

Photothermally-Assisted Fabrication of Fluoride/Graphene Composite Paper Cathodes for High-Energy Lithium-Ion Batteries

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1. Materials and Methods

Graphene oxide (GO)

GO was synthesized from flake graphite (Asbury Carbons, 230U Grade, High Carbon Natural Graphite 99⁺) by a modified Hummers method.^{9,10} The graphite powder (2.0 g) was pre-oxidized by stirring it into a concentrated H₂SO₄ (20 mL) solution in which K₂S₂O₈ (1.0 g) and P₂O₅ (1.0 g) were completely dissolved at 80°C. The mixture, in a beaker, was kept at 80°C for 4.5 h using an oil bath. After the mixture was cooled and diluted with 1 L of DDI (distilled deionized) water, the pretreated product was filtered with a Nylon membrane filter (47 mm diameter, 0.2 µm pore size, Milipore) and washed on the filter until the pH of filtrate water became neutral. The shiny, dark-gray, pre-oxidized graphite was dried in air overnight. Then it was dispersed by stirring into chilled H₂SO₄ (75 mL) in an Erlenmeyer flask in an ice bath. KMnO₄ (10 g) was added slowly with stirring to keep the temperature of reaction mixture below 20°C. The resulting thick, dark green paste was allowed to react at 35°C for 2 h followed by addition of DDI water (160 mL) to form a dark brown solution. To avoid over-flow of the mixture due to rapid temperature rise with foaming by water addition, the flask was chilled in an ice bath and water was added in ~5 mL aliquots with close monitoring of temperature (kept below 50°C). After additional stirring for 2 h, the dark brownish solution was further diluted with distilled water (500 mL), and H₂O₂ (30%, 8.3 mL) was added slowly. The color of the mixture turned bright yellow. The mixture was allowed to settle overnight. The supernatant was decanted and the remaining product was repeatedly centrifuged and washed with DDI water until the pH of the solution became neutral. (At this stage, the Mn concentration in the supernatant was below 0.1 ppm by AAS). Then, the obtained product was diluted to make a ~0.5 % w/w aqueous dispersion for storage.

FeF₃ nanoparticles

FeF₃ nanoparticles were synthesized by a room-temperature co-precipitation approach, modified from a previously reported procedure.¹⁷ 10 mL of NH₄HF₂ (1.5 M) aqueous solution was added to 10 mL of Fe(NO₃)₃ (0.25 M) ethanol solution dropwise, followed by vigorous stirring for 3 h. 50 mL of ethanol was added sequentially, and the white (NH₄)₃FeF₆ products were washed and harvested with ethanol by centrifugation. To convert the (NH₄)₃FeF₆ precursor into FeF₃ nanoparticles, the solid precipitates were vacuum dried at 75°C, followed by calcination at 400°C with a flow of argon (~90 mL min⁻¹) for 2 h.

Photothermally reduced FeF₃/GO (FeF₃/rGO) composites

FeF₃ nanoparticles were dispersed in 1 mL of DDI water by sonication to obtain a homogeneous suspension, and then mixed with a desired amount of the aqueous GO suspension. The mixture was sonicated for another 2 h and vacuum-filtered through an

anodized aluminum oxide (AAO) membrane filter (47 mm diameter, 0.2 μm pore size, Whatman), followed by air drying and detaching from the membrane. The free-standing FeF_3/GO papers were cut by a razor blade into smaller ribbons, and exposed to a single, close-up (<2 mm) digital camera flash (window size of 10 mm $\times$ 20 mm). The typical flash durations ranged from 1-2 milliseconds. The flash energies were measured using a Model PS-100 spectroradiometer, and the typical flash energies applied to the composite papers were calculated by integrating the total fluence (J cm^{-2}) of the irradiance-wavelength plots.

Hydrazine reduced FeF_3/GO ($\text{FeF}_3/\text{H-rGO}$) composites

10 mL of the aqueous GO suspension was mixed with 100 mL of dimethylformamide (DMF) to obtain a stable, light brown suspension by stirring. Chemical reduction of the suspended GO were carried out with hydrazine monohydrate (1 $\mu\text{L}/3$ mg GO) for 12 h at 80°C. Appropriate amount of FeF_3 nanoparticles were dispersed in the resulting homogenous H-rGO suspension by sonication, and the mixture was filtered and vacuum dried at 100°C.

Unsupported (bare) FeF_3 electrodes

The unsupported FeF_3 electrodes were prepared by mixing the FeF_3 nanoparticles, carbon black (Timcal) and poly(vinylidene fluoride) (PVDF) at a weight ratio of 50:35:15 in anhydrous N-methyl-2-pyrrolidone) (NMP) and pasting onto an Al foil.

