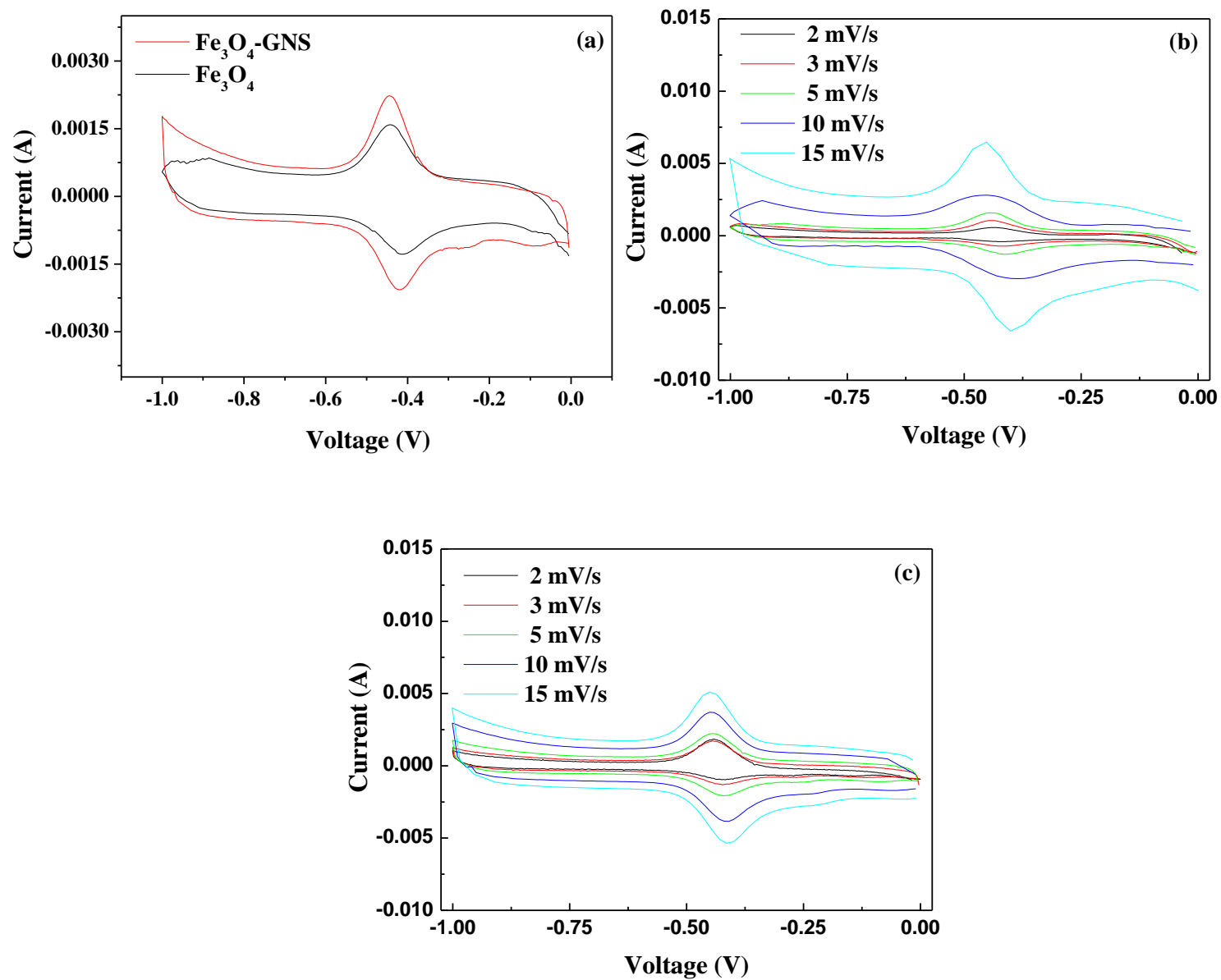


Figure S6. CV curves of (a) Fe_3O_4 and Fe_3O_4 -GNS electrodes in 1 M H_2SO_4 electrolyte at 5 mV/s scan rate between -1-0 V. (b) CV curves of Fe_3O_4 and (c) Fe_3O_4 -GNS electrodes at different scan rates between -1-0 V.

