

## Supplementary Information:

### **Facile preparation of flower-like graphene-nanosheet clusters with the assistance of copper particles and their application in supercapacitor**

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#### ► **Experimental:**

Graphite powder, CuSO<sub>4</sub>·5H<sub>2</sub>O, NaNO<sub>3</sub>, KMnO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> (30%) and H<sub>2</sub>SO<sub>4</sub> were all purchased from Sinopharm Chemicals Reagent Co., Ltd., China and used as received. Phosphate buffer solution (PBS: Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>, 0.1 M, pH = 4.12) was used as the electrolyte for graphene oxide (GO) electrochemical reduction and electrooxidation of copper particles. The GO was synthesized using the classical modified Hummer's method.<sup>1,2</sup> Typically, 1.0 g graphite powder and 0.5 g NaNO<sub>3</sub> were added into 24 mL cooled (0 °C) H<sub>2</sub>SO<sub>4</sub>, after that, 3.0 g KMnO<sub>4</sub> was slowly added under vigorous stirring for 30 min. During this process, the temperature of the mixture was maintained below 20 °C. The mixture was further stirred at 35 °C for 30 min. Then, 46 mL doubly distilled water was slowly added to the system still under vigorous stirring and the temperature of the system was increased to 98 °C, and then the mixture was maintained at that temperature for 15 min, the reaction was

terminated by adding 140 mL doubly distilled water after 10 mL 30% H<sub>2</sub>O<sub>2</sub> solution was added. At last, the oxidized material was purified by washing with 5% HCl solution when filtering until sulfate could not be detected with BaCl<sub>2</sub>. The sample was dried in a vacuum at 40 °C for 12 hours to obtain the final product of GO. To obtain GO aqueous dispersion, 5 mg of as-prepared dried solid product was added to 10 mL doubly distilled water. Then, the system was treated with an ultrasonic homogenizer for 90 min and, after that was centrifuged under 3000 rpm for 30 min. The mass concentration of the obtained aqueous GO dispersion was estimated to be 0.25 mg mL<sup>-1</sup>.

All electrochemical experiments were performed using a CHI 760E electrochemical workstation (Shanghai Chenhua Instrumental Co., Ltd., China) at room temperature. A saturated calomel electrode (SCE), a platinum wire (0.5 mm in diameter), and a glassy carbon (GC) electrode (3 mm in diameter)/ITO glass (ITO-G)/carbon fiber (CF)/gold electrode (3 mm in diameter) were used as the reference, counter and working electrodes, respectively. All the potentials during the electrochemical experiments were versus SCE. The GC electrode was carefully polished with alumina slurry of 0.5 μm in diameter on a polishing cloth and then sonicated in double distilled water bath for several times before use. The cyclic voltammograms (CVs), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were measured in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte at room temperature. The copper particles were electrodeposited from 5 mM CuSO<sub>4</sub> aqueous solution. While the reduction of GO as well as the electrooxidation of Cu were carried out both in PBS solution.

For the fabrication of flower-like graphene-nanosheet clusters (f-GNSCs): First, 10 μL GO ink was uniformly dropped on the surface of a conventional electrode such as GC electrode, ITO-G, CF, or gold electrode followed by electrochemical reduction to GE; Second, copper particles were electrodeposited on the pre-prepared GE layer in 5 mM CuSO<sub>4</sub> solution at a constant potential of -0.4 V for different total charge that passed through the electrodes during the deposition process ( $Q_{\text{dep}}$ ); And then another 10 μL GO ink was added on the surface of Cu/GE also followed by electrochemical

reduction to fabricate a sandwich construction of GE/Cu/GE on electrode. Finally, copper particles were thoroughly removed under a positive potential of 0.1 V for 1000 s, and simultaneously f-GNSCs formed from the surface of the underlying GE layer on the electrode. For comparison, 20  $\mu$ L GO ink was once dropped on a clean GC electrode, dried, and then followed by electrochemical reduction to form the GE/GC electrode. The mass loading of Cu deposited on the electrodes was determined according to the following eq.(1):<sup>3-5</sup>