Characterization

The morphology of as-prepared samples was investigated using Hitachi S-4800-II field emission scanning electron microscopy (FE-SEM), JOEL 2100F field emission transmission electron microscopy (FE-TEM), and Hitachi HD-2300A FE-STEM operated at 200 kV with energy dispersive spectroscopy (EDS) detectors. X-ray diffraction (XRD) patterns were collected by a Scintag XDS2000 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418$ Å) at 40 kV, a step size of 0.01° and a step time of 0.5 s. X-ray photoelectron spectroscopy (XPS) was performed using an Omicron ESCA Probe equipped with an electron flood gun. The $\text{AlK}\alpha$ radiation (1486.6 eV) was used as an excitation source and the binding energy scale was calibrated with respect to adventitious carbon (C1s). Raman spectroscopy was conducted using an Acton TriVista CRS Confocal Raman System with a $\times 100$ objective lens at room temperature and a 514.5 nm laser beam.

The zeta-potential of the GO and FeF_3 aqueous suspensions was measured using a Malvern zeta sizer at 25°C. Thermogravimetric analysis (TGA, Mettler Toledo, TGA/SDTA851^o) was performed on crushed composite papers in air. The samples were heated to 100°C and held at 100°C for 10 min to remove any volatiles and adsorbed water. Then the temperature was ramped to 800°C at the rate of 10°C min^{-1} in flowing air. The weight loss, after correcting for oxidation of FeF_3 , was used to calculate the carbon content. Separate TGA with bare FeF_3 nanoparticles was run at the same conditions to obtain data to correct the weight gain of the composites. Sheet resistance and conductivity measurements were made with a four-point probe technique with an electrode separation of 1 mm using a Keithley 2400 sourcemeter. UV-vis absorbance

spectra of both GO and FeF₃/GO films were collected using a Varian Cary 500 spectrometer.

Electrochemical Test

Electrochemical measurements were carried out using two-electrode coin cells with Li metal as the counter electrode. Microporous glass-fiber membrane (Whatman) was used as separator, and an Al foil was employed to connect the composite papers to external leads. The electrolyte consisted of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v). The cells were assembled in an argon-filled glove box, and galvanostatic measurements were conducted with a BT2000 Potentiostat/Galvanostat system (Arbin Instruments) at various current densities, typically in the voltage range of 1-4.5 V vs Li/Li⁺. Cyclic voltammograms (CV) were recorded over the same voltage range at scan rates of 0.2-10 mVs⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were conducted using a Solartron 1260 impedance analyzer coupled with a Solartron 1286 electrochemical interface by applying an AC voltage of 10 mV amplitude and DC open circuit voltage (OCV) in the frequency range of 1 MHz-0.01 Hz at room temperature.

