

Electronic supplementary information for

Hydrothermal reduction of three-dimensional graphene oxide for binder-free flexible supercapacitors

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Experimental section

Synthesis of graphene oxide (GO) and three-dimensional (3D) reduced graphene oxide

Graphene oxide was prepared by a modified Hummers method as reported elsewhere [1]. Briefly, graphite (5.0g) was added to concentrated sulfuric acid (115 ml) under stirring at room temperature; then adding sodium nitrate (2.5 g), and then the mixture was cooled to 0 °C by immersed in ice-water bath. In order to keep the temperature of the system lower than 20 °C, potassium permanganate (9.0 g) was added slowly to the system under vigorous agitation. Successively, the reaction system was transferred to a 35 °C water bath for about 2 h, then 400ml of water and 20 ml of H₂O₂ (30%) was added together to the system, and then vigorous agitation for about 1 h. The mixture was filtered and washed with 5% HCl aqueous solution (2000 ml) followed by repeated washing with water to remove the acid. The resulting solid was dispersed in water by ultrasonication for about to make a GO aqueous dispersion (2 g/L).

Three-dimensional (3D) reduced graphene oxide (rGO) and H-rGO can be easily prepared using traditional and modified hydrothermal reduction method respectively.

Briefly, 50 ml of 2 g/L GO aqueous dispersion was sealed in a Teflon-lined autoclave and maintained at 150 °C for 5 h, then the autoclave was cooled to room temperature, and then take out the as-prepared three-dimensional (3D) rGO hydrogel. 3ml of 1M hydrochloric acid aqueous solution was added into 50 ml of 2 g/L GO aqueous dispersion under vigorous agitation for about 0.5 h, next, as mentioned above, sealed in a Teflon-lined autoclave and maintained at 150 °C for 5 h, then the autoclave was cooled to room temperature, and then take out the as-prepared three-dimensional (3D) H- rGO hydrogel.

Materials characterizations

SEM (JEOL 6701 field-emission scanning electron microscope operated at 10 kV) and TEM (JEOL JEM-2100F field-emission transmission electron microscope operated at 200 kV) were used to investigate the surface structure and morphology of the as-obtained three-dimensional (3D) reduced graphene oxide rGO and H-rGO. XRD measurements were conducted using CuK α radiation (Rigaku D/max-2500, λ = 1.5405 Å). The nitrogen adsorption and desorption isotherms were obtained at 77.3 K with a Nova 2000e surface area and pore size analyzer. The specific surface area was calculated using the BET model. Raman measurements were conducted using a DXR Raman Microscope (Thermo Fisher Scientific Inc.) with a laser wavelength of 514.5 nm.

Electrochemical characterizations

The electrochemical performances of the symmetric supercapacitors were investigated using a CHI 660D electrochemistry workstation. Electrochemical impedance spectroscopy (EIS) measurements were carried out on the Autolab PG320N at room temperature.

The fabrication of the symmetric binder-free flexible supercapacitors was as follows. Hydrothermal reduction three-dimensional (3D) GO hydrogel was painted on the weighted nickel foam (area of 1.5cm by 5cm or 2.5 by 3cm), then the hydrogel was dried by freeze-drying method, and then press nickel foam and dried materials

together with 10 Mpa pressure, finally, weight the flexible electrode. The mass loading of each electrode is about 1.33 mg cm^{-2} . Two pieces of these electrodes were assembled using Whatman GF/D glass-fiber and 6 M KOH aqueous solutions as separator and electrolyte respectively. In order to control experiments, other electrodes and supercapacitors were fabricated by the same methods.