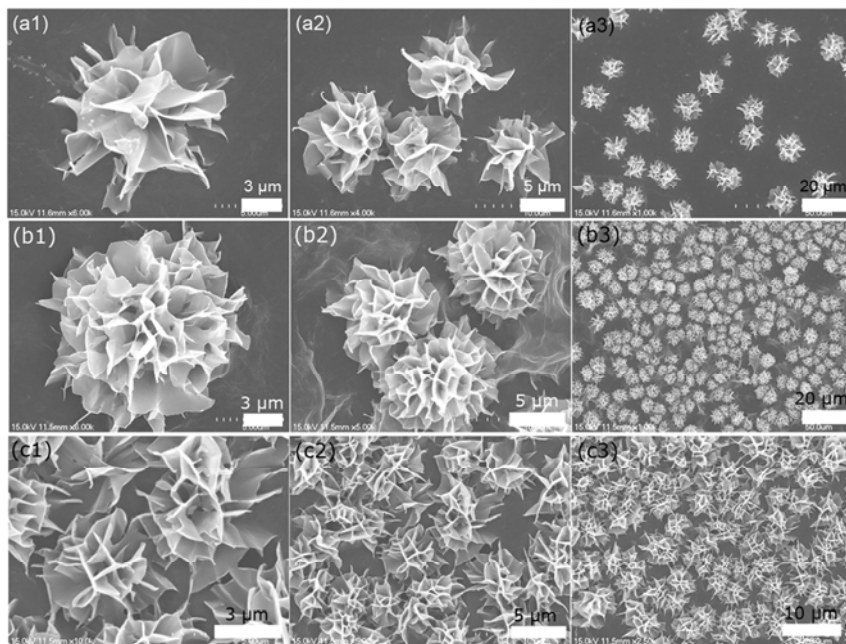
$$W = \frac{(\eta Q_{\text{dep}})M}{FZS} \quad (1)$$

where  $W$  is the mass of deposited Cu particles,  $\eta$  is the current efficiency (assuming as 100% here),  $Q_{\text{dep}}$  is the total charge passed through the electrodes during the deposition process,  $M$  is the molecular weight of Cu,  $F$  is the Faraday constant (96,485 C mol<sup>-1</sup>),  $Z$  is the number of electrons transferred as per Cu atom formed (taken as two for Cu formation), and  $S$  is the surface area of the used electrode.

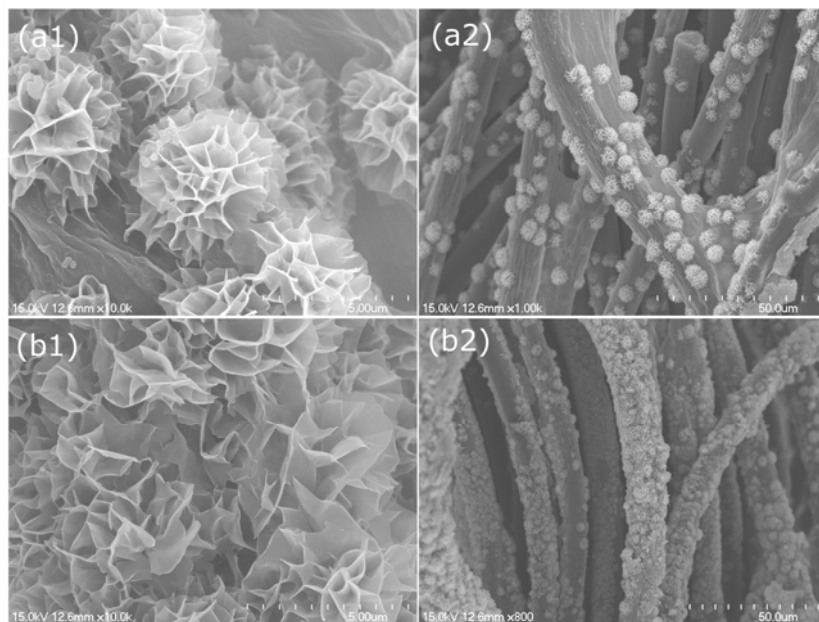
The as-formed f-GNSCs samples were characterized by a scanning electron microscope (SEM, S-4700, Japan), a Renishaw Invia Plus Raman microscope using a 633 nm argon ion laser, and a powder XRD system (XRD, TTR-III) equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm).