2. Result

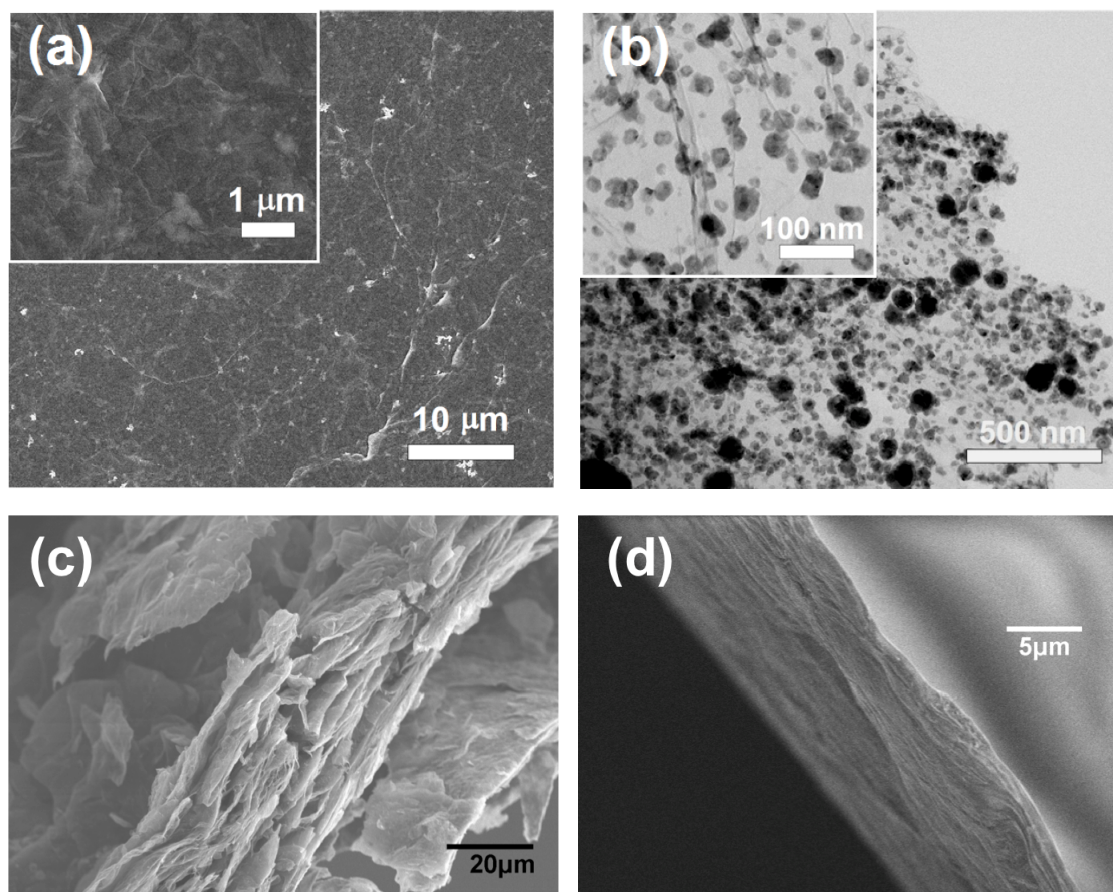


Figure S1. (a) SEM image of the top surface of a FeF₃/GO paper. Inset shows the compact GO sheets wrapping FeF₃ nanoparticles underneath at higher magnification. (b) TEM image of a crushed FeF₃/rGO paper. Inset shows a uniform distribution of FeF₃ nanoparticles at higher magnification. (c) Cross-sectional SEM image of FeF₃/rGO, after photothermal reduction. The flaky and expanded structure is easily observed. (d) Cross-sectional SEM image of FeF₃/H-rGO structure using hydrazine-reduced graphene oxide (H-rGO). The FeF₃/H-rGO structure is much more compact due to the fact that oxygen groups are not removed after paper formation (through thermal or photothermal reduction), and hence most likely suffer from hindered ion diffusion through the structure.

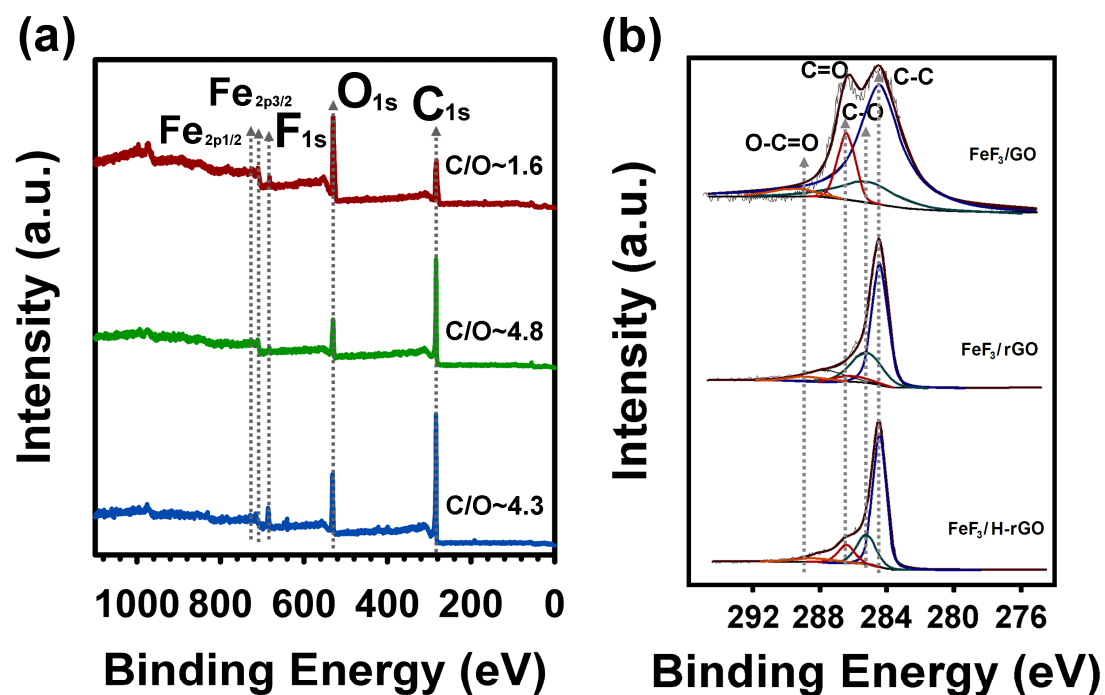


Figure S2. (a) XPS spectra and (b) deconvoluted C_{1s} peak of FeF₃/GO, FeF₃/rGO and FeF₃/H-rGO papers. Peak deconvolution of GO yields a C/O atomic ratio of ~1.6, and the C/O ratio increased to ~4.8 and 4.3 in FeF₃/rGO and FeF₃/H-rGO papers, respectively indicating substantial deoxygenation. The F_{1s}, Fe_{2p}1/2 and Fe_{2p}3/2 peaks were unchanged among the three samples.

