

Supporting Information

Collector and binder-free high quality graphene film as high performance anode for lithium-ion batteries

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Experimental Section

I. Preparation of graphene

The detailed preparation process has been described in our previous report.¹ In order to fully exfoliate graphite into graphene, a solid-exfoliation process was employed to prepare previously exfoliated graphite. Natural flaked graphite was mixed and saturated with acids

consisting of concentrated sulfuric acid and concentrated nitric acid in a volume ratio of 4:1. The reaction system was stirred with excess FeCl_3 or NH_4NO_3 (>0.25 g/ml in the mixture) for 24 h to form the intercalated graphite compound. The concentration of nitric acid should be maintained at 10 mol/L (as higher concentrations will reduce the conductance of the resulting graphene). The mixture was then carefully vacuum filtered and washed with deionized water for 5 times until the pH of the solution was 6. After being dried at 60°C in a vacuum oven for 2 h, the graphite was loaded in a ceramic vessel, placed in a microwave oven, and irradiated at 500 W for 90 s. Under microwave irradiation, the precursors expanded rapidly, accompanied by “lightening.”

In a typical synthesis of graphene, the PEG was dispersed in chlorosulfonic acid (CSA) and ultrasonicated for 10 min, forming a stable dispersion which attributed to the protonation of the graphitic material. The dispersion was allowed to settle for 2 h, allowing better intercalation of CSA. Then, hydrogen peroxide was slowly added into the dispersion to react with the intercalated CSA. The generated O_2 , HCl , and SO_3 gases exfoliated the graphite to form grapheme sheets (GS). Excess hydrogen peroxide is needed to ensure that CSA is quenched completely. After washing out the acid, the GS floated to the top of water and could be easily collected by filtration. Before use, the GS were dispersed in water by sonication and spray dried at 100°C .

Then, as-prepared graphene, nano carbon fiber and carbon black were dispersed in ethenol with a mass ratio of 80:10:10. The concentration of graphene is 1 mg mL⁻¹. The dispersion was probe-sonicated for 30 min, then vacuum filtration of the as-prepared dispersion results in the formation of a uniform graphene film with an areal density of about 3.5 mg cm⁻².

II. Structural and electrochemical characterization

X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda=1.54$ Å). The accelerating voltage was set at 40 kV with 30 mA flux at a scanning rate of 8° min⁻¹ in the 2 θ range of 20–70°. X-Ray photoelectron spectroscopy (XPS) analysis was conducted on a VG ESCALAB MK II spectrometer (VG Scientific, U.K.) employing a monochromatic Mg K α source ($h\nu=1253.6$ eV). Peak positions were internally referenced to the C(1s) peak at 284.6 eV. Scanning electron microscope (SEM) images were performed on a XL 30 ESEM FEG scanning electron microscope at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were carried out on a Hitachi-600 TEM with an accelerating voltage of 100 kV. Raman spectra were recorded with a Renishaw 2000 system using an Argon ion laser operating at 514.5 nm with a CCD detector.

For the electrode fabrication, the graphene film without a copper current collector was used as the working electrode. For comparison, the commercial MCMB, acetylene black, and poly(vinylidene difluoride) (PVDF) in NMP with a mass ratio of 80:10:10 were mixed into a homogeneous slurry with mortar and pestle, and then the obtained slurry was casted onto copper current collector (10- μ m-thick Cu foil; KeJing Group) using the doctor blade technique. The electrolyte consisted of a solution of 1 M LiPF₆ in EC/DMC (1:1 v/v) provided by Guangzhou Tinci Materials Technology Co. Ltd. Polypropylene (Celgard 2400) were utilized as separators and pure lithium metal foil was used as counter electrode. 2032 type coin cells were assembled in an argon-filled glovebox. The cells were tested on a multi-channel battery test system (NEWARE CT-3008) in the voltage ranges of 0.01–1.2 V vs. Li/Li⁺ at room temperature. Cyclic voltammetry was recorded on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China).

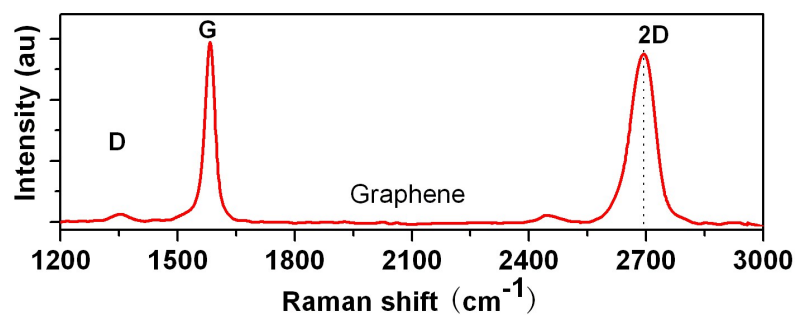


Figure S1. Raman spectra of the as-prepared graphene on a SiO₂ substrate.

