

## Electronic Supplementary Materials

### **Preparation of reduced graphite oxide with high volumetric capacitance in supercapacitor**

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## Experimental

### Synthesis of GO

GO was synthesized by the modified Hummers method from natural graphite (325 mesh)<sup>1,2</sup>. Briefly, natural graphite powder (12 g),  $K_2S_2O_8$  (10 g), and of  $P_2O_5$  (10 g) were stirred in 48 mL of  $H_2SO_4$  at 80 °C for 5 h, washed several times with deionized water and dried in air overnight. Then  $KMnO_4$  (55 g) was slowly added to the graphite powder solution with 480 mL of  $H_2SO_4$  at 0 °C. After vigorous stirring at 35 °C for 2 h, 1000 mL of deionized water was added into the solution, and then the solution was stirred at 35 °C for additional 2 h. Deionized water (2 L) was added and followed by 50 mL of 30%  $H_2O_2$ . The color of mixture changed into brilliant yellow along with bubbling. The mixture was left overnight leaving yellow-brown precipitates. The resulting precipitates was dialyzed for 2 weeks and dried at 40°C in vacuum to get dried GO.

### Synthesis of RGO-HD

Dried GO (1.6g) was dispersed under the ultrasonication in 800 mL deionized water to form a homogeneous solution.  $Zn(NO_3)_2 \cdot 6H_2O$  (1.49g) and  $NH_4HCO_3$  (0.89g) was added into the solution, and then the solution was stirred for 12 h to obtain a homogeneous mixture. After centrifugation the mixture was placed in a muffle furnace at 350°C for 4 h. The resulting product was immersed in HCl (10 M) and stirred for 12 h to form a black precipitate. The resulting precipitate was washed and filtered with deionized water until the filtrate is neutral. After filtration, the black product was freeze-dried in a freeze drier for 2 days to get reduced graphite oxide with high density (denoted as RGO-HD).

### Characterization

The powder X-ray diffraction (XRD) measurements of the samples were performed on a Rigaku D/max 2500 X-ray powder diffractometer using a graphite monochromator with Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The data were collected between scattering angles ( $2\theta$ ) of 5–80° at a scanning rate of 4°/min. The microstructure and morphology were characterized by the scanning electron microscope (SEM) using a Hitachi S4800 scanning electron microscope. Fourier transform infrared spectroscopy (FT-IR) were conducted on Bruker E55 FT-IR spectrometer in the range of 4000–400  $cm^{-1}$ . The Raman spectrum was carried out on a Renishaw inVia spectroscopy (514 nm excitation in the range of 1000–2000  $cm^{-1}$ , 20 mW

laser power). Thermogravimetric analysis (TG) measurements were performed in NETZSCH5 STA 449C thermogravimetric analyzer at a heating rate of 10 °C·min<sup>-1</sup> in air atmosphere for all the samples except otherwise stated. N<sub>2</sub> adsorption/desorption isotherms were obtained by a gas adsorption analyzer (ASAP 2020, Micromeritics Instrument Co. USA) at 77K. The true density is obtained from an AccuPyc II 1340 (Micromeritics Instrument Co. USA). X-ray photoelectron spectroscopy measurement was performed on a PHI Quantera scanning X-ray microprobe, and the binding energy is calibrated with C1s = 284.8eV. Methylene blue (MB) adsorption method was used to evaluate the specific surface area of RGO-HD in aqueous solution.<sup>3</sup>

## Electrochemical Measurements

Symmetrical two-electrode configuration was used to evaluate electrochemical performance of as prepared samples. RGO-HD electrodes were constructed by mixing the as prepared RGO-HD, conductive carbon and polytetrafluoroethylene (60% emulsion, Aldrich) in the weight ratio of 85 :10 : 5. The mixture was prepared as slurry in ethanol and coated onto nickel foam (1 cm× 1 cm piece) with spatula. The electrodes were dried at 120 °C overnight and then pressed at a pressure of 5 MPa for 1 min. The two-electrode symmetric cell was assembled in a Swagelok cell, with microporous polypropylene as separator between the electrodes. The electrolyte was 6 M KOH aqueous solution. Assembled cells were allowed to soak electrolyte overnight. The weight of the active material on each electrode was ~ 10 mg.

The cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation (Princeton P4000, Ametek, USA). The galvanostatic charge/discharge of the assembled cells was performed on an ARBIN battery testing unit (BTS 2000) in the potential range of 0–1V. All the measurements were carried out at room temperature.

The gravimetric specific capacitance  $C_g$  of electrode material is calculated according to

$$C_g = \frac{2I\Delta t}{mV}$$

in which  $I$  is the discharging current,  $\Delta t$  is the discharging time,  $m$  is the mass of active materials in single electrode, and  $V$  is the voltage of supercapacitor.

The apparent particle density is calculated according to the following equation<sup>4-7</sup>

$$\rho = \frac{1}{V_{total} + 1/\rho_t}$$

$$C_v = \rho C_g$$

$\rho$  is apparent particle density,  $\rho_t$  is true density of graphene ( $1.93 \text{ g} \cdot \text{cm}^{-3}$ ),  $V_{\text{total}}$  is total volume estimated from  $\text{N}_2$  adsorption/desorption ( $V_{\text{total}} = 0.197 \text{ cm}^{-3} \cdot \text{g}^{-1}$ ).  $C_v$  is volumetric specific capacitance and  $C_g$  is the gravimetric specific capacitance. (Notably, the values of  $C_v$  and  $C_g$  are based on pure active materials in the electrode).

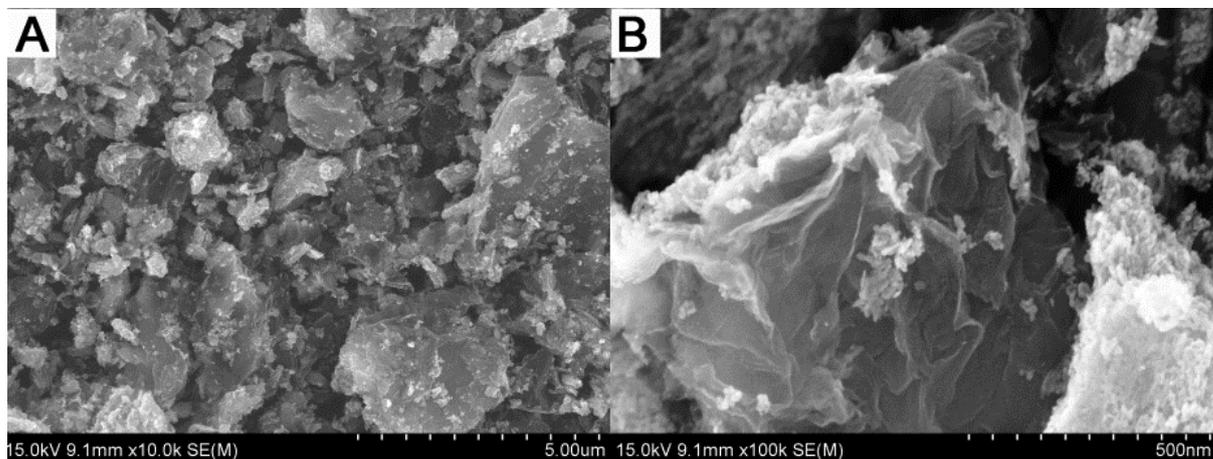
The gravimetric energy density and power density (based on pure active materials in the electrode) according to equation  $E_g = C_g V^2 / (8 \times 3.6)$  and  $P_g = E_g / \Delta t$ , respectively. ( $E_g$  is gravimetric energy density,  $\Delta t$  is the discharging time,  $P_g$  is gravimetric power density). The volumetric energy density and power density are calculated according to equation  $E_v = C_v V^2 / (8 \times 3.6) = \rho C_g V^2 / (8 \times 3.6)$  and  $P_v = E_v / \Delta t$  ( $C_v$  is volumetric specific capacitance,  $E_v$  is volumetric energy density,  $\Delta t$  is the discharging time,  $P_v$  is volumetric power density).