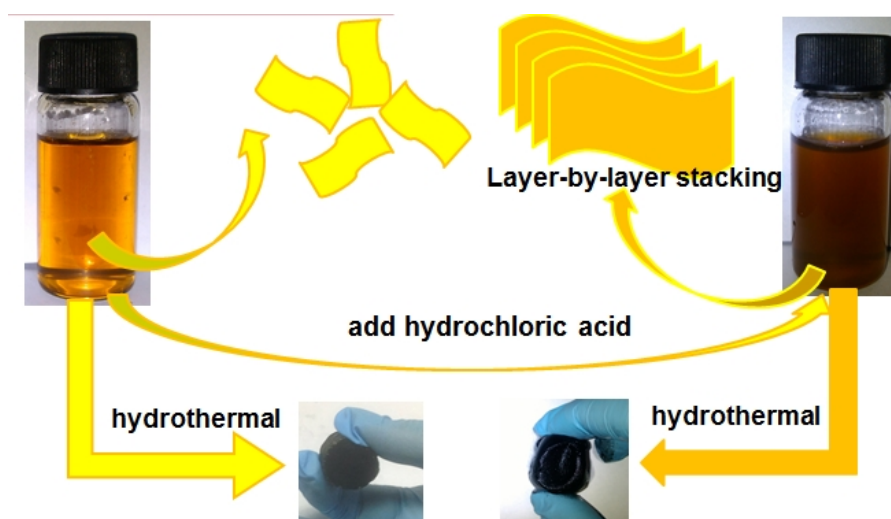


Fig. S1 Scheme of traditional and modified hydrothermal reduction process for the preparation of three-dimensional (3D) graphene.

