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Electronic Supplementary Information

Oxidizing Metal Ions with Graphene Oxide: The *In-situ* Formation of Magnetic Nanoparticles on Self-Reduced Graphene Sheets for Multifunctional Applications

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1. Materials and Characterization

Materials: Graphite powders (300 mesh) was purchased from Sigma-Aldrich. Sulfuric acid (98%), Sodium nitrate, and Iron(II) chloride tetrahydrate were bought from Sigma-Aldrich and used as received. Potassium permanganate was obtained from Fisher.

Characterization: Scanning electron microscopic SEM was performed using Nova nanoSEM 600, while transmission electron microscopy (TEM) observation was undertaken under JEOL JEM-2100 microscope at an acceleration voltage of 200 kV. Atomic force microscopic images were obtained by Agilent 5500 AFM. X-ray diffraction (XRD) was carried out using Miniflex II Desktop X-ray Diffractometer. The thermogravimetric analysis was made on a TA instrument with a heating rate of 10 °C in air. UV-vis spectra were collected using Beckman coulter DU 640 spectrophotometer. Fourier transform infrared spectra (FTIR) were recorded on a PerkinElmer spectrum GX FTIR system. X-ray photoelectron spectroscopic (XPS) measurements were performed on a VG Microtech ESCA 2000 using a monochromic Al X-ray source (97.9 W, 93.9 eV). Solid-state Magic Angle Spinning Nuclear Magnetic Resonance analyses were performed with a Varian VNMR 500 MHz NMR spectrometer operating at 125.62 MHz.

2. Sample Preparation

In a typical experiment, GO was prepared by acid oxidation of graphite powder according to the modified Hummers' method. Briefly, 3 g of 300 mesh graphite powders (Aldrich) was added to 70 ml sulfuric acid (98%), followed by the addition of 1.5 g sodium nitrate at room temperature. The mixture was then cooled down to 0 °C. Thereafter, 9 g KMnO₄ was slowly added to the mixture under vigorously stirring below 20 °C and kept stirring for 30 minutes at about 35 °C. Upon completion of the reaction, 15 ml of 30% H₂O₂ was added to the reaction vessel. Subsequently, the reaction mixture was filtered through a PVDF filter membrane with a pore size of 0.22 μm, washed consecutively with 1 M HCl and DI water, and further purified by dialysis. Finally, the resultant dispersion in water was ultrasonicated for 1 hour, followed by centrifugation at 4000 rpm for 30 minutes to produce GO. Then, the GO was used as an efficient oxidizing reagent to oxidize Fe²⁺

from FeCl_2 or FeSO_4 to form $\text{Fe}_3\text{O}_4/\text{rGO}$ via the spontaneous *in-situ* deposition of Fe_3O_4 nanoparticles onto the self-reduced GO surface (Scheme 1).

3. TEM Image of Fe_3O_4 Nanoparticle

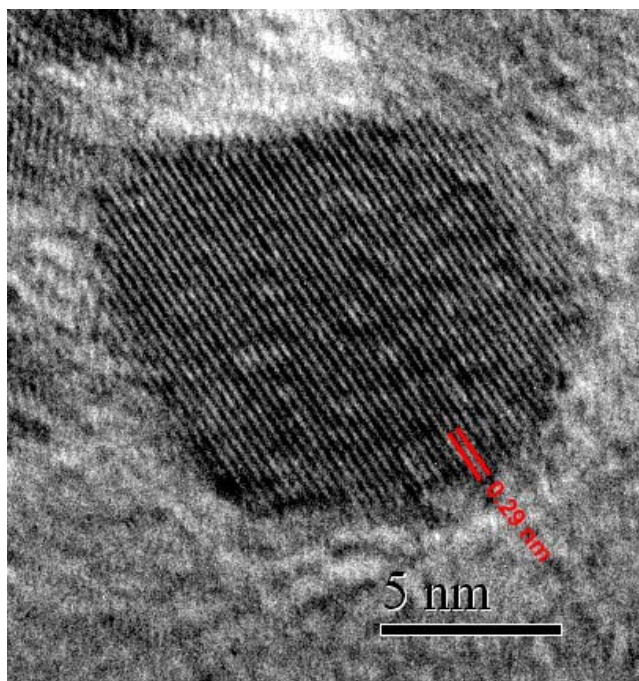


Figure S1. A HRTEM image of an individual Fe_3O_4 nanoparticle in $\text{Fe}_3\text{O}_4/\text{rGO}$.

4. Solid C^{13} NMR Spectra of GO Before and After Reduction

Solid-state Magic Angle Spinning Nuclear Magnetic Resonance analyses of graphene oxide and reduced graphene oxide were performed with a Varian VNMR 500 MHz NMR spectrometer (^1H frequency) operating at 125.62 MHz. The dried powder Samples were packed into 4 mm silicon nitride rotors with PTFE end caps spinning at 10 kHz. 3k to 12k FID transients were averaged using 8 sec relaxation delay and $4.0 \mu\text{s}$ 90° pulse width without decoupling. ^{13}C chemical shifts were corrected by using hexamethylbenzene ($\delta_{\text{CH}_3} = 17.3 \text{ ppm}$) as an external reference.

