Supporting Information

Controlled Partial-Exfoliation of Graphite Foil and Integration with MnO_2 Nanosheets for Electrochemical Capacitors

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Calculations

Capacitance calculated based on constant current charge/discharge profile

Areal and gravimetric capacitance of a single electrode from the constant current charge/discharge profile are calculated from equation S1 and S2, respectively:

$$C_a = \frac{It}{S\Delta U} \qquad \text{(Equation S1)}$$

$$C_g = \frac{It}{m\Delta U} \qquad \text{(Equation S2)}$$

Where C_a is the areal capacitance (mF/cm^2) and C_g is the gravimetric capacitance, S is the area of electrode (cm^2), I represents the discharge current density (mA), m is the mass of active material (mg), t is the discharge time (s) and ΔU is the potential window (V).

Areal energy density and power density of a single electrode

Areal energy density (E, Wh/m^2) and power density (P, W/m^2) were calculated using the following two equations:

$$E = \frac{10000}{2 \times 3600 \times 1000} C_a (\Delta U)^2 \qquad \text{(Equation S3)}$$

$$P = \frac{3600E}{t} \qquad \text{(Equation S4)}$$

Where C_a is the areal capacitance (mF/cm^2), ΔU is the potential window (V) and t is the discharge time measured in constant current charge-discharge profiles (s).

Supplenmentary Figures

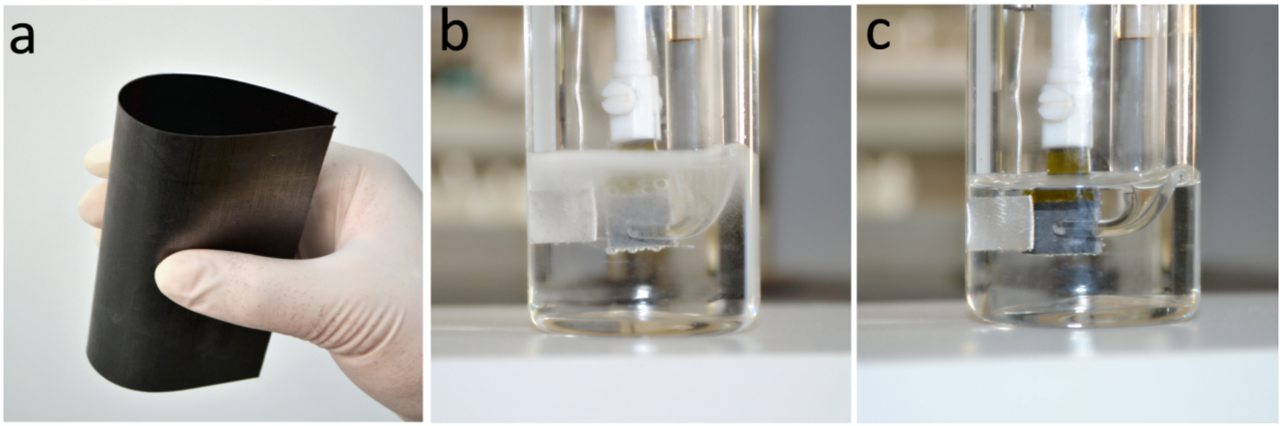

Figure S1 Digital photographs of a piece of flexible graphite foil (a), primary exfoliation process (b), and secondary exfoliation process (c) carried out in a three-electrode electrochemical reactor.

