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Approaching the theoretical capacitance of graphene through copper foam integrated three-dimensional graphene networks

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I. Supporting experimental details

1. Experimental Section

1.1 Materials and chemicals: Graphite flakes ($\approx 20 \mu\text{m}$), phosphorus pentoxide (P_2O_5 , $\geq 98\%$), potassium permanganate (KMnO_4 , $\geq 99\%$), 1, 2-dichloroethane and tetraethylammonium tetrafluoroborate ($\geq 99\%$) were obtained from Sigma-Aldrich and used as received. High-purity Cu plate ($\geq 99.99\%$) with 1 mm thickness was purchased from Goodfellow Cambridge Limited (London). Prior to use, Cu plates were treated with dilute HCl and acetone repeatedly to obtain clean and hydrophilic surfaces. Other chemicals used in this work were at least of analytical grade in purity. Except some electrochemical experiments were performed in organic media, phosphate buffer solutions (PBS, 1 M, pH 7) were used as supporting electrolyte for all electrochemical measurements including voltammetric, charge/discharge and impedance spectroscopy. All solutions used were prepared with Millipore water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) produced by Milli-Q system.

1.2 Instrumental details: All voltammetric and charge/discharge measurements were carried out with a CHI 760C electrochemical workstation equipped with a Faradaic cage. Electrochemical impedance spectroscopy (EIS) was performed using an Autolab System (Eco Chemie, Netherlands) controlled by the NOVA 1.10 software. All electrochemical measurements (otherwise mentioned) were performed in 1 M phosphate buffer solution (PBS) under neutral condition (pH 7) with a three-electrode system consisting of the target systems as working electrode, saturated calomel electrode (SCE) as reference electrode, a platinum coiled wire with a large surface area as counter electrode X-ray diffraction (XRD) analysis was carried out with a Bruker DB Advance diffractometer unit. Scanning electron microscopic (SEM) images were acquired by a FEI Quanta 200 ESEM FEG field emission scanning electron microscope. Atomic force microscopic (AFM) images were recorded in the tapping mode using a 5500AFM system (Agilent Technologies, Chandler, AZ).

1.3 Synthesis of graphene oxide. Single-layered graphene oxide (GO) was prepared by a two-step procedure. In the first step pre-oxidised graphite was prepared and in the second step exfoliation and strong oxidation was performed. Graphite powder (10 g) was slowly added into concentrated H_2SO_4 solution (15 ml) containing P_2O_5 (5 g) and $\text{K}_2\text{S}_2\text{O}_8$ (5 g) kept in a hot water bath (80°C) under strong stirring for 3 h. After cooling to room temperature and

diluting with Milli-Q water, the dark green mixture was obtained. The mixture was then filtered and washed several times until pH of waste solutions reaching neutral. Pre-oxidized graphite powder was collected and dried in air at room temperature overnight. In the second step, pre-oxidized graphite powder (1.0 g) was slowly added to concentrated H₂SO₄ solution (25 ml) maintaining the temperature at 0 °C. Solid KMnO₄ (3.0 g) was then added to the mixture under slow stirring and maintaining the temperature below 20 °C. After removing the ice-water bath, the mixture was heated at 35 °C under stirring for 2 h, to which Milli-Q water (50 ml) was then added. After a few minutes, Milli-Q water (150 ml) and 5 ml 30% H₂O₂ solution were further added to the mixture, leading to the solution color changed rapidly to bright yellow. The mixture was then washed with 10% HCl solution (v/v, 250 ml) and filtered to remove residual metal ions. The raw GO suspended in Milli-Q water was centrifuged at a high rotation speed (10000 rpm). The supernatant containing highly dispersed and stable GO nanosheets was collected. To remove residual salts and acids, the sample was further dialyzed using a dialysis tube (with a cut-off molecular weight of 12000-14000) for 7 days by regularly replacing water bath with fresh Milli-Q water 2-3 times per day.

1.4 Electrochemical reduction of GO on CuF. Electrochemical behaviour of GO dispersions was checked by cyclic voltammetry (CV) first, in order to obtain the optimal potential window for electroreduction of GO nanosheets under the present conditions. A cathodic peak around -0.9 V (vs SCE) was observed, resulting from the electroreduction of oxygen-containing groups (e.g. hydroxyl and epoxy groups) on GO sheets. Similar electrochemical behaviour for 3D GO@CuF electrodes was observed. Namely, GO@CuF displayed a large cathodic peak at -0.9 V with an onset reduction potential at -0.8 V as shown in Figure S2. The successive potential cycling between -0.3 V and -1.1 V resulted in that the cathodic peak at -0.9 V denominated gradually and disappeared after about 50 cycles. Thus, the 50 potential switching cycles were used in this work to ensure sufficient conversion of GO into rGO.

2. Fabrication of supercapacitor electrodes:

First, CuF thin film was generated on Cu foil (or plate) by galvanostatic electrodeposition.¹ In a typical preparation procedure, a piece of high-purity and clean Cu foil (with an active area of 0.125 cm²) was used as a substrate (cathode) for the deposition of CuF and another

piece of Cu foil used as a counter electrode (anode). A constant current density (e.g. 2 A cm⁻²) was applied to cathode and anode in an electrochemical cell containing 0.4 M CuSO₄ and 1.5 M H₂SO₄ for different deposition time (20 to 60s). The distance between anode and cathode was fixed at 1 cm. GO was synthesized from graphite flakes according to our previously developed procedure.^{2,3} *Secondly*, for self-assembly of GO nanosheets on CuF, a 10 μL stock solution of GO (1 mg mL⁻¹) was drop-cast over CuF and the sample electrode was incubated at 4 °C at least 12 h for slow drying. The resulting electrode was washed with Milli-Q water, denoted as GO@CuF (or 3DGO@CuF). In the final step, GO@CuF was electrochemically reduced by potential cycling (Fig. S2) to obtain rGO@CuF (or 3DrGO@CuF). The reduction peak at -0.9 V (vs SCE) corresponding to oxygen containing functionality of GO completely disappeared after 50 cycles, indicating that GO was fully converted to rGO

3. Surface area measurements.

Real surface area of the 3DrGO@CuF material was measured by popular voltammetry approach for porous electrodes.⁴ First, voltammetry curves are recorded at different scan rates in the potential window applied to calculate specific capacitance. The current in the middle of the potential range is taken into account and is plotted as a function of scan rate (Figure S11). The slope obtained from the curve is the differential capacitance (total value) of the electrode interface.

$$C_{\text{total}} = dQ/dE = I dt/dE = I/(dE/dt) \quad (1)$$

The capacitance obtained from the curve is then compared with reference value (C*). In this case, the reference value is considered the theoretical capacitance value, which is 21 μF/cm².

$$\text{Surface area (A)} = C_{\text{total}}/C^* \quad (2)$$

The calculated surface area found in this method is about 1000 m²/g for 3DrGO@CuF materials.

II. Supporting data

Table S1. Summary of key performance parameters for supercapacitor electrodes fabricated and tested with various experimental conditions

| Supercapacitor electrodes | CuF film thickness ^{a)} (μm) | GO loading amount ($\mu\text{g cm}^{-2}$) | Electrolytes | Current density applied (A g^{-1}) | Specific capacitance (F g^{-1}) | Power density (kW kg^{-1}) | Energy density (Wh kg^{-1}) |
|---------------------------|--|---|--------------|---|--|---------------------------------------|--|
| rGO@CuF | 100 (40 s) | 80 | 1 M PBS | 10 | 366 | - | - |
| rGO@CuF | 125 (50 s) | 80 | 1 M PBS | 10 | 387 | - | - |
| rGO@CuF | 150 (60 s) | 80 | 1 M PBS | 1 | 623 | 0.3 | 31 |
| rGO@CuF | 150 (60 s) | 80 | 1 M PBS | 10 | 416 | 3 | 21 |
| rGO@CuF | 150 (60 s) | 80 | 1 M PBS | 20 | 355 | 6 | 18 |
| rGO@CuF | 150 (60 s) | 160 | 1 M PBS | 10 | 259 | - | - |
| rGO@CuF | 150 (60 s) | 400 | 1 M PBS | 10 | 130 | - | - |
| CuF alone ^{b)} | 150 (60 s) | 0 | 1 M PBS | 1 | 110 | - | - |
| GO@CuF ^{c)} | 150 (60 s) | 80 | 1 M PBS | 1 | 234 | - | - |

^{a)} The value in the parentheses describe the deposition time of CuF used for corresponding materials;

^{b)} The Cu foam alone electrodes were used as reference system; ^{c)} GO@CuF is the electrodes loaded with GO but without electrochemical reduction.