In view of practical application, the volumetric capacitance based on the electrode (not merely based on the active material) is preferred. The volumetric capacitance based on the electrode was evaluated by the equation of  $C_{ve} = \rho_e \times C_e$ . ( $C_e = C/m_e$ ,  $C$  is the capacitance delivered by single electrode,  $C_e$  is the specific capacitance based on the mass of single electrode,  $m_e$  is the mass of single electrode in symmetric cell (the total mass of the current collector, binder, conductive carbon black and active material). ( $\rho_e = m_e / V_e$ ,  $\rho_e$  is apparent density of the electrode,  $m_e$  and  $V_e$  are the mass and volume of a single electrode, respectively).

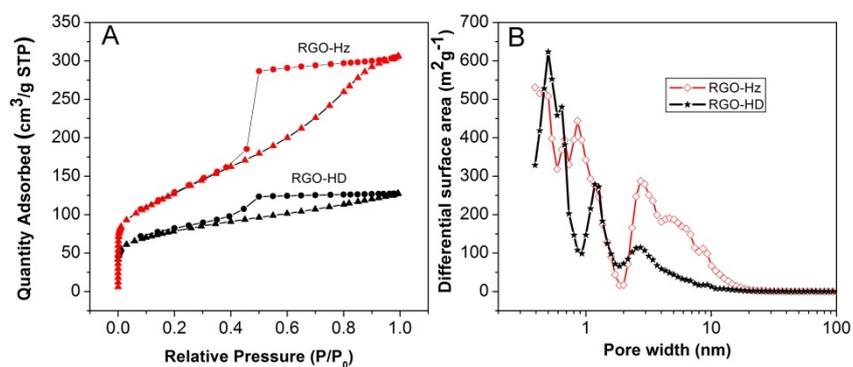
For as fabricated supercapacitor using RGO-HD, the apparent density of the electrode in which nickel foam was used as current collector is  $2.67 \text{ g} \cdot \text{cm}^{-3}$ , and the  $C_e$  is  $23.5 \text{ F} \cdot \text{g}^{-1}$  based on single electrode. Thus the volumetric capacitance based on the electrodes is about  $62.7 \text{ F} \cdot \text{cm}^{-3}$ .



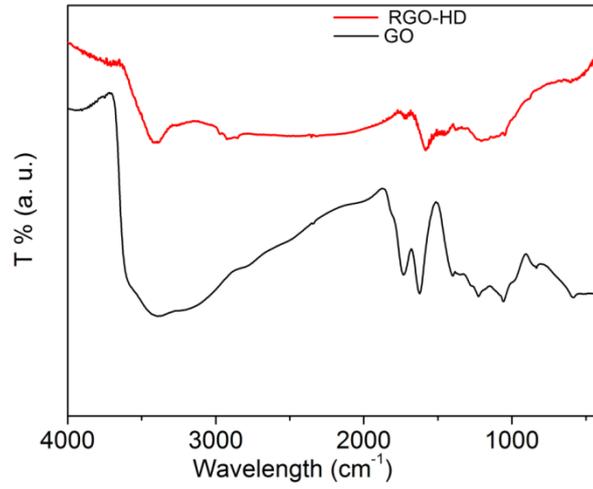
**Fig. S1** Digital image of RGO prepared by thermal reduction<sup>8</sup> (1) and RGO by hydrazine reduction (denoted as RGO-Hz) according to literature<sup>9,10</sup> (2) and RGO-HD (3) with same weight (20mg).