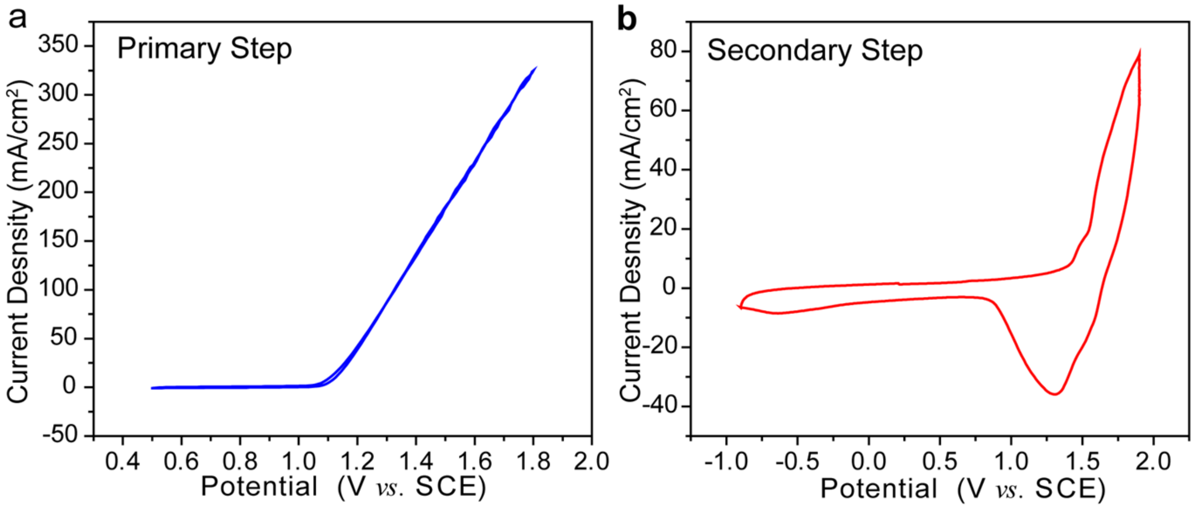

Figure S2 CV profiles of the primary exfoliation (a) and ACV profile of the secondary exfoliation (b) processes collected at a scan rate of 20 mV/s.

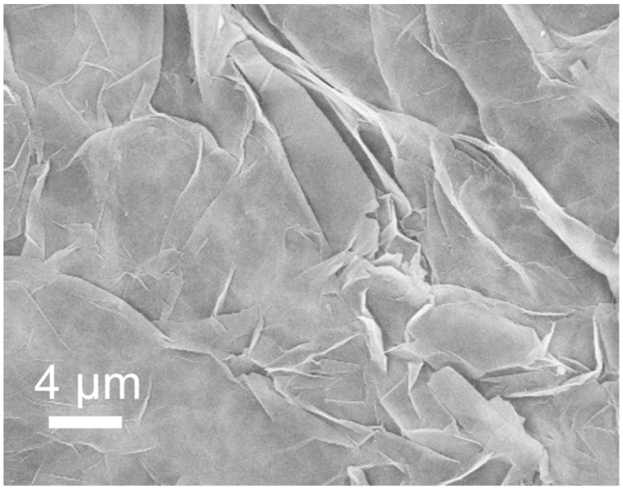

Figure S3 SEM image showing the morphology of graphite foil after second-step-only exfoliation.

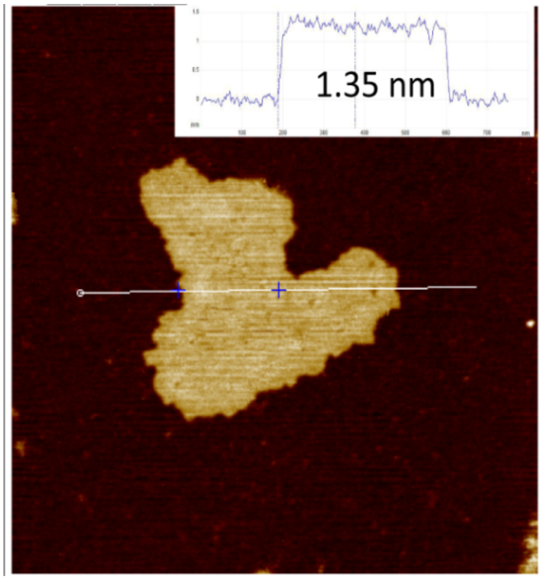

Figure S4 AFM image of a piece of graphene sheet exfoliated from the FEG substrate. Inset shows the height profile of AFM image corresponding to the line shown in this image.