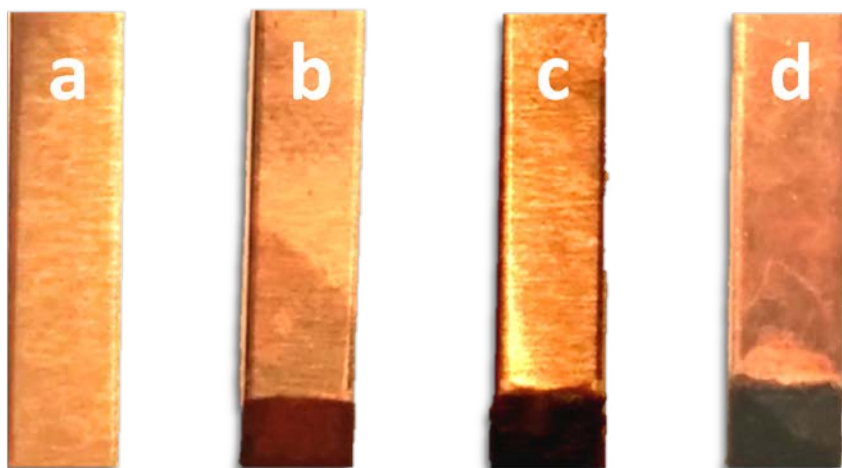


Figure S1. Digital photo images of (a) Cu foil, (b) CuF, (c) GO@CuF and (d) rGO@CuF.

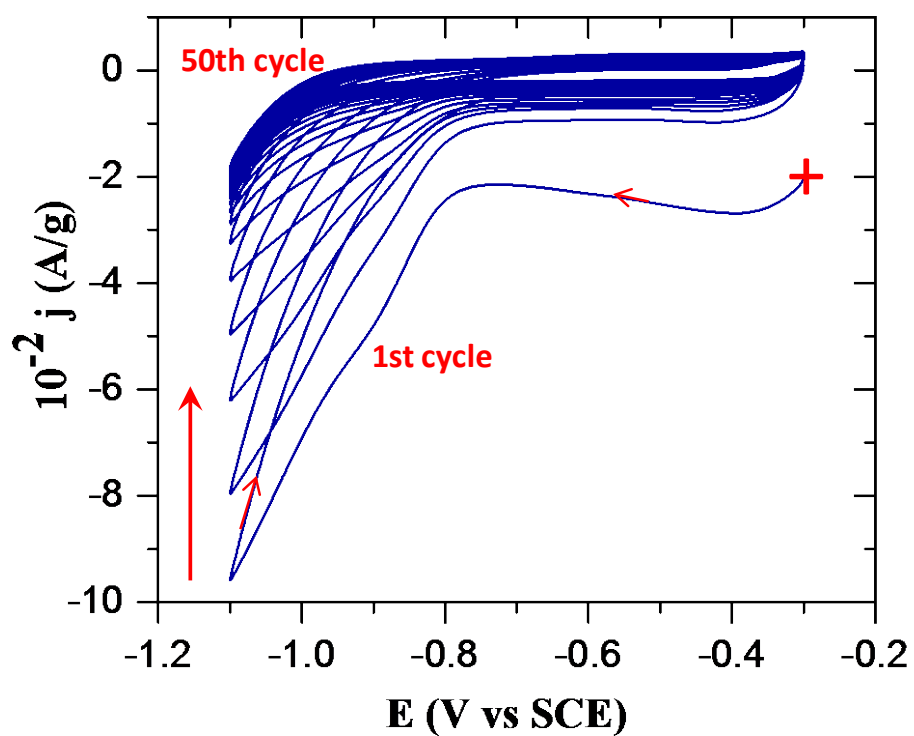


Figure S2. Electrochemical reduction of GO: Potential cycling of GO@CuF electrode for the electrochemical reduction of GO to rGO in 1 M PBS (pH 7).

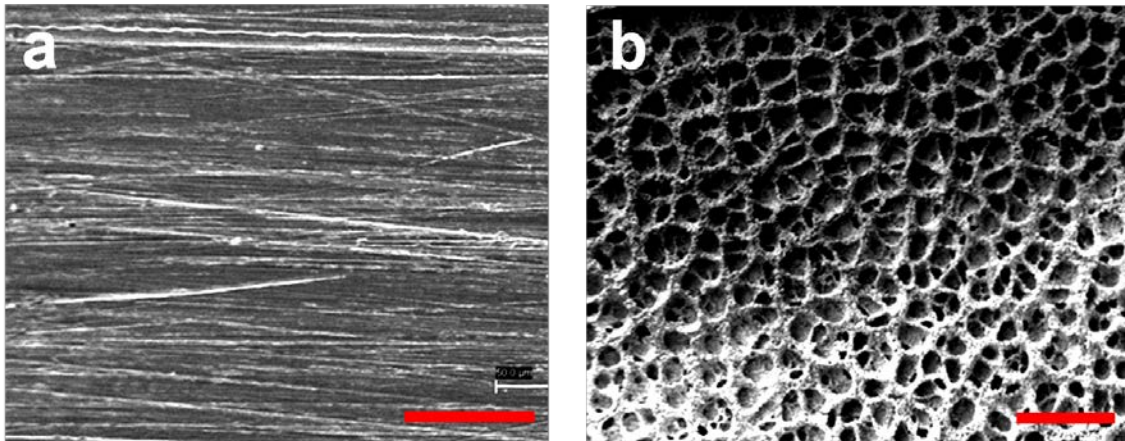


Figure S3. SEM images of Cu plate and foam: (a) Cu plate before depositon and (b) after CuF formation on Cu plate by the EC deposition. The scale of bars: 100 μm (a), 400 μm (b).