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3. B. Habibi and M. Pournaghi-Azar, *J. Solid State Electrochem.*, 2010, **14**, 599.
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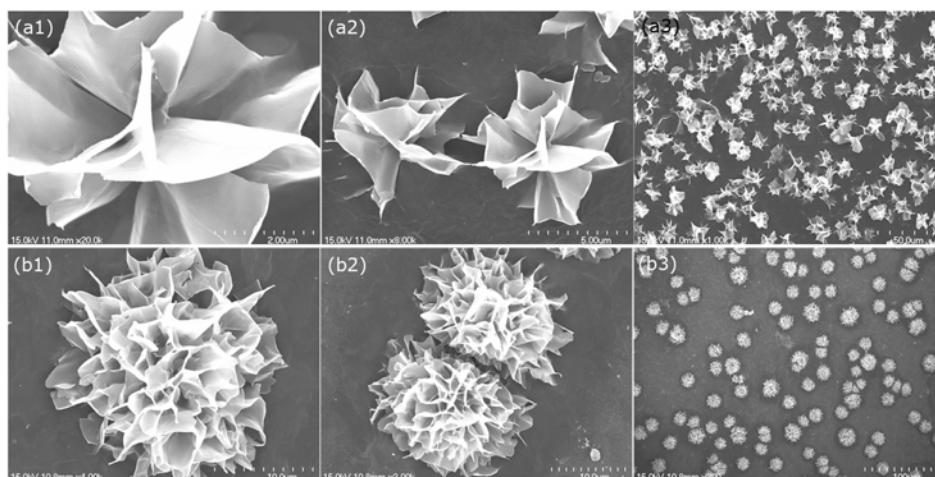
► **SEM characterization:**



**Fig. S1** SEM images of f-GNSCs on ITO glass (ITO-G) in different magnification prepared with Cu mass loading of (a1-a3) 0.024, (b1-b3) 0.048 and (c1-c3) 0.096 mg cm<sup>-2</sup>, respectively.

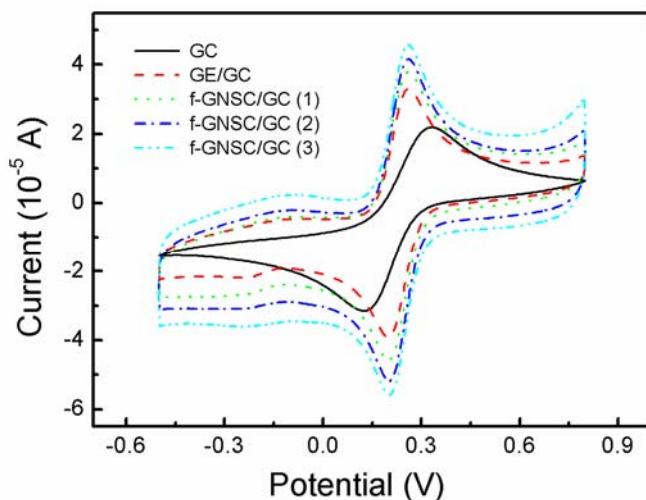


**Fig. S2** SEM images of f-GNSCs on carbon fibers (CFs) in different magnification prepared with Cu mass loading of (a1-a2) 0.024 and (b1-b2) 0.048 mg cm<sup>-2</sup>, respectively.