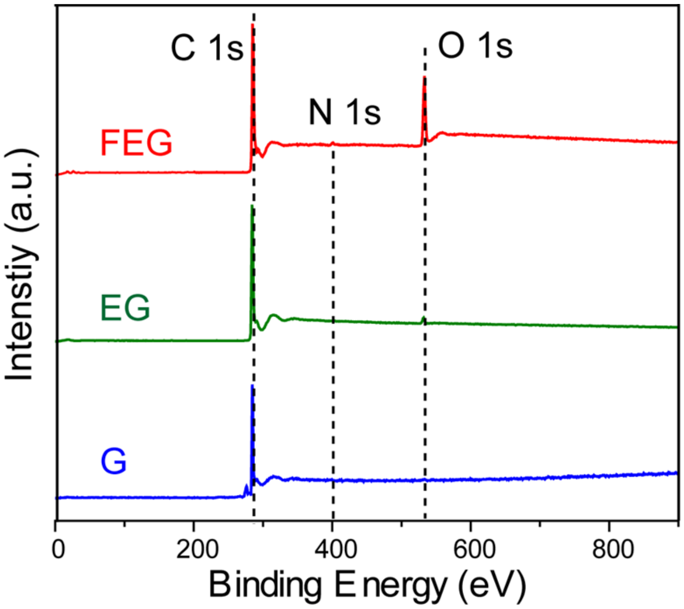

Figure S5 XPS survey spectra of G, EG, and FEG.

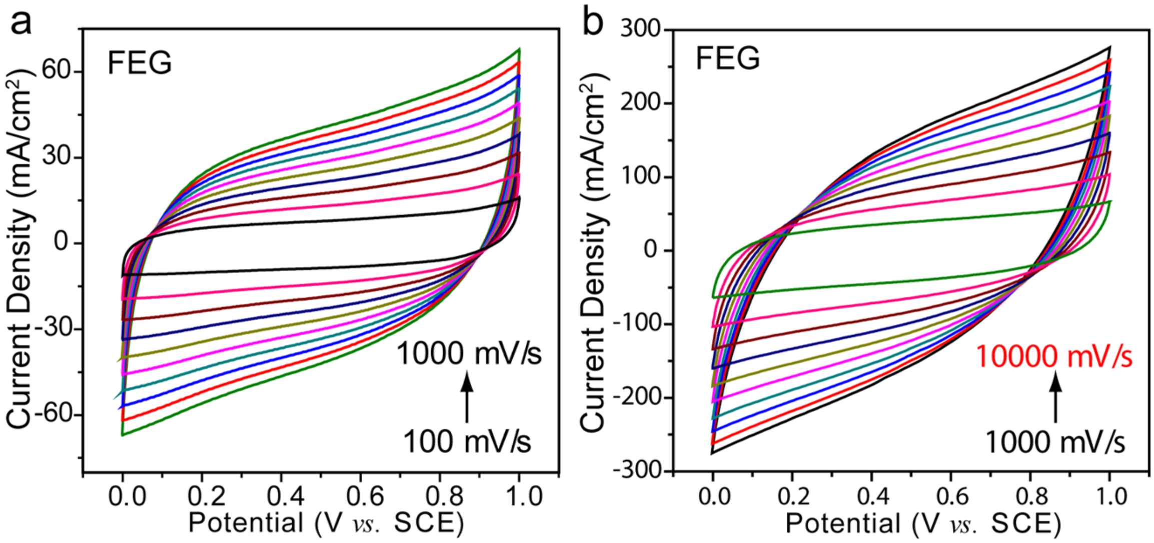

Figure S6 CV curves of FEG substrate collected at various scan rates in 3 M KCl aqueous electrolyte: from 100 mV/s to 1000 mV/s (a) and from 1000 mV/s to 10000 mV/s (b).

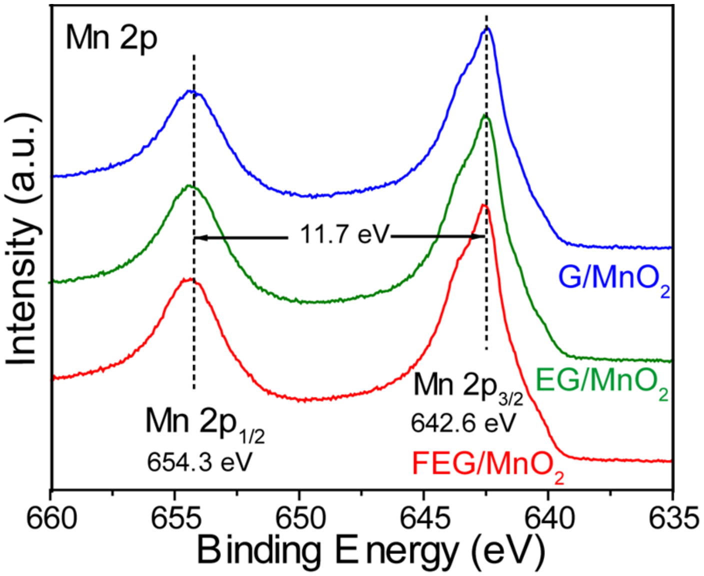

Figure S7 Mn 2p XPS spectra of G/MnO_2, EG/MnO_2, and FEG/MnO_2.