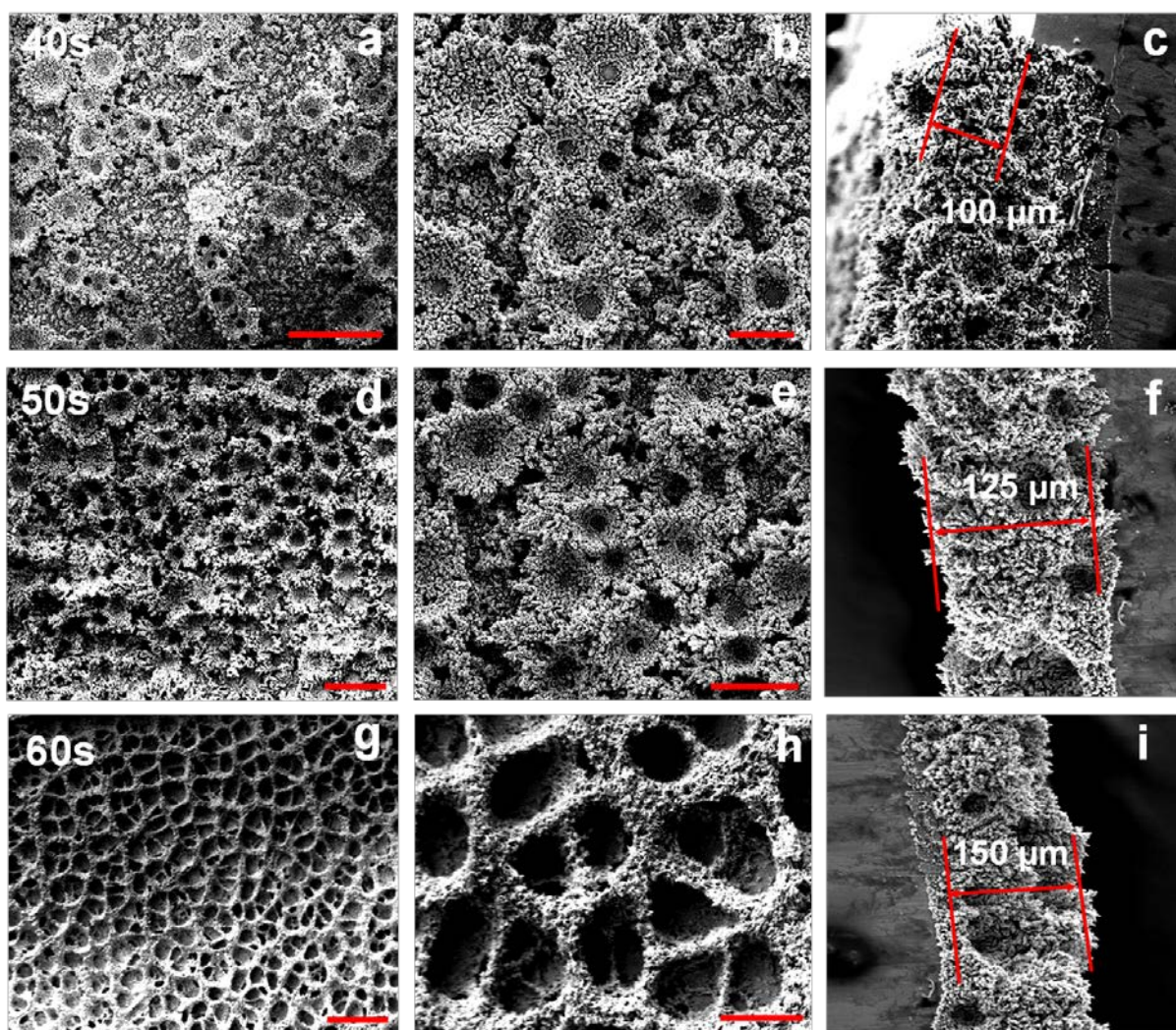


Figure S4. SEM images of Cu foam at different deposition time: (a, b and c) are the CuF with deposition time of 40 s. (d, e and f) are the CuF with deposition time of 50 s. (g, h and i) are the CuF with deposition time of 60 s. (c, f and i) are the corresponding cross-sectional SEM images. Scale bars: a) 150μm, b) 50μm, d) 200μm, e) 150μm, g) 300μm and h) 100μm.

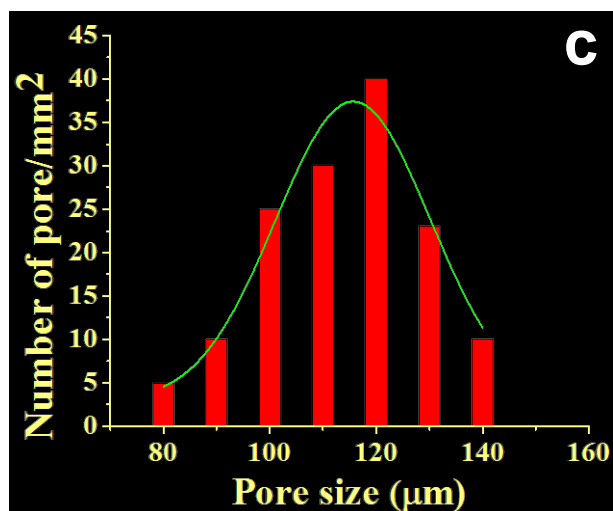
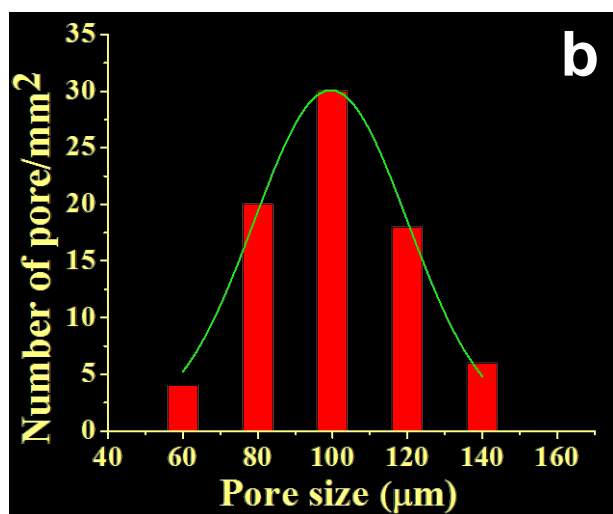
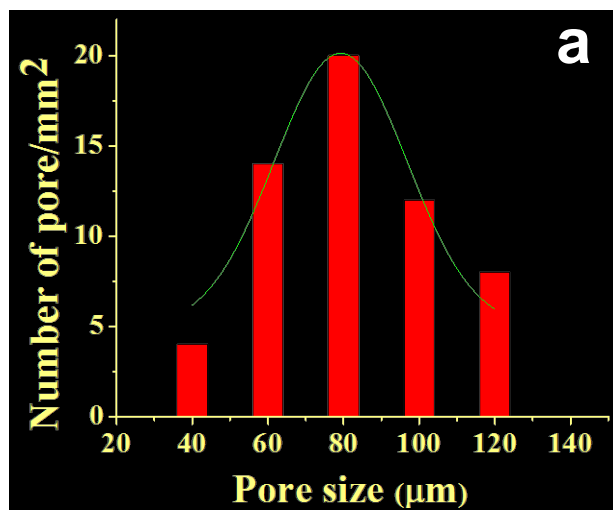


Figure S5. Histograms of the pore size distribution of CuF prepared with different deposition time: (a) 40 s, (b) 50 s, and (c) 60 s.

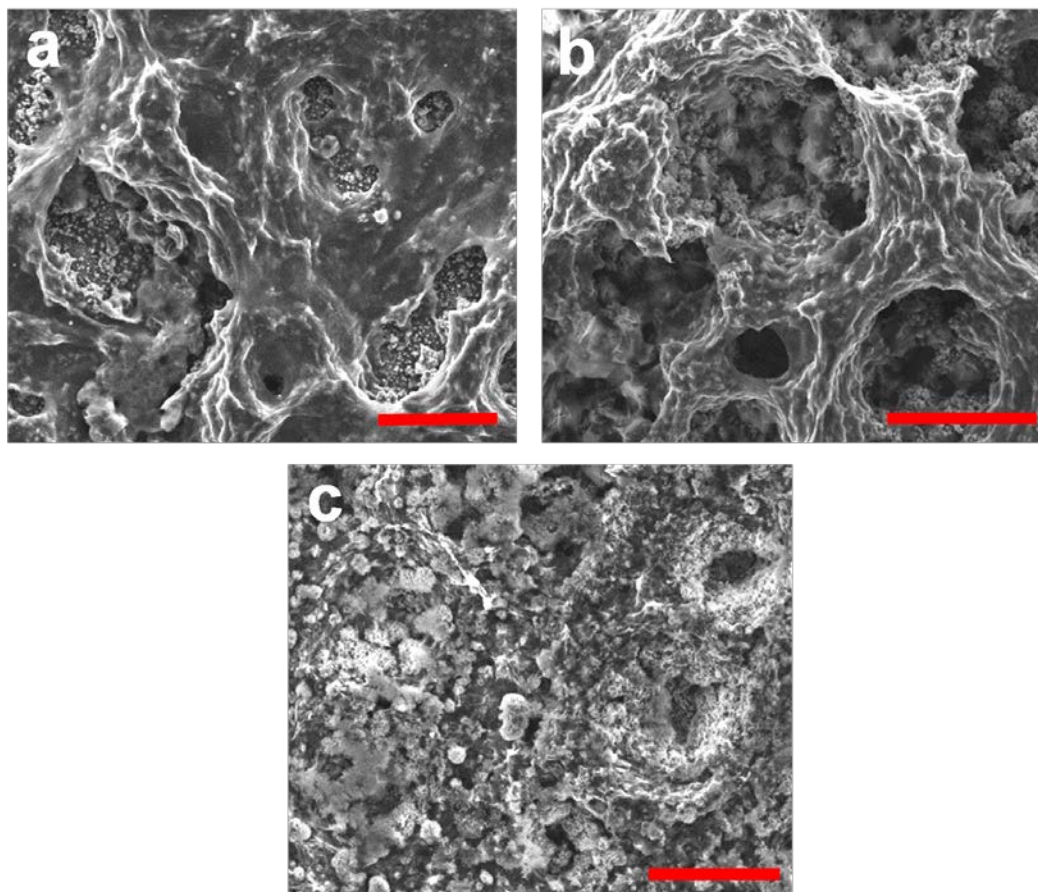


Figure S6. SEM images of rGO@CuF at different deposition time of CuF, (a) 40 s, (b) 50 s and (c) 60 s with same GO loading of 0.08 mg/cm^2 . Scale bars: a) $50 \mu\text{m}$, b) $100 \mu\text{m}$ and c) $100 \mu\text{m}$.