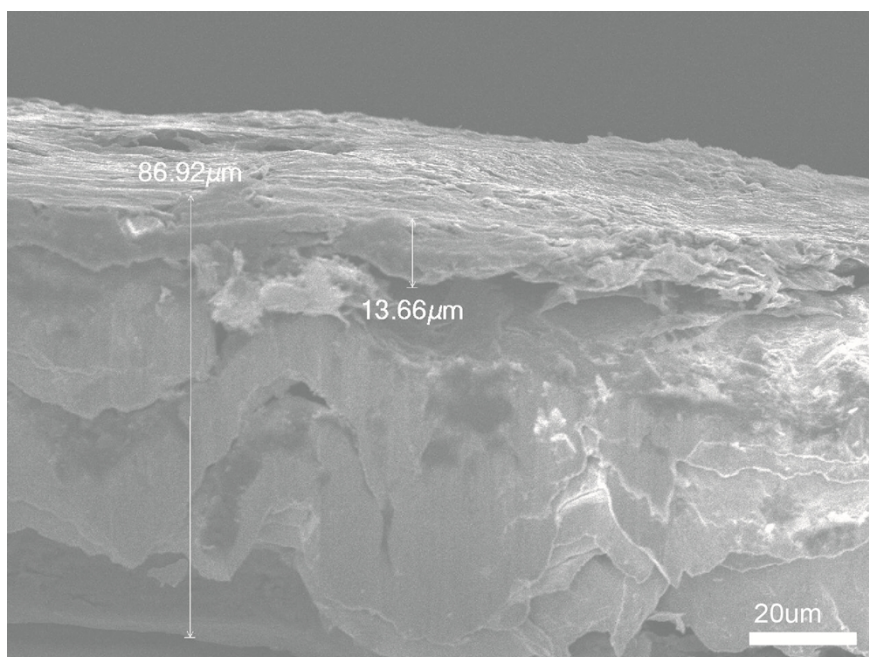


Figure S2. SEM image of the cross section of the prepared electrode

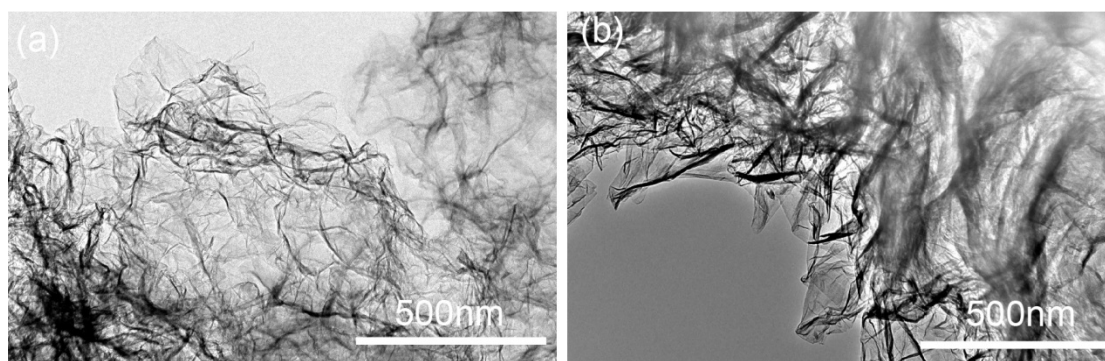


Fig. S3 TEM images of (a) rGO, (b) H-rGO

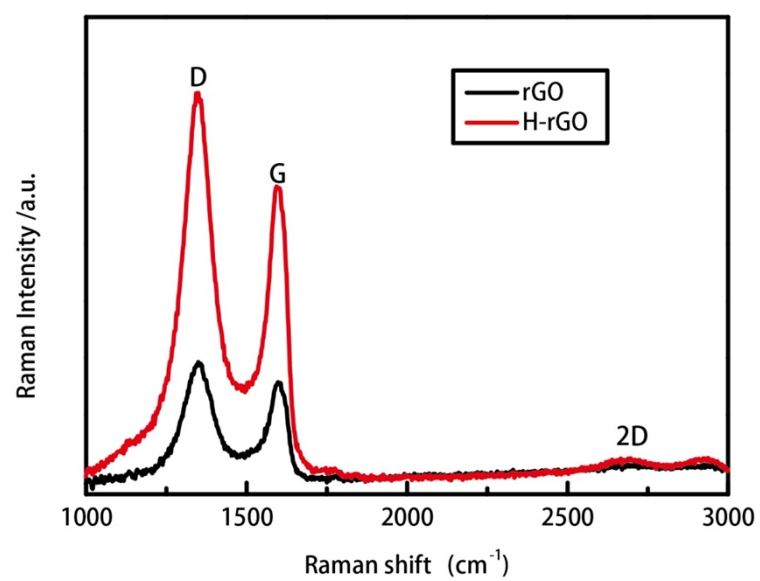


Fig. S4 Raman spectra of rGO and H-rGO

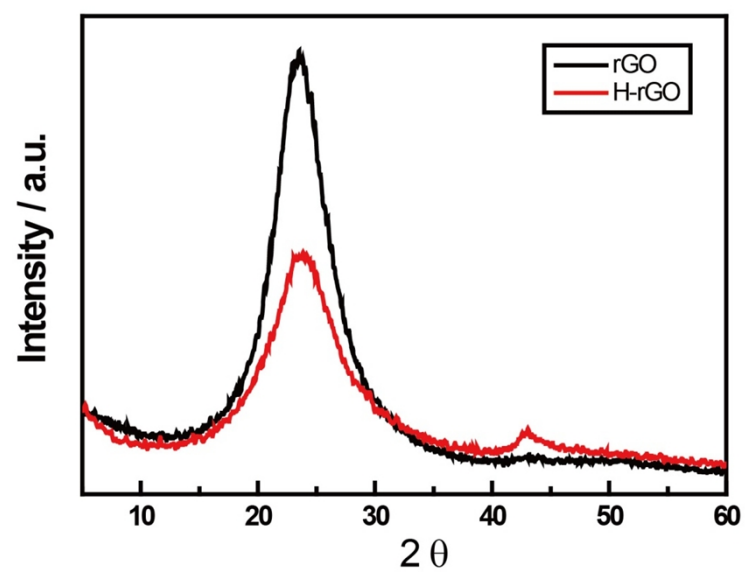


Fig. S5 X-ray diffraction pattern of rGO and H-rGO

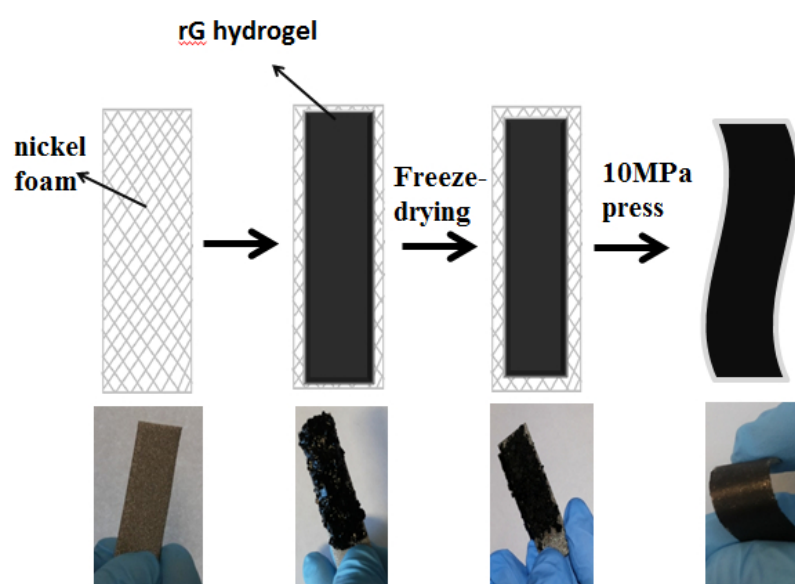


Fig. S6 Scheme of preparing flexible binder-free electrodes.