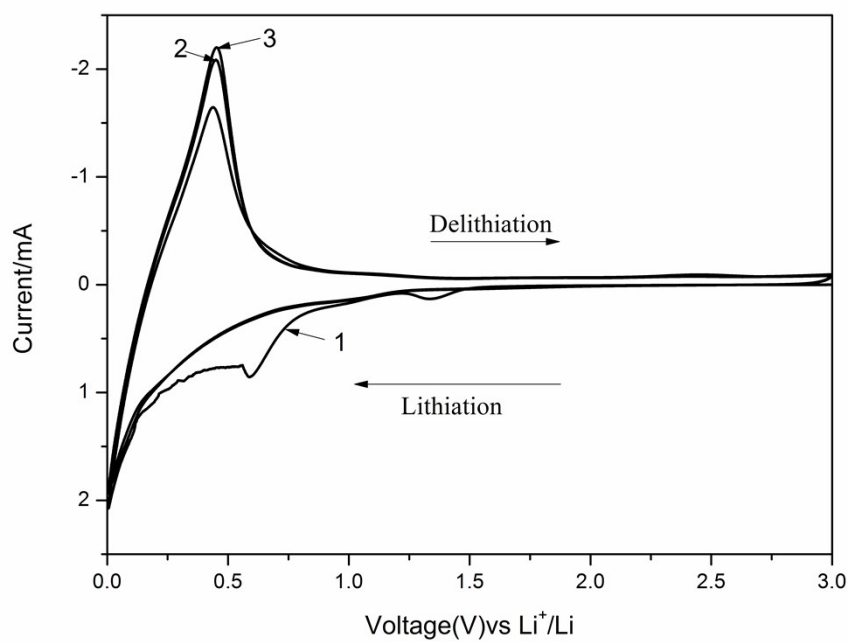


Figure S2. Cyclic voltammetry profiles of the commercial MCMB at a 1 mV s⁻¹ scan rate (voltage range: 0.01 V–3.0 V).

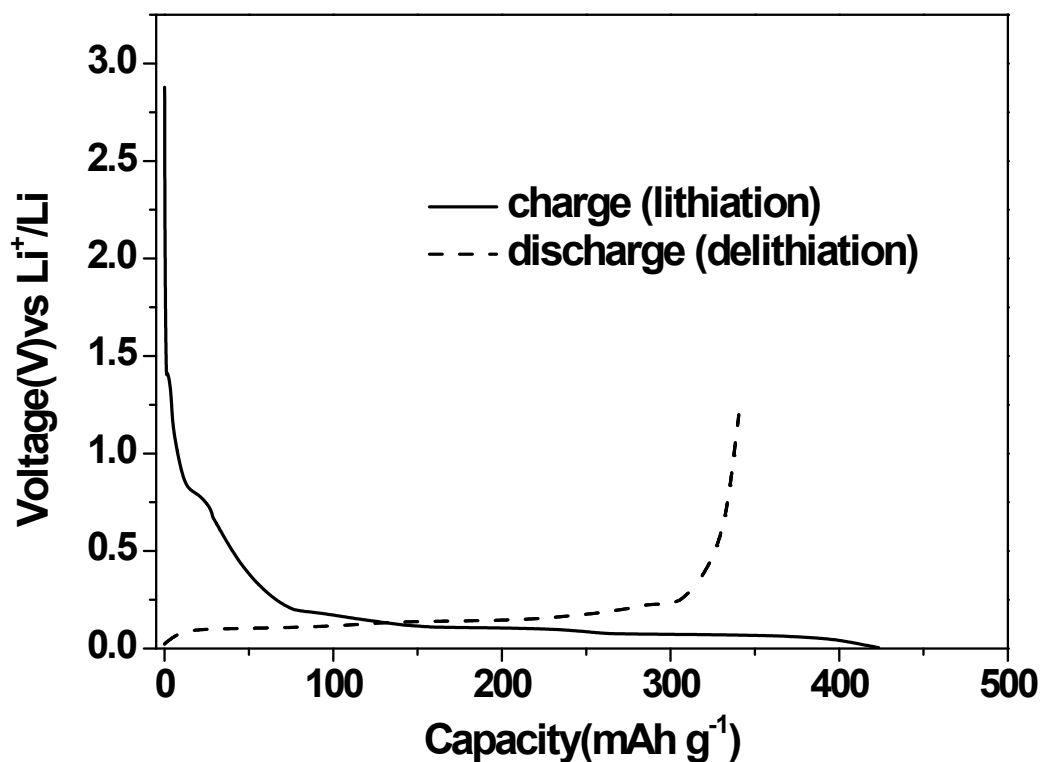


Figure S3. Galvanostatic charge–discharge curves of MCMB for the first cycle between 0.01 V and 1.2 V versus Li^+/Li at 0.1 C.