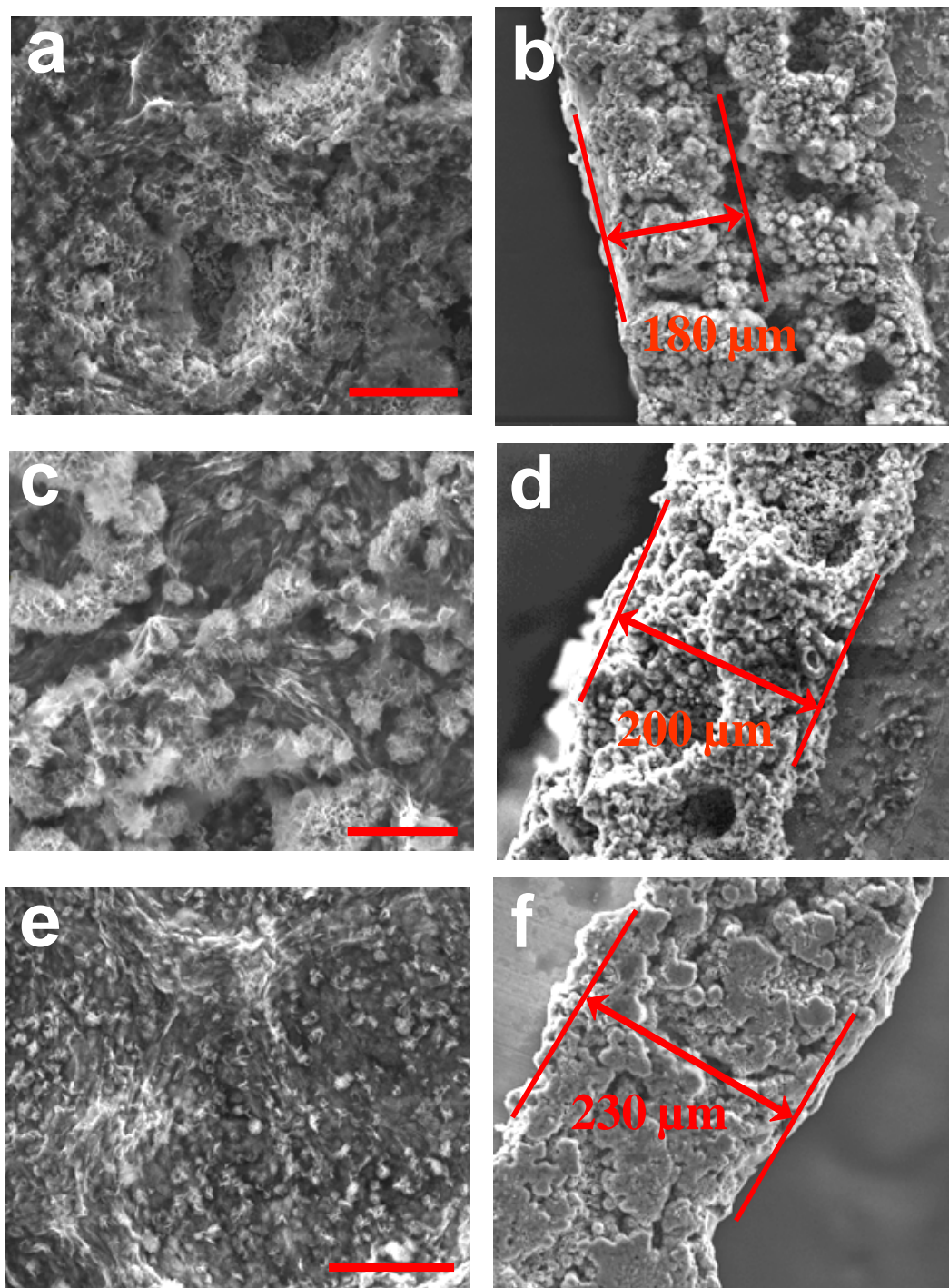


Figure S7. SEM images of rGO@CuF with different loading of GO. The loading of GO was 0.08 mg/cm^2 (a, b), 0.16 mg/cm^2 (c, d), and 0.4 mg/cm^2 (e, f) with the same CuF samples prepared using 60 s deposition time. (b, d and f) are the corresponding cross-sectional images of (a, c and e), respectively. Scale bars: a) $80 \text{ }\mu\text{m}$, c) $80 \text{ }\mu\text{m}$, e) $80 \text{ }\mu\text{m}$.

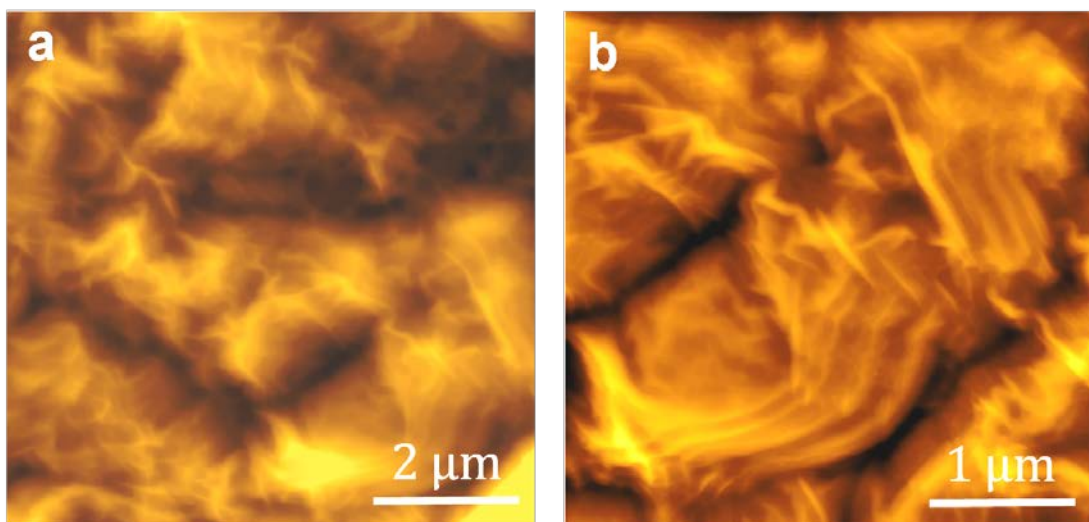


Figure S8. High-resolution AFM images of 3DGO@CuF on Cu supports, i.e. before electrochemical reduction.