Solid state ^{13}C MAS NMR reflects the extent of graphene oxide reduction. Figure S2 shows ^{13}C NMR spectra of graphene oxide and reduced graphene oxide (rGO), obtained by HCl washing to remove Fe_3O_4 from the $\text{Fe}_3\text{O}_4/\text{rGO}$ composite, respectively. Three

distinct resonances dominate the spectrum of graphene oxide: the resonance centered at 134 ppm corresponds to unoxidized sp^2 carbons; the 60 ppm resonance is a result of epoxidation, and the 70 ppm is from hydroxylated carbons. For graphene oxide with a low degree of oxidation, the latter resonances overlap, and a weak broad resonance corresponding to carbonyl carbons is observed at 167 ppm. After reduction, the 60 ppm, 70 ppm and 167 ppm resonances all disappears. The peak at 134 ppm shifts to 123 ppm because of the change in the chemical environment of the sp^2 carbons. The resonance centered at 116 ppm come from the PTFE end caps of the solid state NMR rotor.

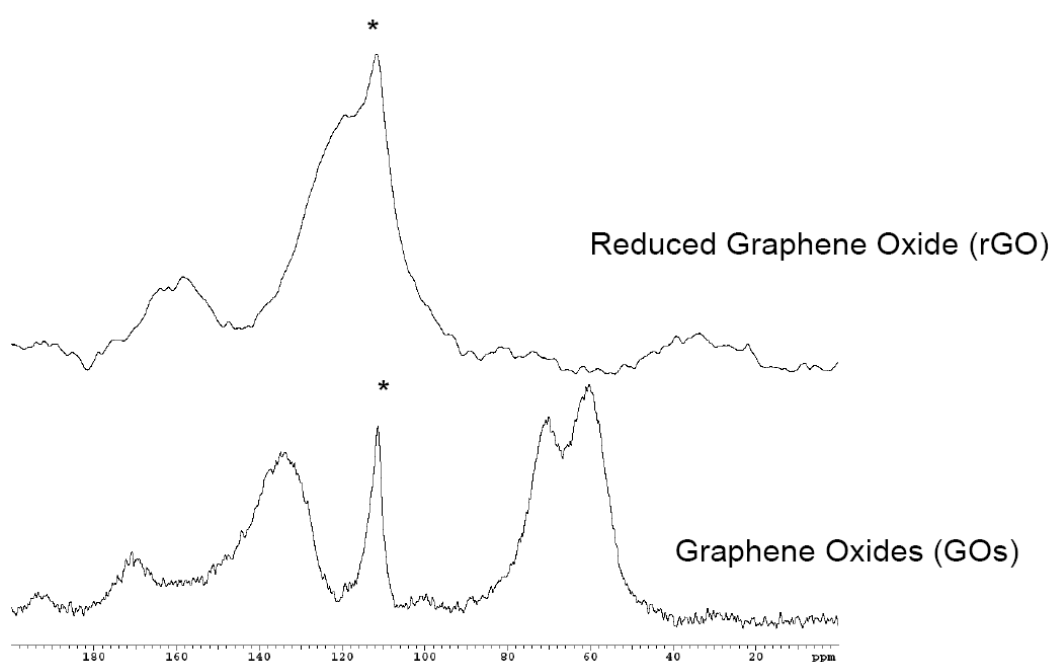


Figure S2. Solid state ^{13}C MAS NMR spectra (125.62 MHz; 10 k rpm) of graphite oxide and graphene; *indicates resonance from the PTFE end caps.

To overcome the possible surface-area loss through π - π stacking in GN or rGO electrodes, we have recently developed self-assembled GO/carbon nanotube layer-by-layer films for high-performance supercapacitors with nanotubes bridging between graphene sheets to serve as fast electronic and ionic conducting channels for a high rate capability and to ensure the access of the intrinsically large surface area of GO for a high capacitance. Since the rGO-supported Fe_3O_4 nanoparticles can not only serve as separators to gain the intrinsically large surface area of rGO (Figure 1d) but also impart

pseudo-capacitance, the newly-developed $\text{Fe}_3\text{O}_4/\text{rGO}$ sheets are of great promise for charge storage applications. Thus, we performed the cyclic voltammetric (CV) measurements on rGO and $\text{Fe}_3\text{O}_4/\text{rGO}$ in KOH electrolyte (6 M) at 20 °C. As expected, Figure S3 shows a much higher electric double-layer capacitance (EDLC), along with additional Faradic pseudo-capacitance, for the $\text{Fe}_3\text{O}_4/\text{rGO}$ hybrid than that of the rGO obtained from $\text{Fe}_3\text{O}_4/\text{rGO}$ by HCl washing to remove Fe_3O_4 . This, together with the observed magnetic property, implies some potential energy storage and even biomedical applications for the newly-developed $\text{Fe}_3\text{O}_4/\text{rGO}$.

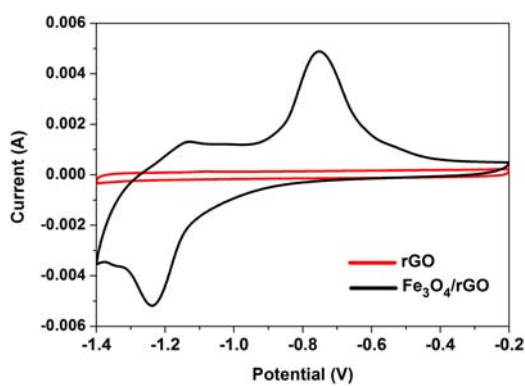


Figure S3. CV curves measured on glassy carbon (GC) electrodes in an aqueous KOH (6 M) solution at a scan rate 50 mV/s for $\text{Fe}_3\text{O}_4/\text{rGO}$ and rGO obtained by HCl washing to remove Fe_3O_4 from $\text{Fe}_3\text{O}_4/\text{rGO}$.