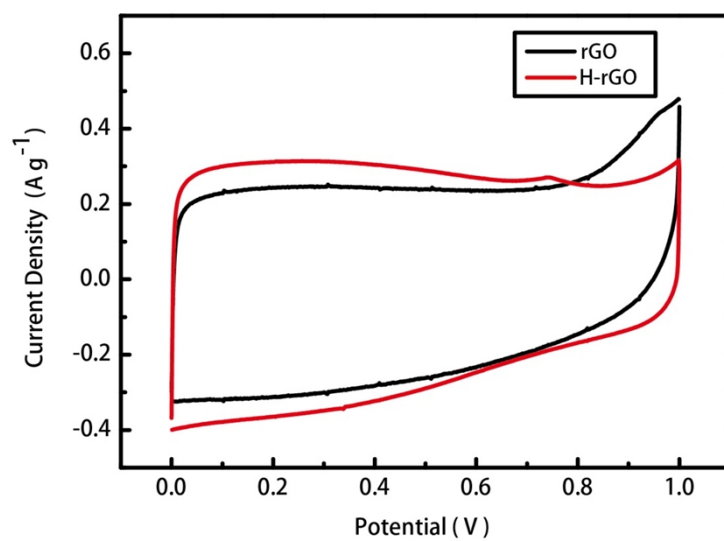


Fig. S7 Cyclic voltammograms of rGO and H-rGO at a scan rate of 5 mV s⁻¹.

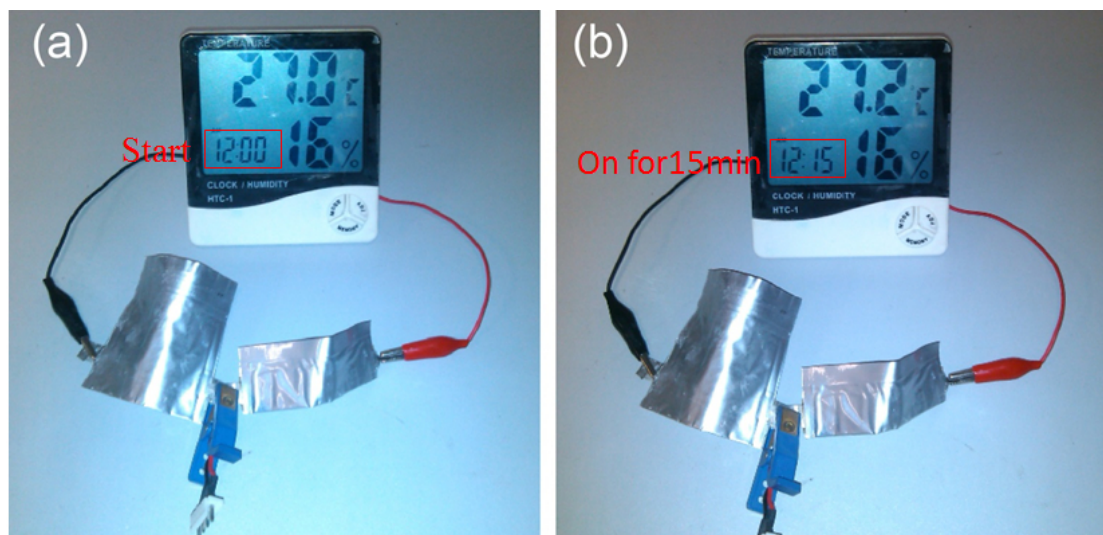


Fig. S8 Digital images of how long the digital temperature and humidity meter can work powered by the two devices connected in series. (a) start. (b) on for 15 min.

Reference

- [1] Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* 2008, 8, 3137.