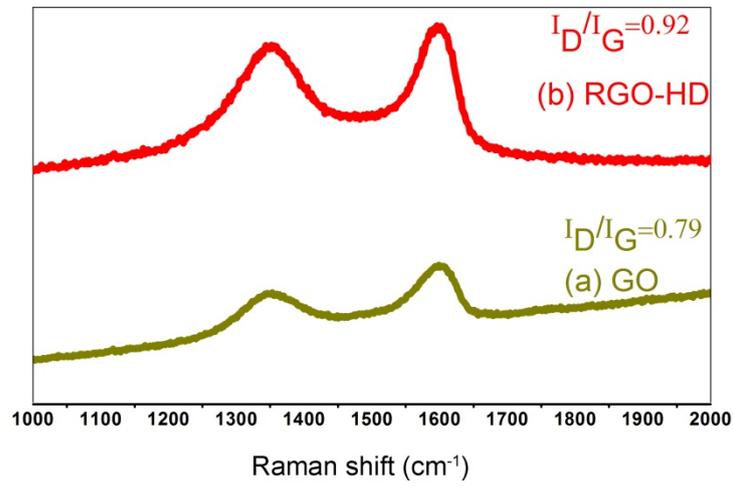
**Fig. S2** SEM images of RGO-HD/ZnO composites (A) at low magnification; (B) at high magnification.



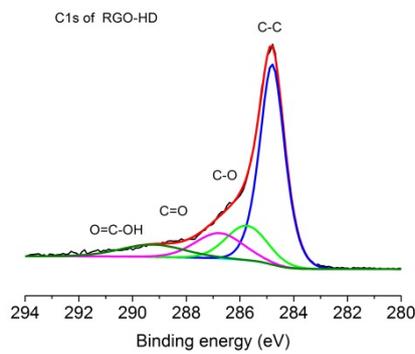
**Fig. S3** Isotherm adsorption/desorption curves of RGO-HD and RGO-Hz at 77K (A); Pore size distribution of RGO-HD and RGO-Hz calculated according to NLDFT model (B).



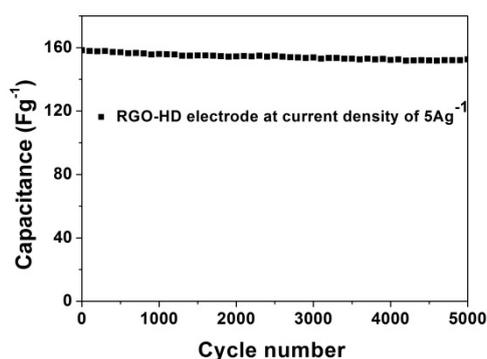
**Fig. S4** FT-IR spectra of GO and RGO-HD.



**Fig. S5** Raman spectra of GO and RGO-HD.



**Fig. S6** C1s XPS profile of RGO-HD sample.



**Fig. S7** Cycle performance of RGO-HD electrode at current density of  $5\text{Ag}^{-1}$ .

**Table S1** Relative concentrations of functional components obtained from curve fitting the C1s XPS Spectrum of RGO-HD

Functional groups	C-C	C-O	C=O	O=C-OH
concentration	63.2%	14.6%	14.0%	8.2%

#### REFERENCES

1. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, A. D. Gorchinskiy, *Chem. Mater.* 1999, **11**, 771.
2. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339
3. M. J. McAllister, J.-L. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme and I. A. Aksay, *Chem. Mater.*, 2007, **19**, 4396-4404.
4. P. Walker and W. Kotlensky, *Can. J. Chem.*, 1962, **40**, 184-188.
5. H. Itoi, H. Nishihara, T. Kogure, T. Kyotani, *J. Am. Chem. Soc.* 2011, **133**, 1165-1167
6. J. Yan, Q. Wang, C. Lin, T. Wei, Z. Fan, *Adv. Energy Mater.*, 2014, doi: 10.1002/aenm.201400500
7. Y. Tao, X. Xie, W. Lv, D.-M. Tang, D. Kong, Z. Huang, H. Nishihara, T. Ishii, B. Li, D. Golberg, F. Kang, T. Kyotani and Q.-H. Yang, *Sci. Rep.*, 2013, **3**, 2975
8. Q. Du, M. Zheng, L. Zhang, Y. Wang, J. Chen, L. Xue, W. Dai, G. Ji and J. Cao, *Electrochim. Acta*, 2010, **55**, 3897-3903

9. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558-1565.
10. Y. Li and X.-M. Li, *RSC Adv.*, 2013, **3**, 2398-2403.