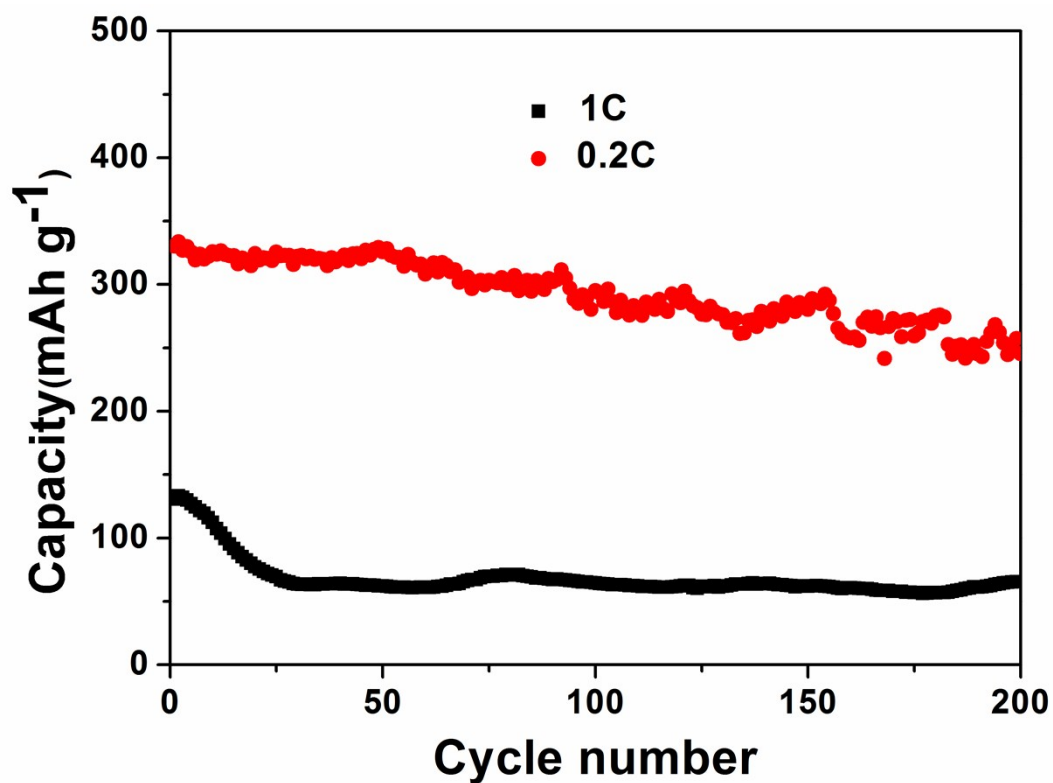


Figure S4. Cycling performance of the MCMB at different current densities

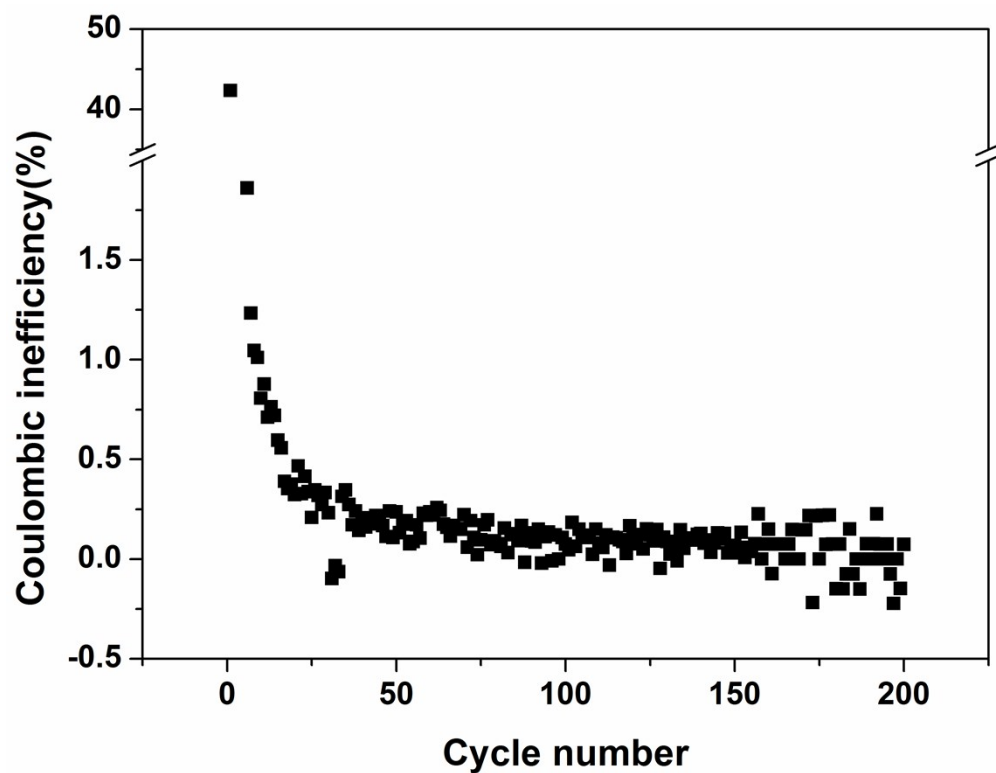


Figure S5. Coulombic inefficiency data as a function of cycle