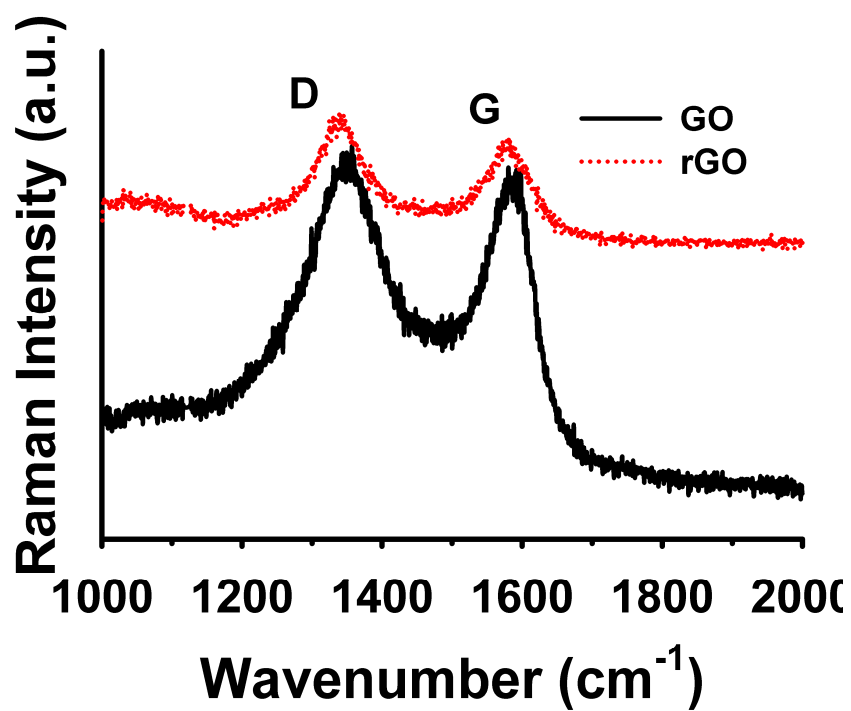


Figure S3. Raman spectra of GO and rGO papers showing little changes in the intensity ratios of the D and G bands before and after photothermal reduction.

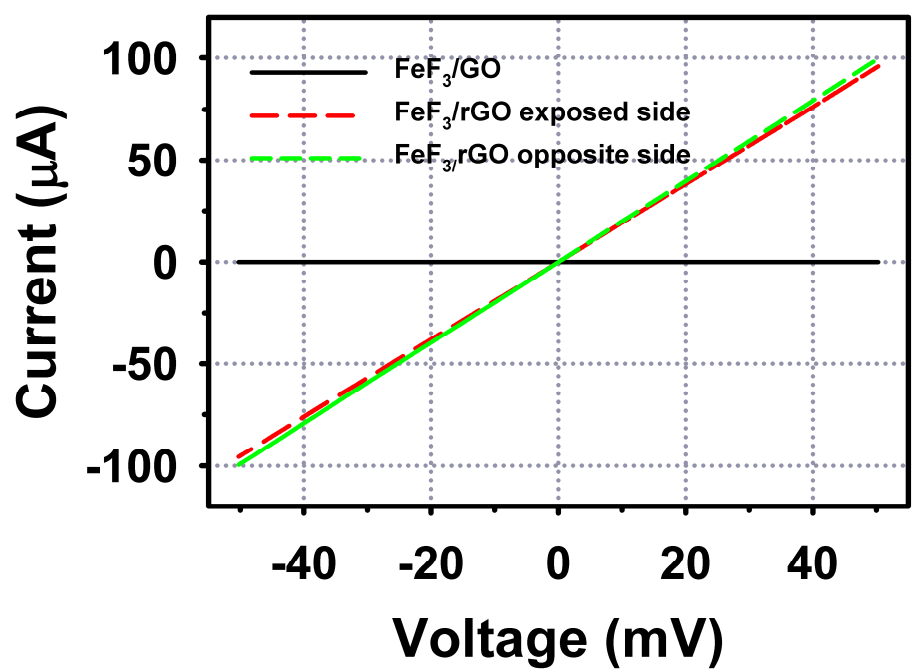


Figure S4. I-V curves obtained by four-point transport measurements of FeF_3/GO and FeF_3/rGO papers at room temperature.