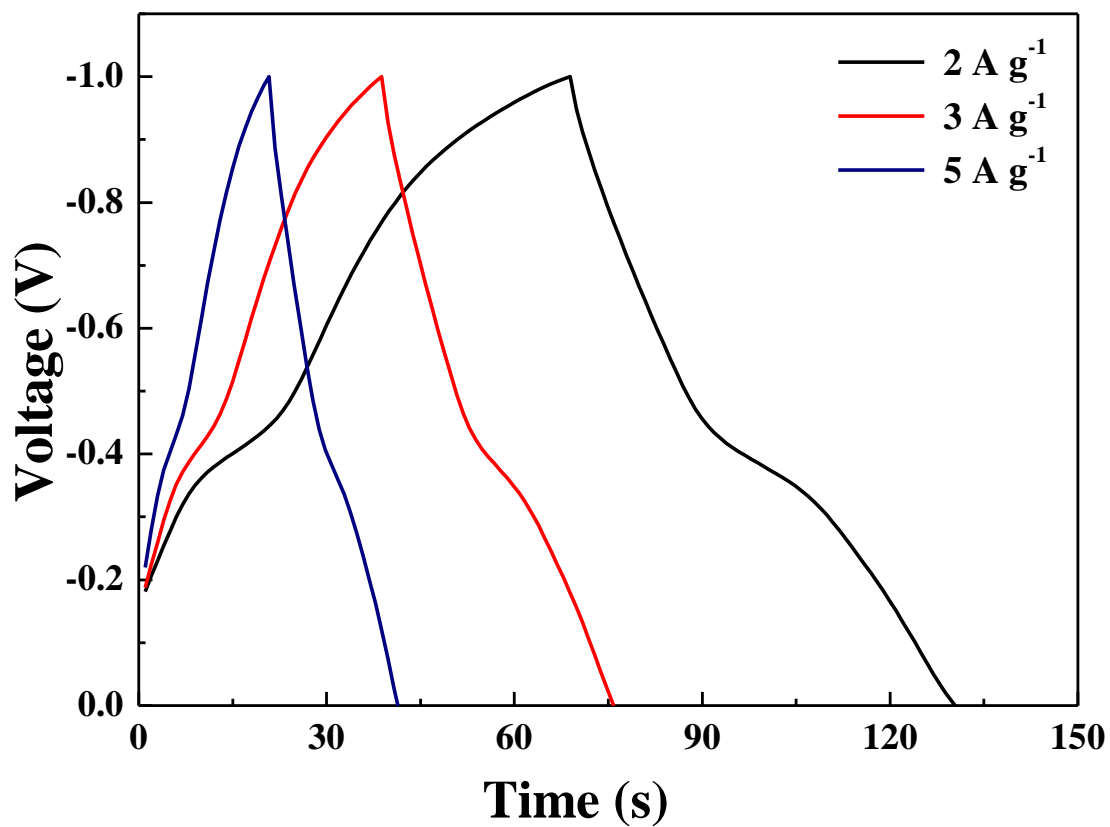


Figure S7. Charge discharge traces of Fe₃O₄-GNS electrode at various current densities between -1.0 V in 1M H₂SO₄ in three electrodes cell configuration.