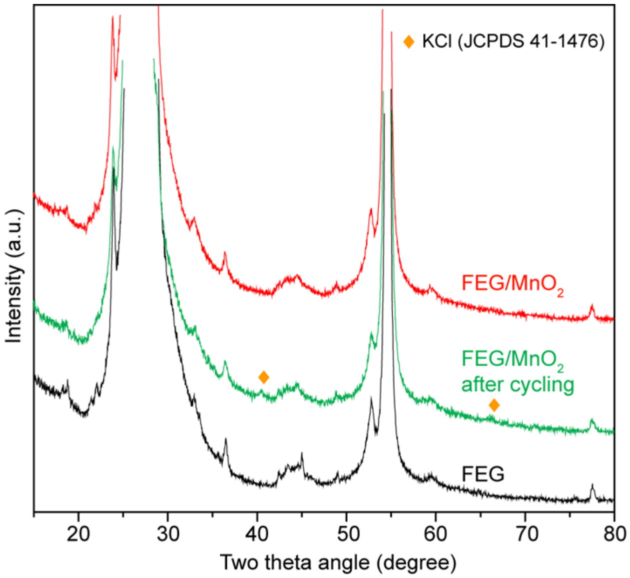

Figure S8 XRD spectra collected for FEG/MnO_2 before and after cycling test.

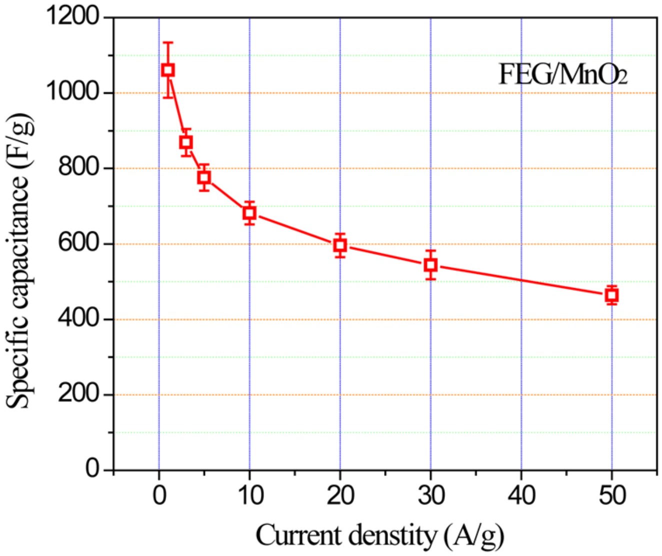

Figure S9 Specific capacitance of FEG/MnO_2 at different current densities with error bars (calculated from three parallel samples) for each capacitance.