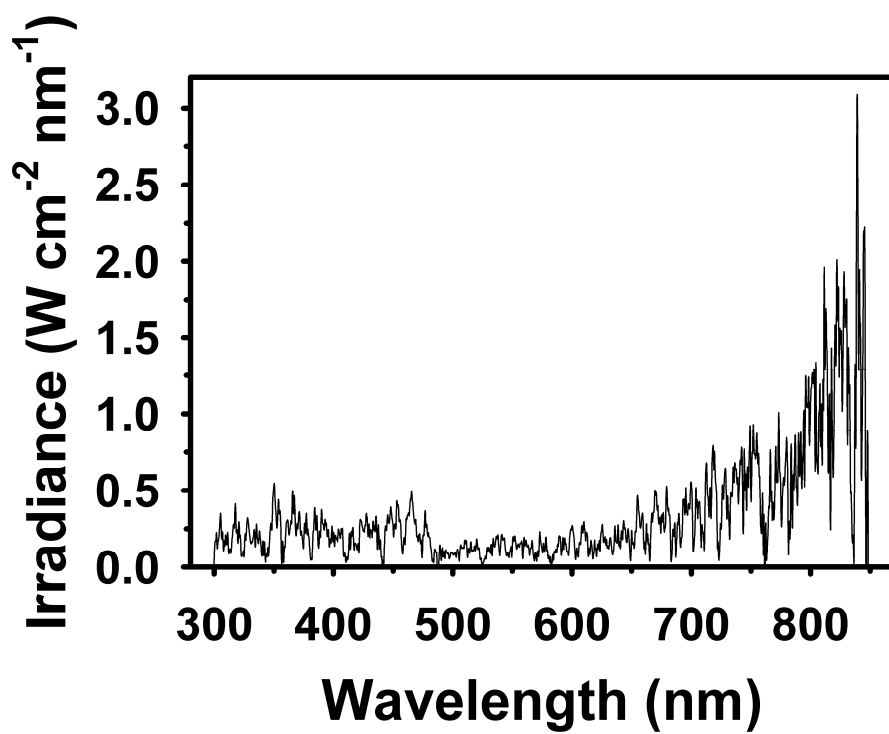


Figure S5. Light intensity spectrum of a single camera flash used in this preparation at a distance < 2 mm.

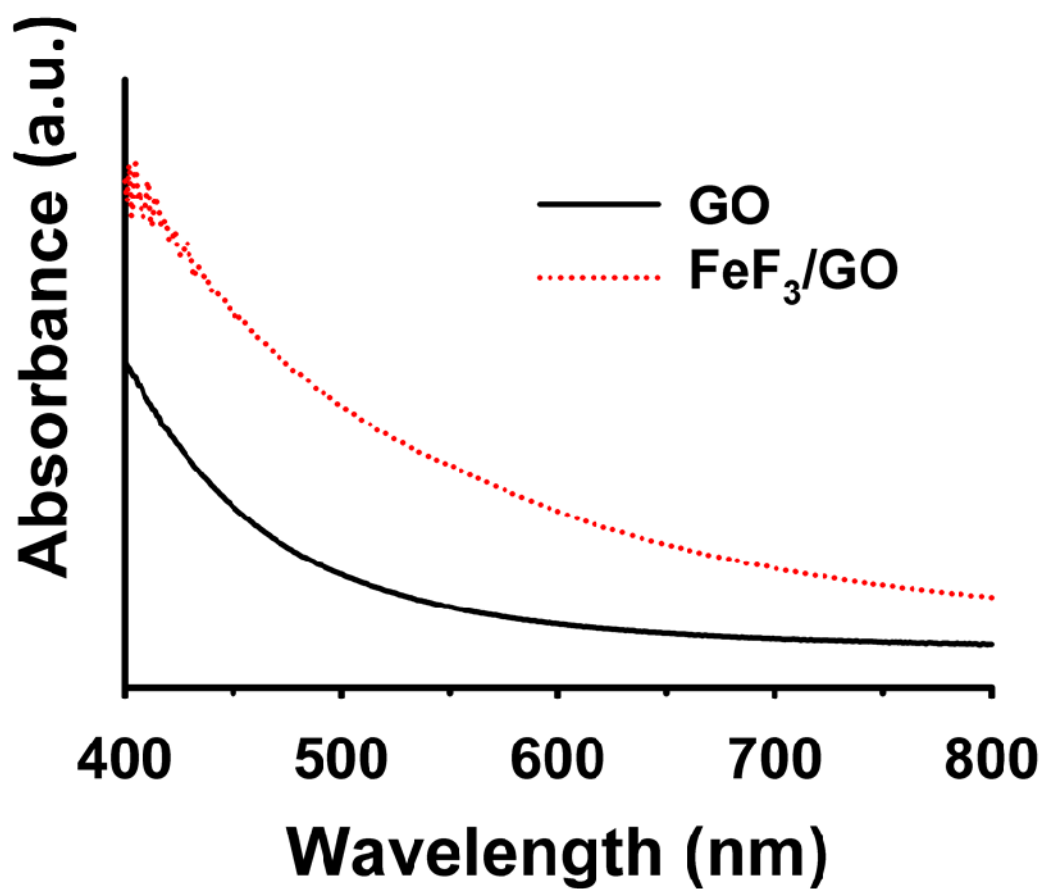


Figure S6. UV-vis spectra of GO and FeF₃/GO papers. An estimate of ~85% of the incident light was absorbed by a FeF₃/GO paper over the visible light range of 400-800 nm.