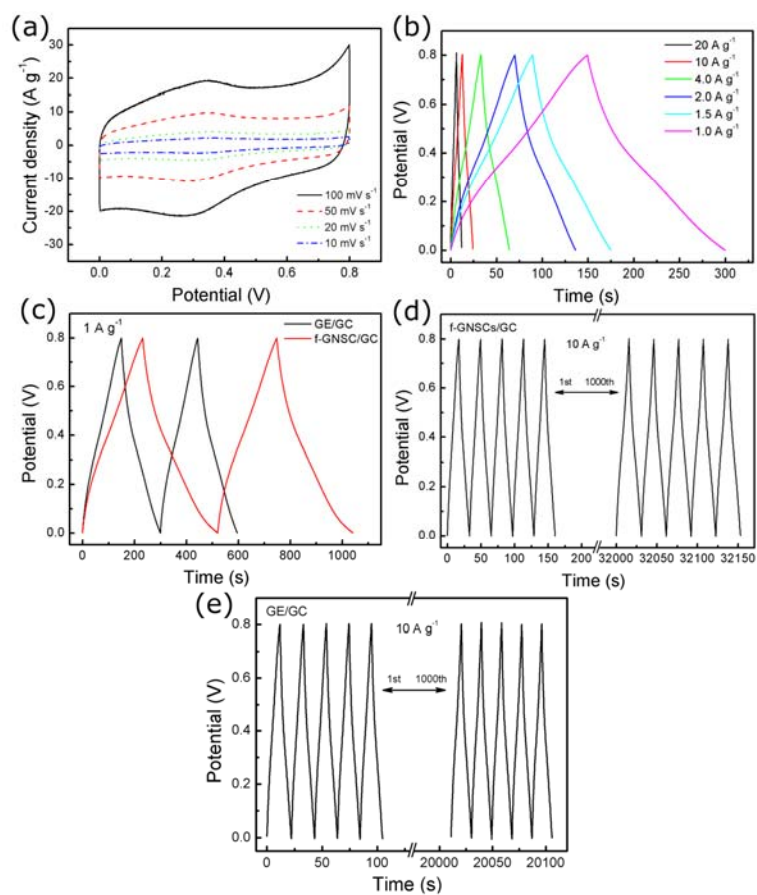


**Fig. S3** SEM images of f-GNSCs on gold electrodes in different magnification prepared with Cu mass loading of (a1-a3) 0.024 and (b1-b3) 0.048 mg cm<sup>-2</sup>, respectively.

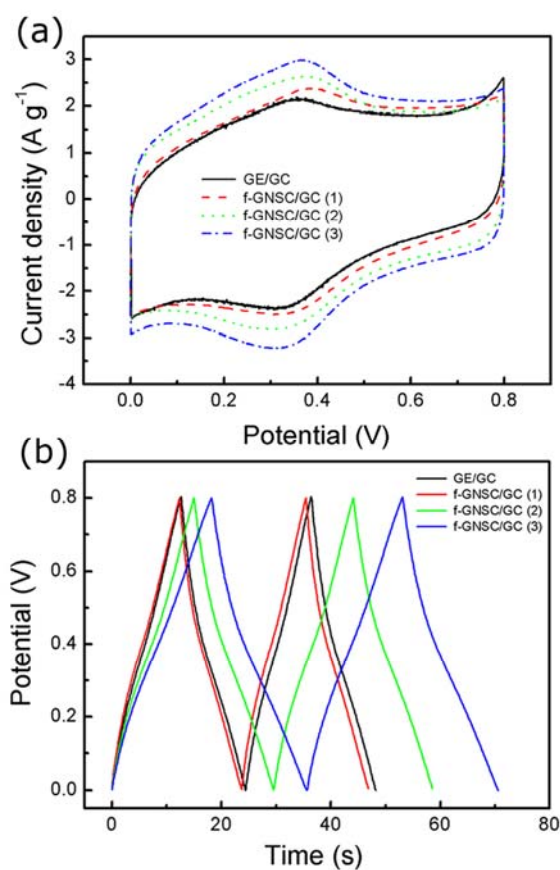
► **Electrochemical characterization:**



**Fig. S4** CVs (the second run recorded) of the bare GC, GE/GC, and f-GNSC/GC electrodes in 5 mM K<sub>3</sub>Fe(CN)<sub>6</sub> aqueous solution containing 1 M KCl at scan rate of 20 mV s<sup>-1</sup>. f-GNSC/GC (1), f-GNSC/GC (2), and f-GNSC/GC (3) were obtained with the mass loading of 0.024, 0.048, and 0.096 mg cm<sup>-2</sup> copper particles, respectively.



**Fig. S5** (a) CVs and (b) charge-discharge curves of GE/GC; (c) charge-discharge curves of f-GNSC/GC and GE/GC at 1 A g<sup>-1</sup>; the long-term cycling charge-discharge curves of (d) f-GNSC/GC and (e) GE/GC electrodes at 10 A g<sup>-1</sup>.



**Fig. S6** (a) CVs of GE/GC and f-GNSCs/GC electrodes in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at scan rate of 10 mV s<sup>-1</sup>; (b) charge-discharge curves of GE/GC and f-GNSCs/GC electrodes recorded in 1 M H<sub>2</sub>SO<sub>4</sub> with a constant current density of 10 A g<sup>-1</sup>. f-GNSC/GC (1), f-GNSC/GC (2), and f-GNSC/GC (3) were obtained with the mass loading of 0.024, 0.048, and 0.096 mg cm<sup>-2</sup> copper particles, respectively.