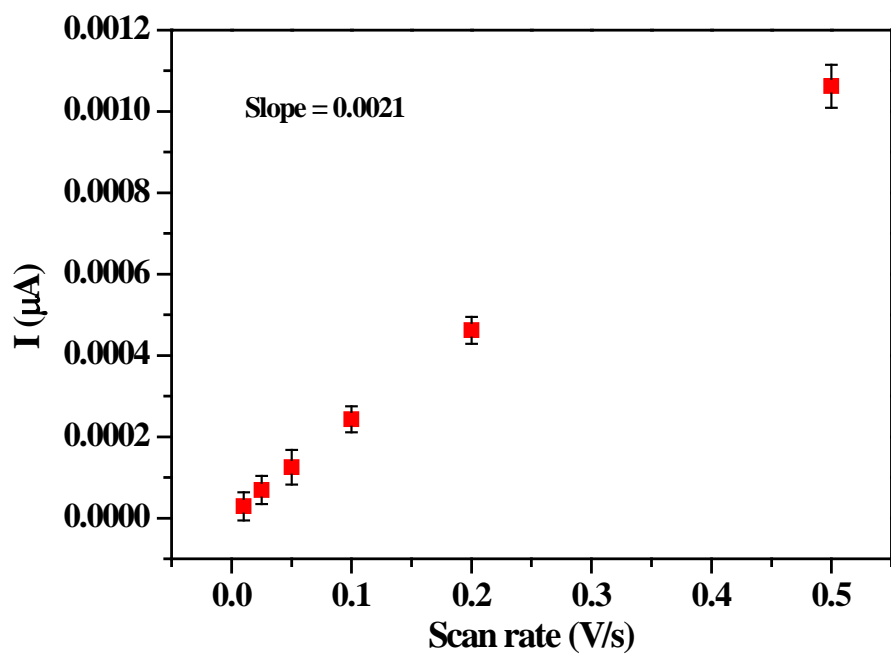


Figure S9. Surface area measurements: Plot demonstrating the voltammetry current vs scan rates

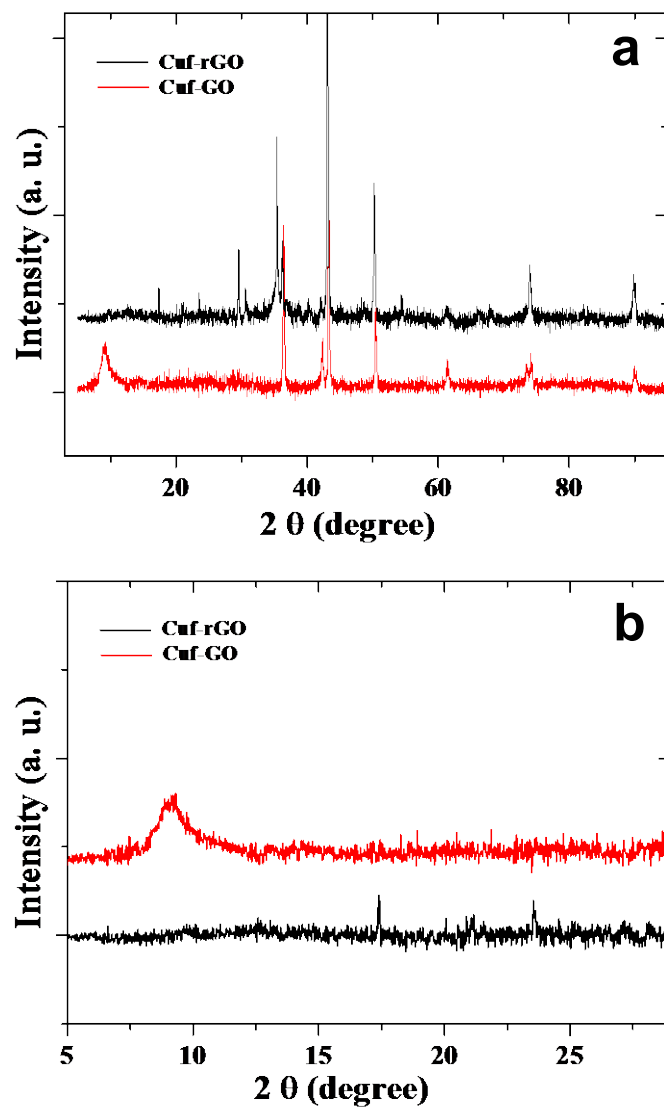


Figure S10. Comparison of XRD spectra of GO@CuF (red) and rGO@CuF (black) on Cu substrates: (a) full spectra and (b) in the region of smaller angles

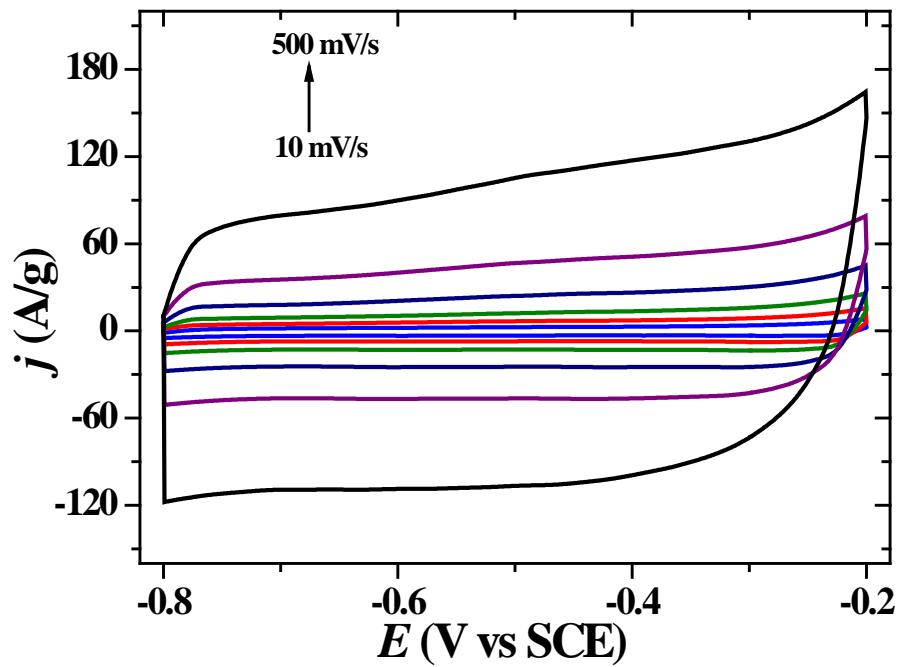


Figure S11. Cyclic voltammograms of 3DrGO@CuF electrodes in 1 M PBS obtained at different scan rates of 10 to 500 mV/s.

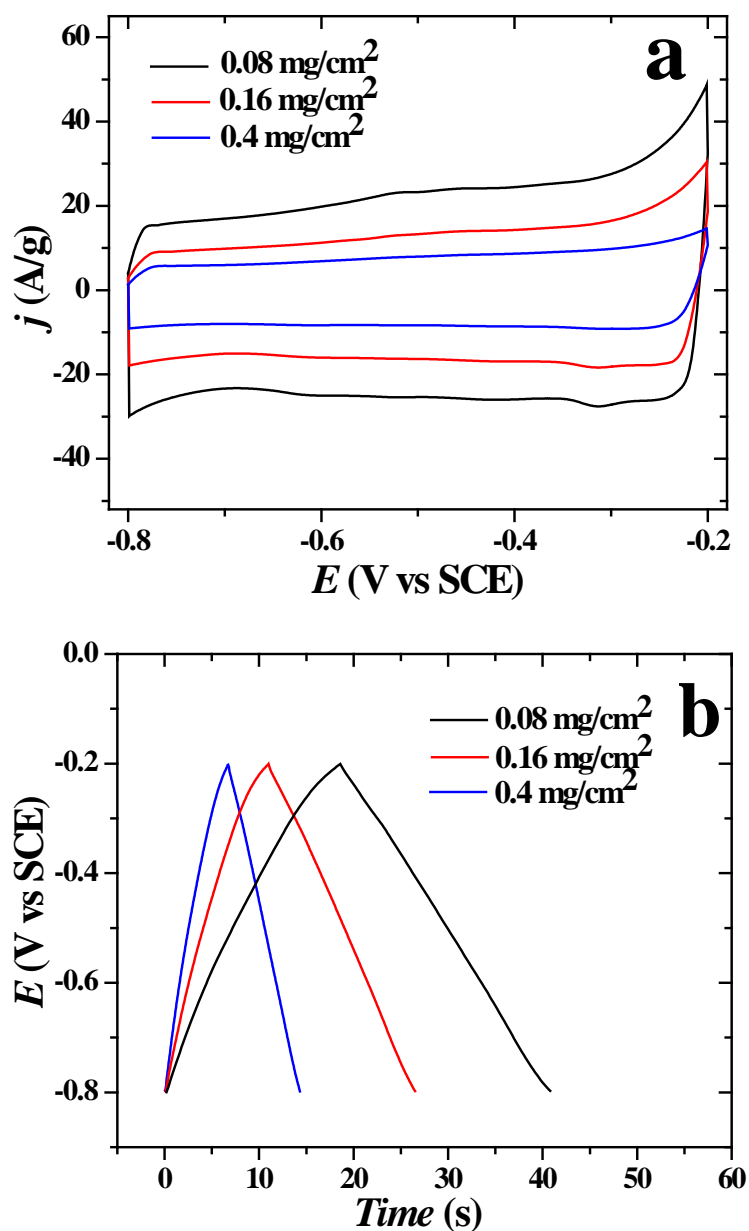


Figure S12. Cyclic voltammograms with a scan rate of 100 mV/s (a) and charge-discharge responses with current density of 1 A/g (b) of 3DrGO@CuF electrodes with different loading of GO as indicated in the figures with same CuF deposition time of 60s in 1 M PBS.