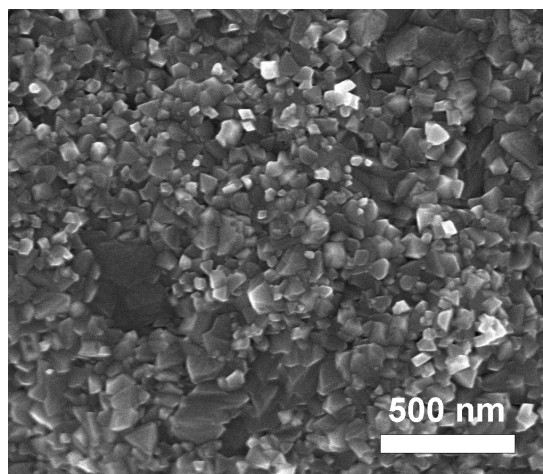


Figure S7. SEM image of FeF₃/GO papers heated at 400°C in Ar, showing emergence of bulk metallic Fe particles on the film surface. This implies that heating in H₂ would cause FeF₃ reduction.

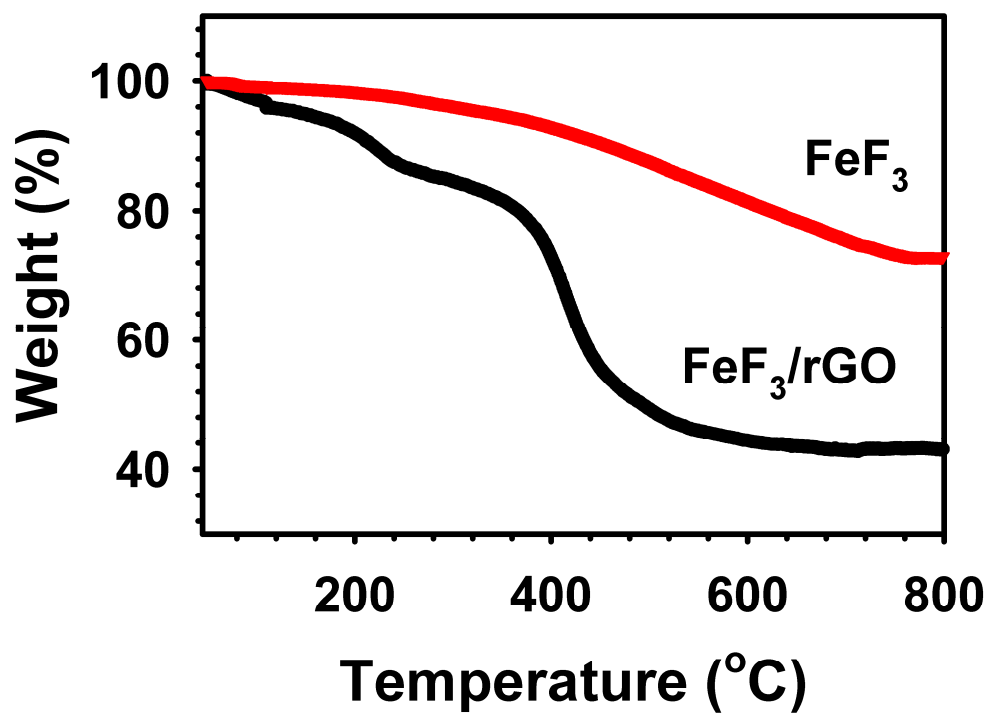


Figure S8. TGA curves of FeF₃ and FeF₃/rGO papers.