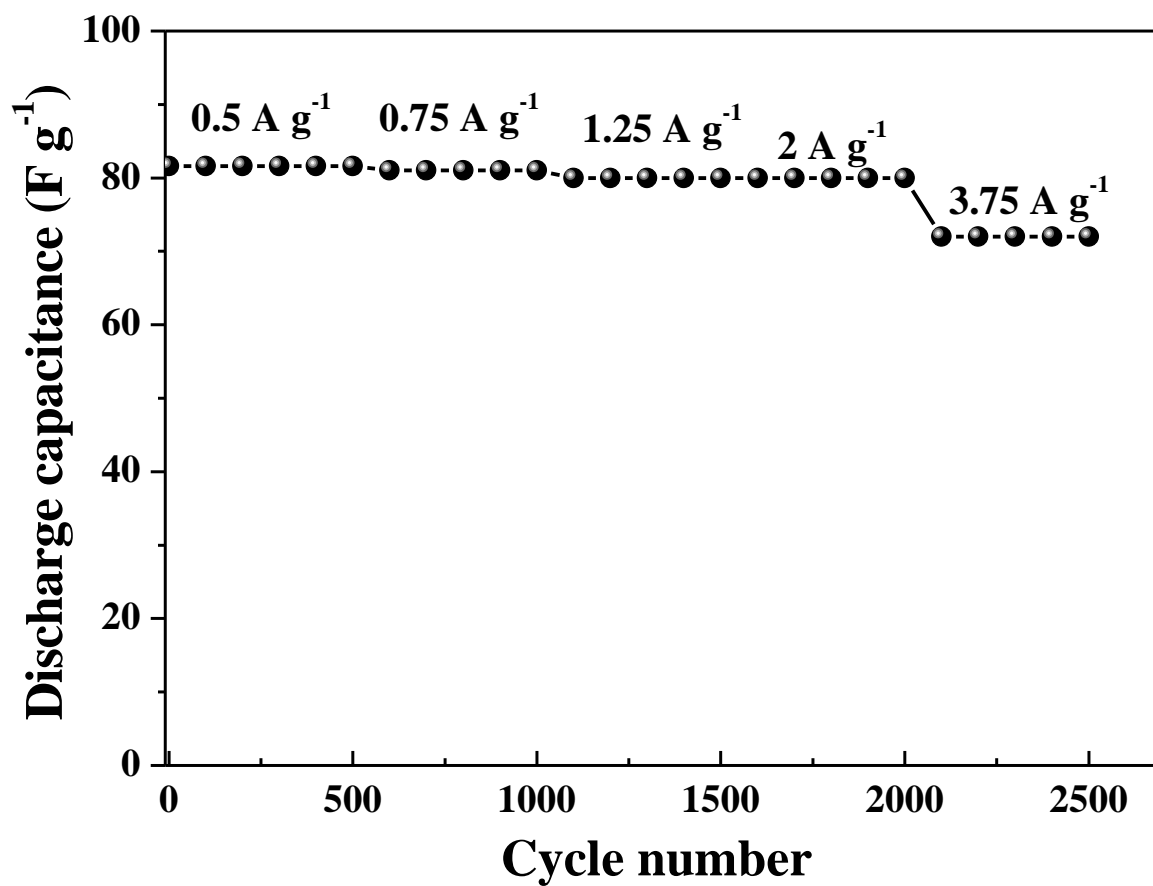


Figure S8. Rate performances of Fe₃O₄-GNS symmetric cell at various current densities between 0-1 V.

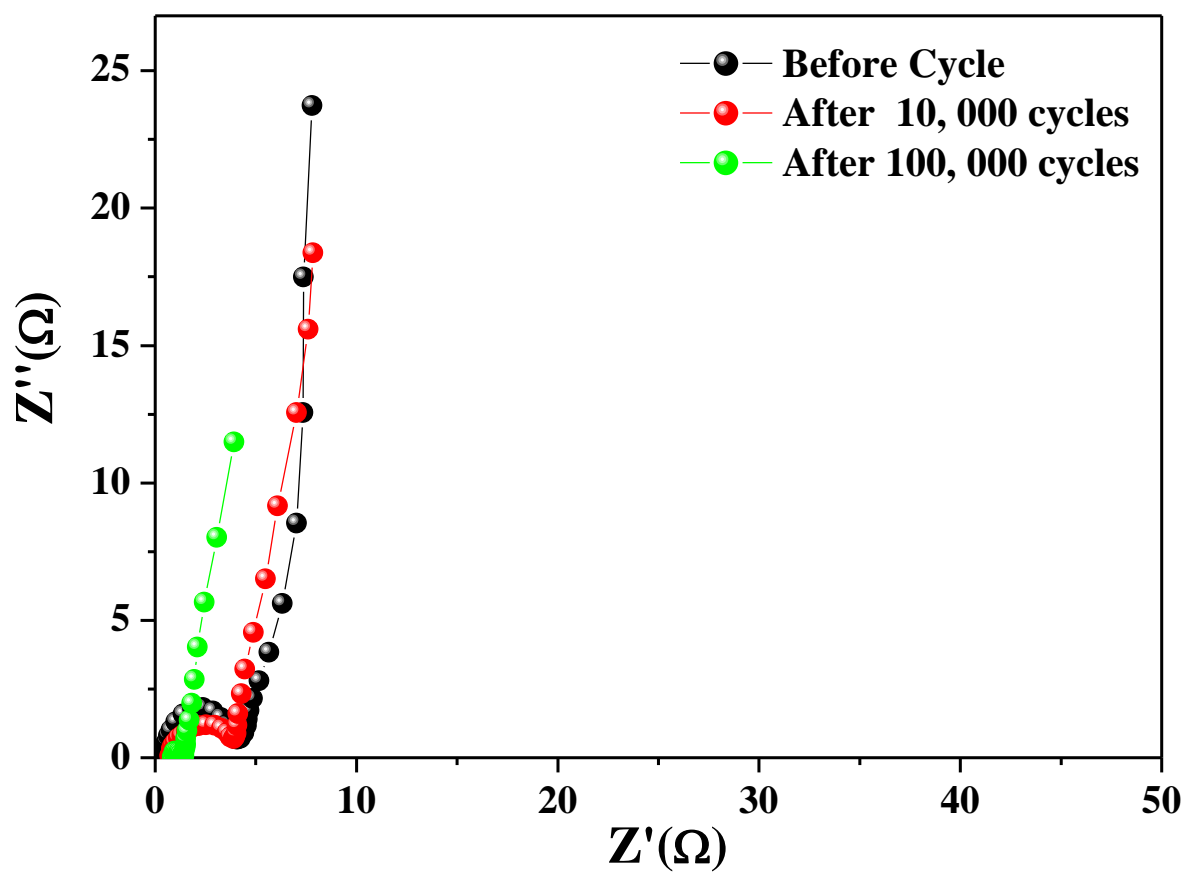


Figure S9. Nyquist plots of Fe_3O_4 -GNS symmetric cell recorded before and after 10,000 and 100,000 cycles at 3.75 A g^{-1} current density for between 0-1 V.