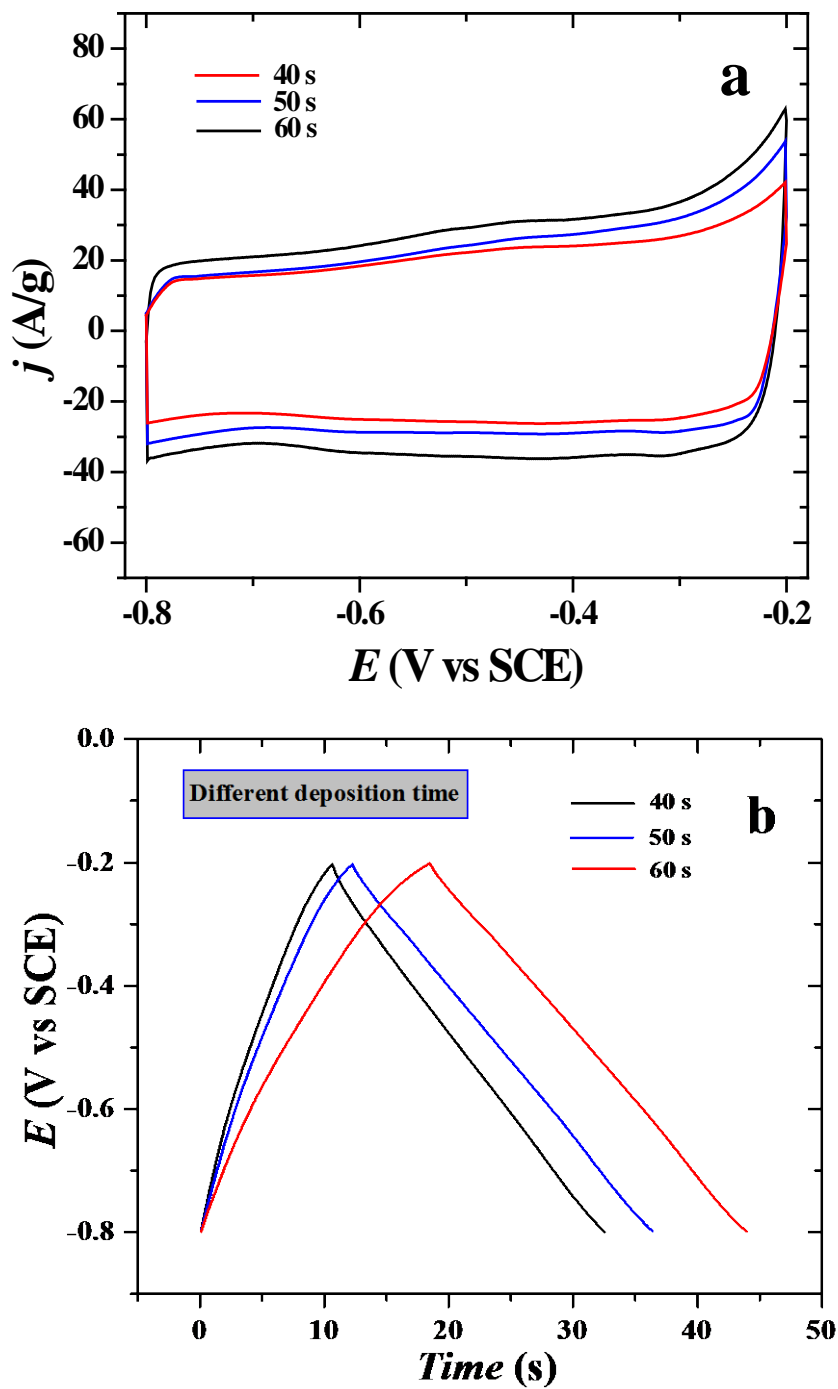


Figure S13. Cyclic voltammograms with a scan rate of 100 mV/s (a) and charge-discharge responses with current density of 1 A/g (b) of 3DrGO@CuF electrodes with different CuF deposition time as indicated in the figures with same GO loading of 0.08 mg/cm² in 1 M PBS.

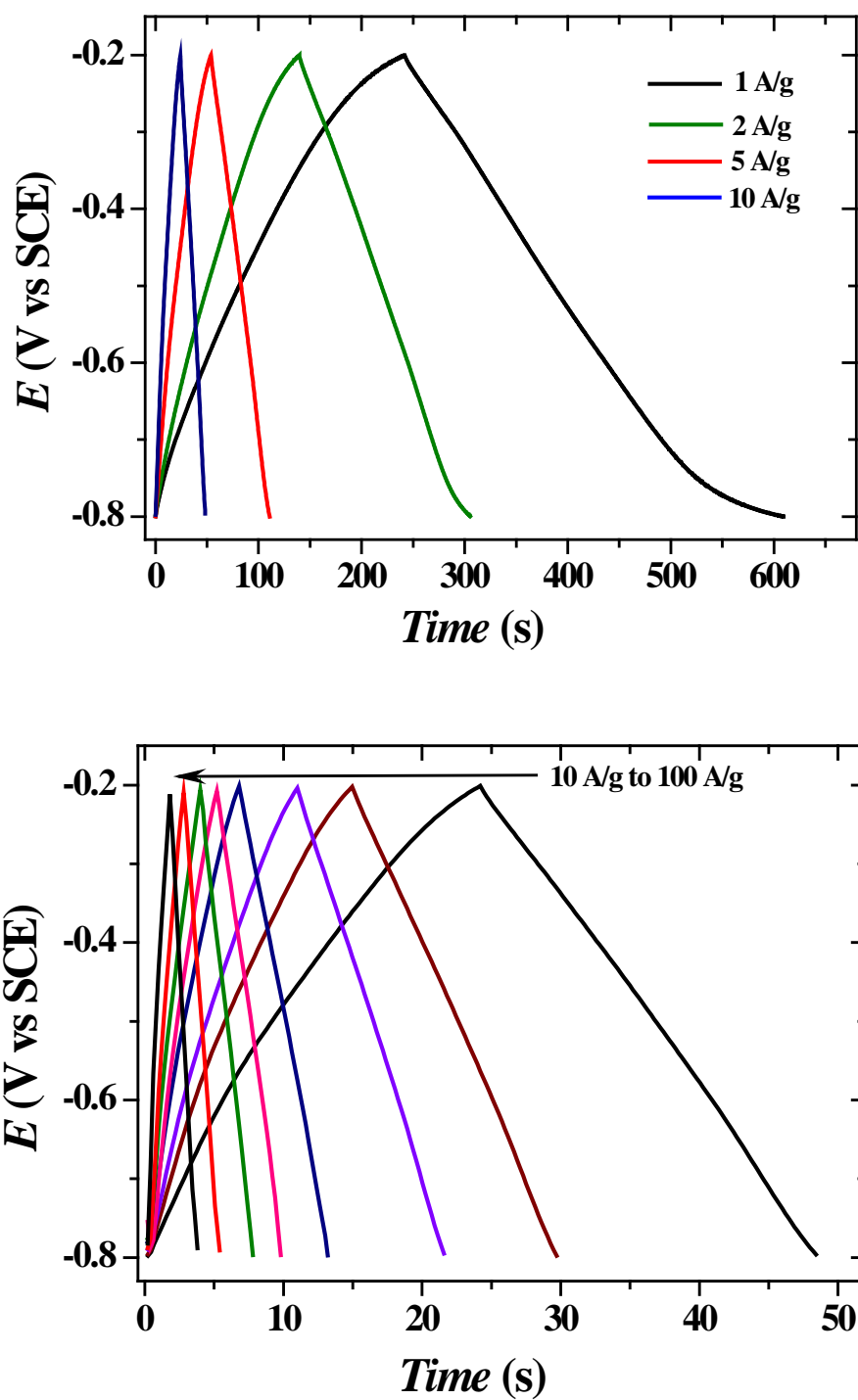


Figure S14. Comparison of charge-discharge responses of rGO@CuF electrodes in 1 M PBS obtained at different current densities.