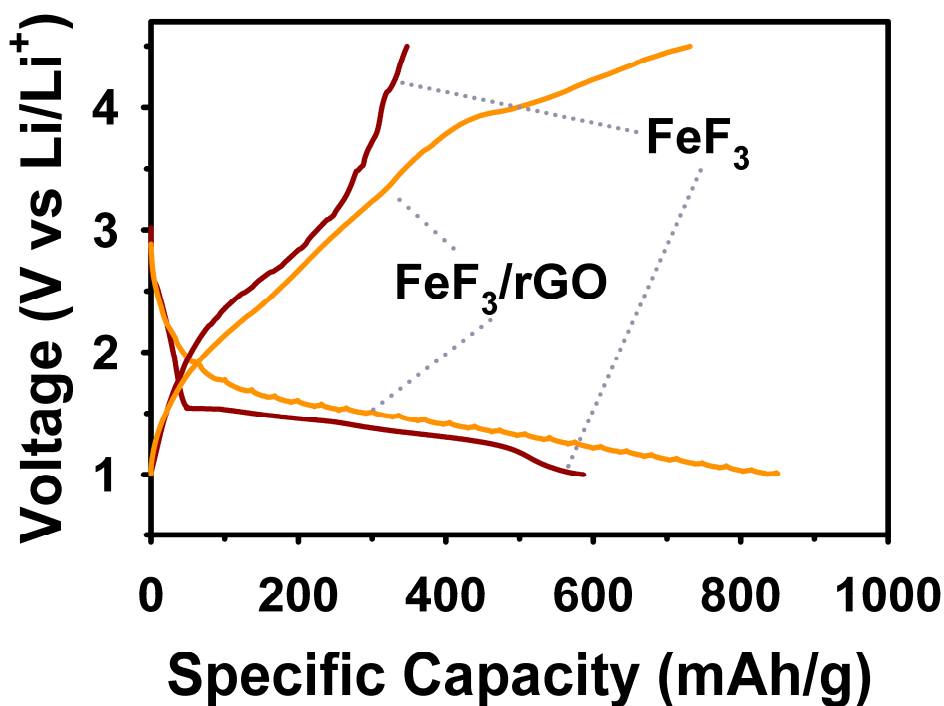


Figure S9. First galvanostatic charge/discharge profiles of unsupported FeF_3 and FeF_3/rGO paper cathodes at a current density of 20 mA g^{-1} . The specific capacity of unsupported FeF_3 cathode was calculated using the active material mass, and the specific capacity of FeF_3/rGO paper was calculated using the total mass.

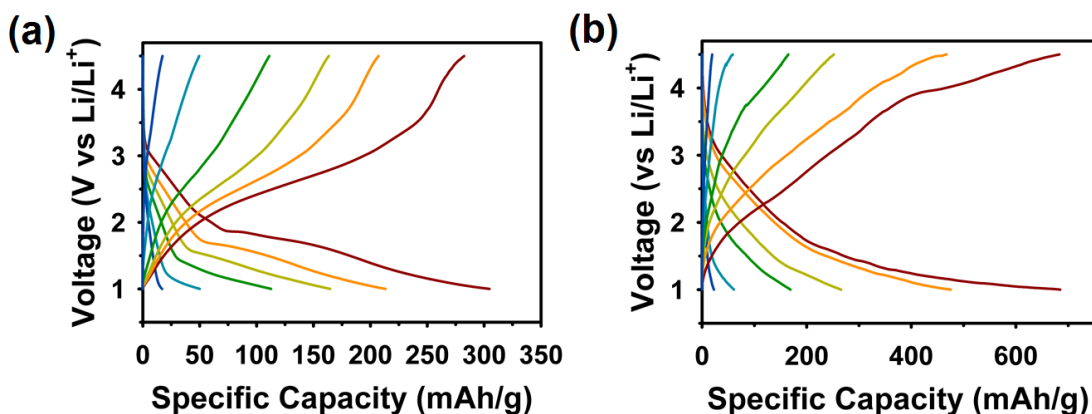


Figure S10. Fifth-cycle galvanostatic charge/discharge profiles of (a) unsupported FeF_3 cathodes and (b) FeF_3/rGO papers between 1-4.5 V at current densities of 20, 50, 100, 200, 500, 1000 and 2000 mA g^{-1} .

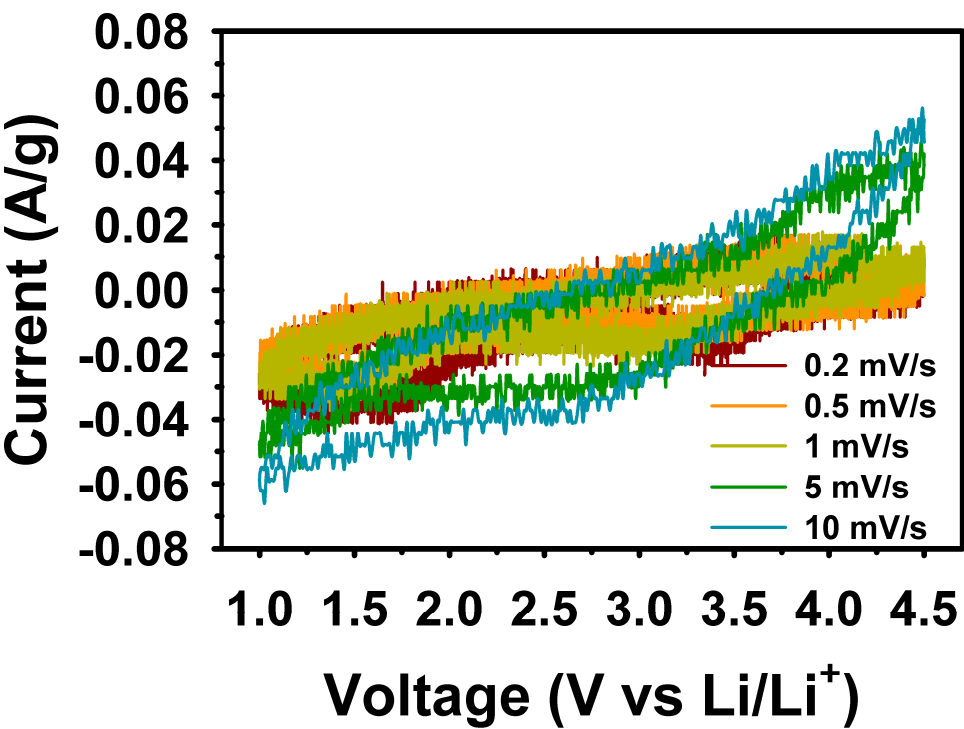


Figure S11. CV curves of photothermally reduced rGO papers at different scan rates.