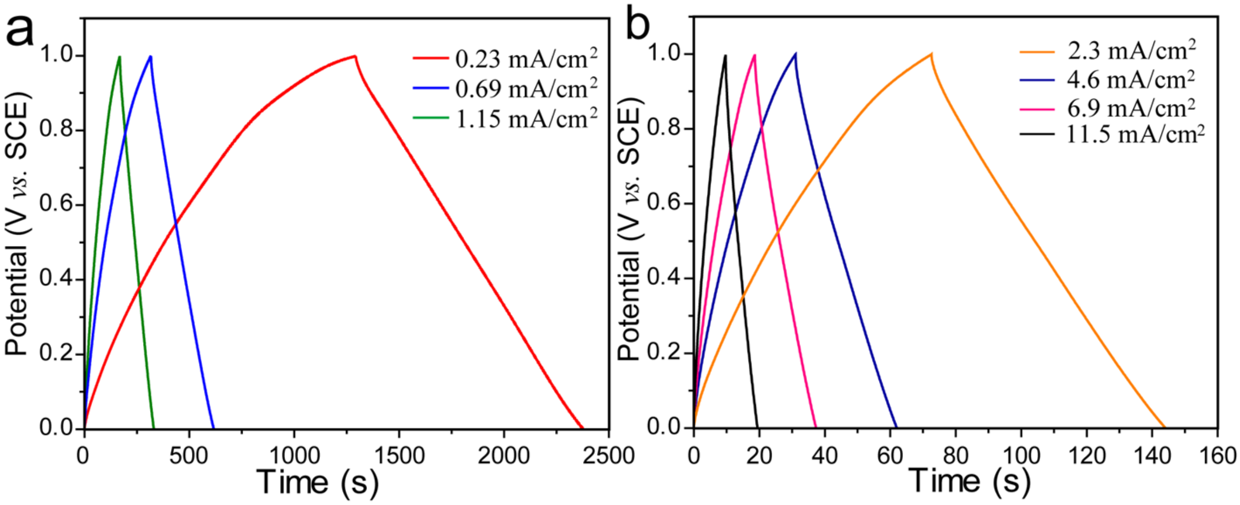

Figure S10 Constant current charge/discharge profiles of FEG/MnO_2 at various current densities from 0.23 mA/cm^2 to 1.15 mA/cm^2 (a) and from 2.3 mA/cm^2 to 11.5 mA/cm^2 (b).

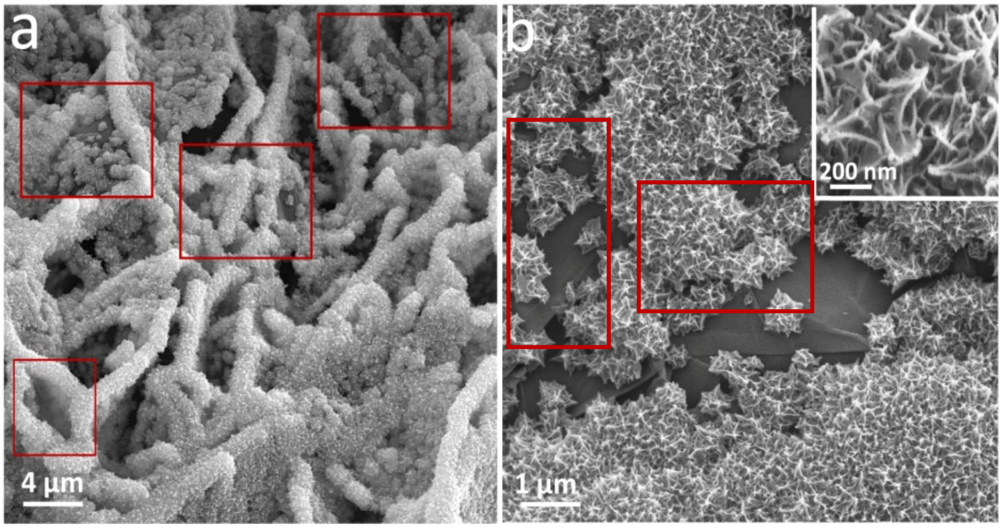

Figure S11 SEM images of EG/MnO_2 (a) and G/MnO_2 (b). Inset of (b) showed the morphology of deposited MnO_2 nanosheets. Red boxes highlight the exposed area of substrate.

Here we proposed the following reasons to explain the morphology of the three electrodes. The lattice structure of graphene is much different from that of MnO_2. Hence the electro-deposition of MnO_2 on graphene sheets is a heterogeneous reaction, causing the slow formation of embryonic nuclei on graphene surface for MnO_2 to grow. Once there are several MnO_2 nuclei formed, it will be much easier for Mn^{2+} to diffuse to the already formed MnO_2 nucleus and grow rather than to elsewhere because the growth of MnO_2 nanosheets on MnO_2 nucleus is homogeneous. As a result, MnO_2 nanosheets tend to accumulate around the nucleation sites and finally lead to non-uniformity. What's more, locally aggregated MnO_2 cluster is unfavorable for pseudo-capacitors since it is hard for electrons to diffuse through thick and poorly conductive layers. However, the oxygen-containing functional groups on FEG surface could capture Mn^{2+} in the electrolyte through the coordination bonding between oxygen atoms and manganese ions. Thus, the enrichment of Mn^{2+} ions on graphene surfaces as well as the highly efficient charge transfer property of FEG will facilitate the simultaneous formation and provide plenty of transient, nanoscale ordered regions for MnO_2 nucleation, and favor the growth of MnO_2 nanosheets to form uniform nanoarrays.