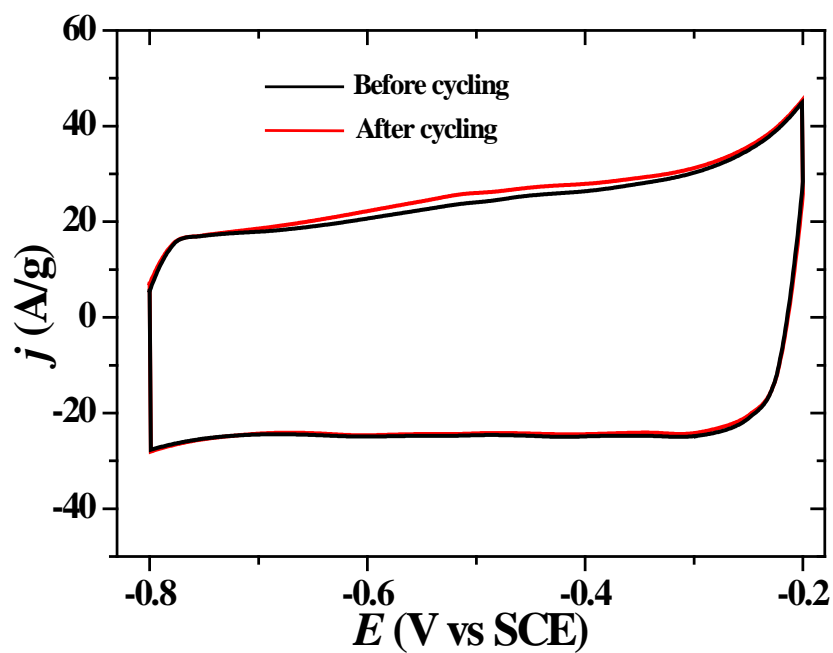


Figure S15. Comparison of cyclic voltammograms of rGO@CuF electrodes before (black) and after (red) 2000 charge/discharge cycles.

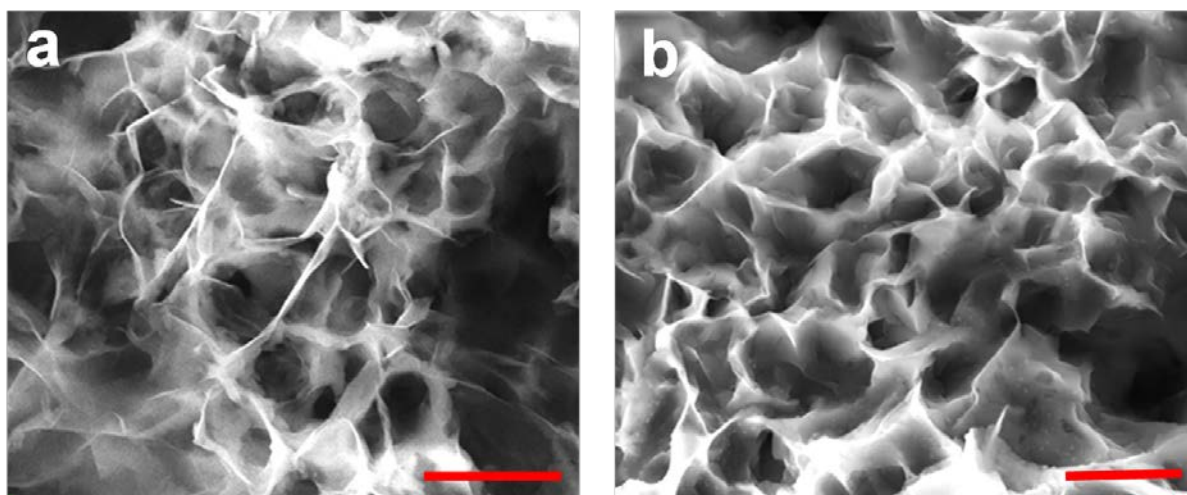


Figure S16. Comparison of SEM images of 3DrGO@CuF material before (a) and after (b) 2000 charge/discharge cycles.

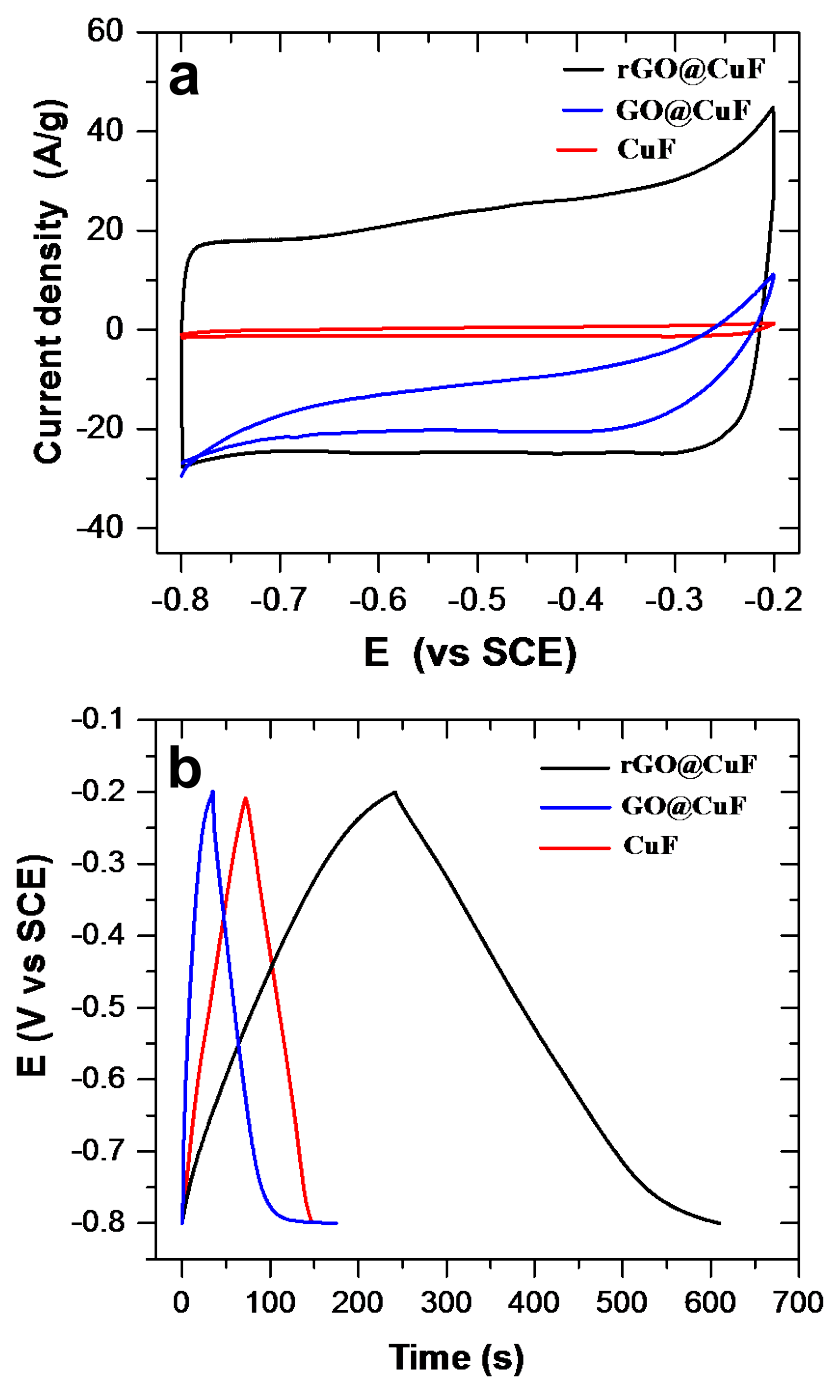


Figure S17. (a) Cyclic voltammograms with a scan rate of 100 mV/s and (b) charge-discharge curves at a current density of 1 A/g for CuF (red), GO@CuF (blue) and rGO@CuF (black) electrodes performed in 1 M PBS.