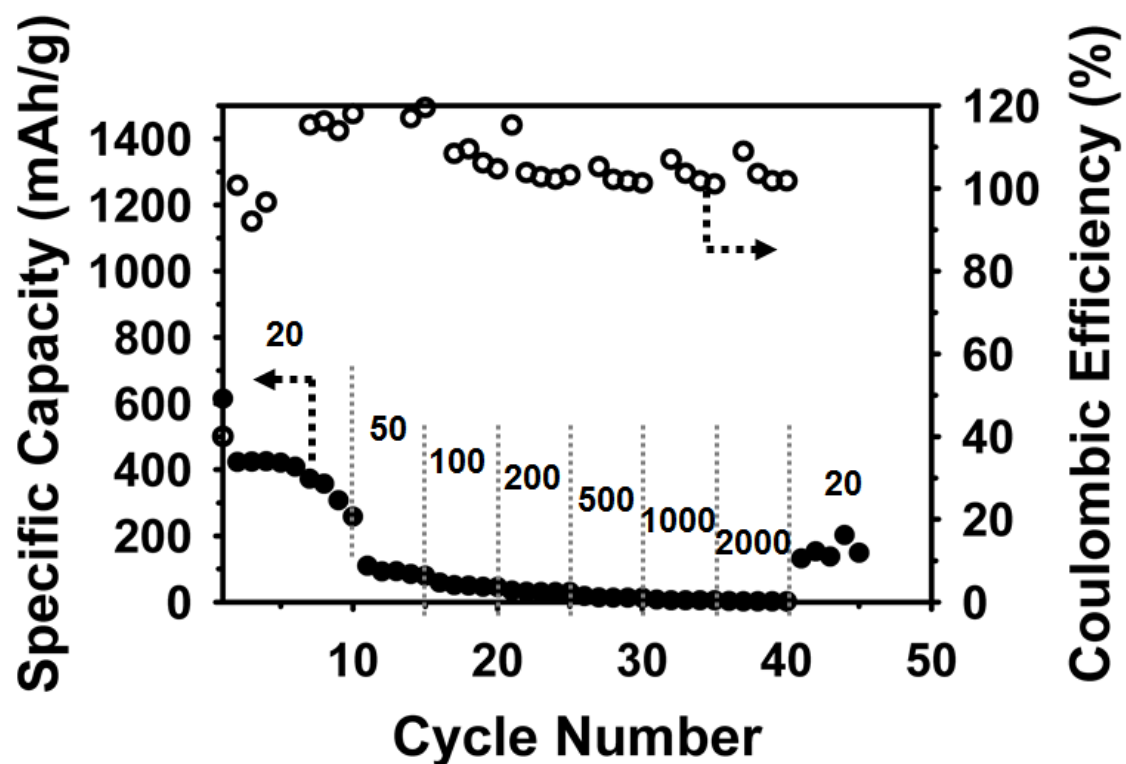


Figure S12. Specific discharge capacity and coulombic efficiency of photothermally reduced rGO papers between 1-4.5 V at current densities of 20, 50, 100, 200, 500, 1000 and 2000 mA g⁻¹.

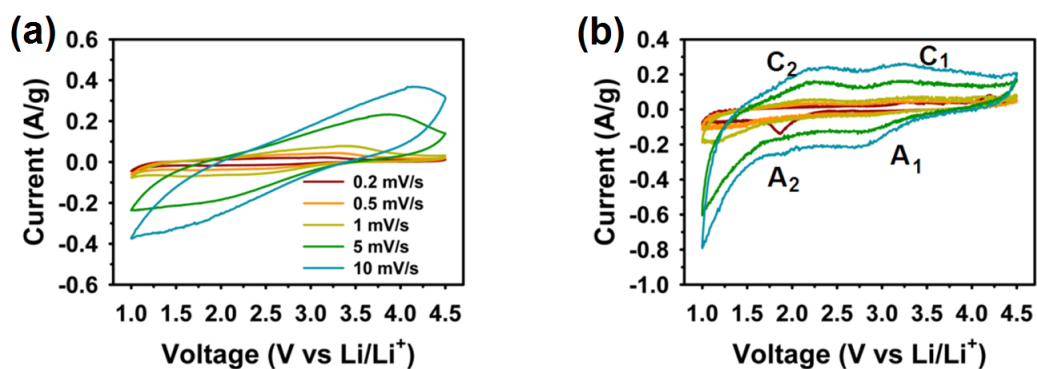


Figure S13. Cyclic voltammogram curves of (a) unsupported FeF₃ cathodes and (b) FeF₃/rGO papers at different scan rates.