number for the as-obtained graphene film at 0.2 C

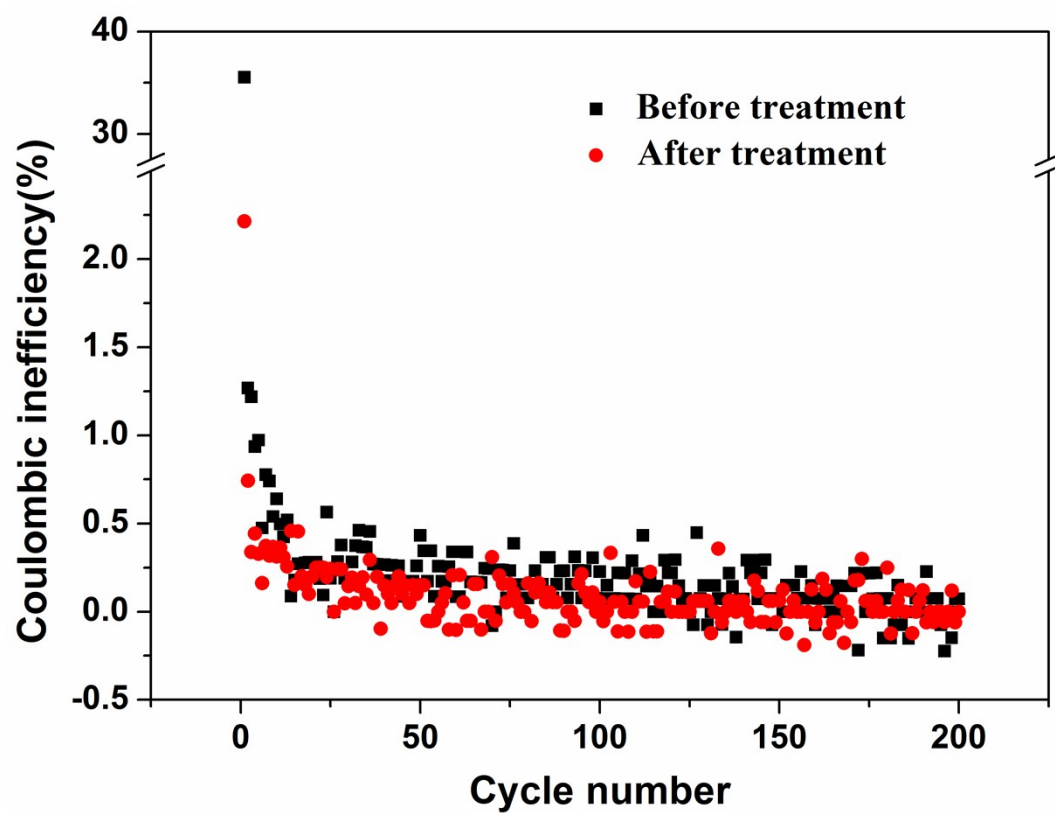


Figure S6. Coulombic inefficiency data as a function of cycle number for the graphene film at 1C before and after a surface treatment