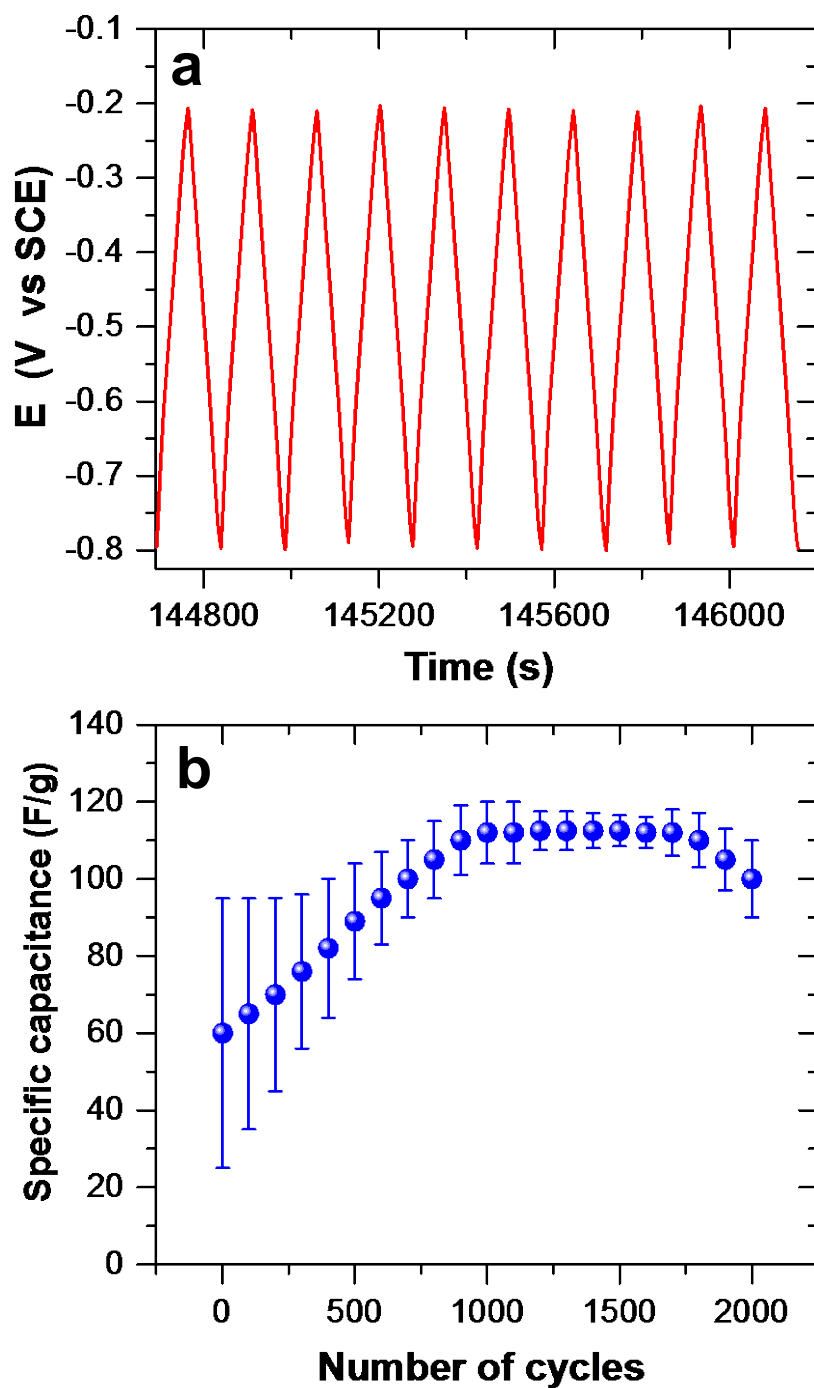


Figure S18. (a) Successive charge-discharge curves of pure CuF electrodes at a current density of 1 A g^{-1} in 1M PBS. (b) Change of specific capacitance over the charge-discharge cycles.

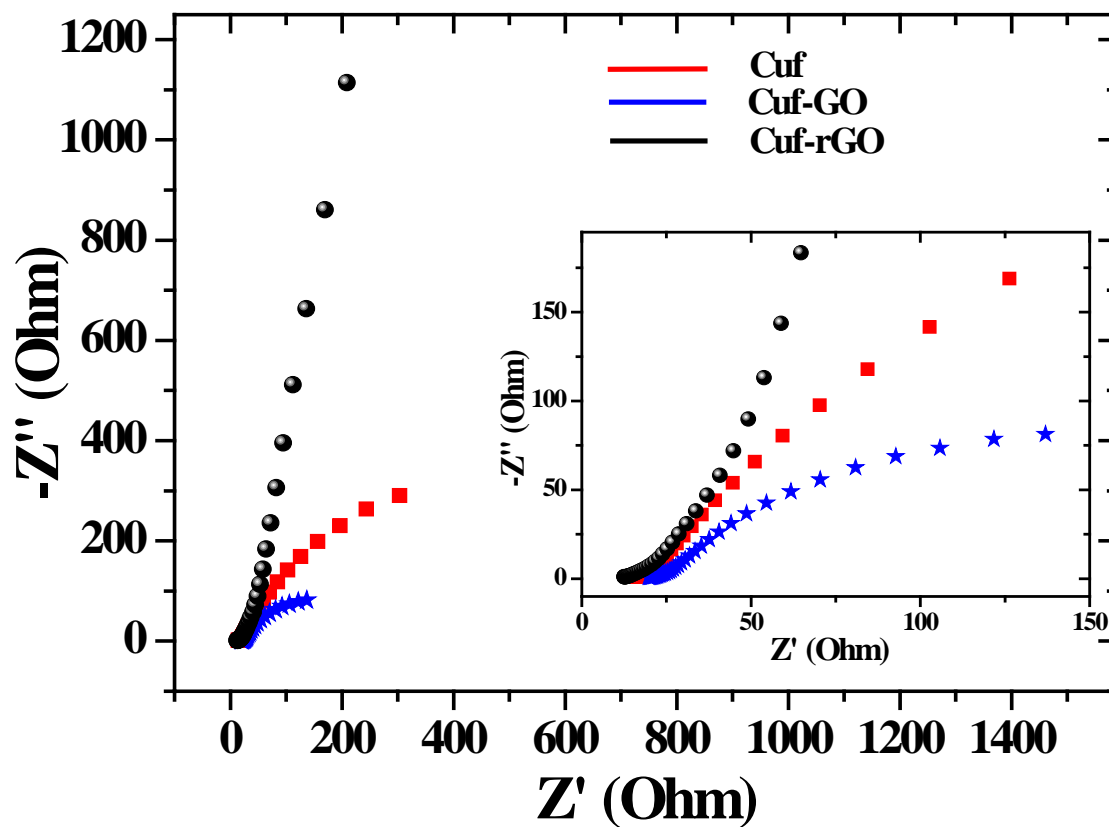


Figure S19. Comparison of electrochemical impedance spectra of CuF (red), GO@CuF (blue) and rGO@CuF (black) electrodes in 1 M PBS. EIS was obtained at open circuit potential (OCP). Inset shows the spectra in the high-frequency region.

III. References

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