

Supplementary Material (ESI) for Journal of Materials Chemistry

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Electronic Supplementary Information (ESI)

## Facile synthesis of hydrogenated reduced graphene oxide via hydrogen spillover mechanism

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### Experimental Section

**Chemicals.** Commercially available Natural flake graphite, sulfuric acid (95-98%), potassium permanganate, hydrogen peroxide, nickel powder (<150 µm, 99.99% trace metals basis) and hydrochloric acid (36.5-38%) were purchased from Sigma-Aldrich and used as received. Other reagents were of analytical grade and were used as received without further purification. All aqueous solutions were prepared with deionised distilled (DD) water (>18.2MΩ.cm) from a Milli-Q Plus system (Millipore).

**Synthesis of GO.** Graphene oxide (GO) was synthesized by chemical exfoliation method followed by our previous work.<sup>1</sup> The resultant suspension was extensively washed with DD water and dilute HCl until the pH of the filtrate was neutral and subsequently centrifuged (3000 rpm) in order to remove residual unexfoliated graphite and oxidizing agents. GO slurry was then freeze-dried and stored in a vacuum oven at room temperature.

**Synthesis of HRGO.** Dry GO powder (75 mg) was initially dispersed in DD water (100 ml) under sonication (15 min). Subsequently, Ni powder (1250 mg) was added to the GO suspension in a round bottom (RB) flask and re-sonicated (10 min) followed by stirring (200 rpm for 15 min) under ambient conditions. Finally, 70.0 ml of conc. HCl was slowly poured to the above solution and continuously stirred for next 24 hrs. After the completion of reaction final product was centrifuged (6000 rpm, 15 min) to remove any remaining Ni and HRGO was repeatedly washed with DD water and dried at 70°C in oven.

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<sup>1</sup> G. Goncalves, P. A. A. P. Marques, C. M. Granadeiro, H. I. S. Nogueira, M. K. Singh, and J. J. A. Gracio, *Chem. Mater.*, 2009, **21**, 4796.

**Characterization techniques.** Phase purity and presence of crystalline phases of GO and HRGO samples were analysed by X-ray diffraction (XRD) analysis (Rigaku Geigerflex D/Max, C Series, Tokyo, Japan; CuK $\alpha$  radiation;  $2\theta$  angle range 5–75°; step 0.02°/s). The FTIR spectra of GO, HRGO and RGO were recorded using a Bruker Tensor 27 FT-IR spectrometer by mixing the sample KBr (Aldrich, 99%, FT-IR grade). X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 200A, VG Scientific (UK). For analysis, an achromatic Al (K $\alpha$ ) X-ray source operating at 15 kV (300 W) was used, and the spectrometer was operated in CAE mode with 20 eV pass energy. Data acquisition was performed with a pressure lower than 10<sup>-6</sup> Pa. Spectral analysis was performed using the XPS Peak software with Gaussian–Lorentzian peak shape. The binding energies of XPS spectra were determined by curve deconvolution using non-linear least squares fitting routine after a Shirley-type background subtraction. The Raman spectra were obtained at room temperature in back scattering configuration with a Jobin-Yvon Lab Ram HR equipped with a Multichannel air cooled (-70°C) CCD detector. An objective of x40 magnification was used to focus the surface of sample excited with the 532 nm HeCd laser line. The samples for TEM were prepared by dipping an aliquot of suspension (HRGO in acetone, 0.1 mg/ ml) on to a carbon-coated copper grid. A conventional high-resolution (HR) TEM (JEOL 2200F TEM) was performed to analyse the crystallinity and quality of HG sample. Results were collected at 200 kV with a point resolution of 0.16 nm. For electrical measurements HRGO film (1mg/ ml acetone) was prepared on SiO<sub>2</sub> substrate by drop coating and dried at 60°C in oven for 2h. Current vs. Voltage (I/V) curve was measured using two probe Keithley electrometer (model 617) at 300 K. During the measurements the samples were maintained inside a cryostat, in helium gas, to improve the heat transfer and eliminate the moisture. Also, to avoid errors due to leakage resistance we used a guarded configuration to minimize those effects. The resolution of our equipment was 0.1 fA (femto-ampere), with extremely low input offset current. To achieve high accuracy, in particular for lower current ranges, we initialised the instrument, using the zero check and zero correct facilities. Shielding of the circuit under test is also done, to minimize noise pickup. Moreover, the resistance of the samples was very high, when compared with electrode contacts and therefore it will not affect the accuracy of the measurements. Capacitance measurement was carried out by using an Agilent 4294A LCR precision impedance analyser with frequency range from 40 to 1MHz at 300k. For measuring the capacitance one of the electrodes was formed by a metal plane in bottom of the bulk, just on the substrate. The dimension was, from the point of view of the electrical measurement, the area of the film, which is about 0.5 cm<sup>2</sup>. The second electrode was applied by silver painting, in the top of the film. Dimensions were maintained for all the samples. The thermogravimetric (TGA) analysis was carried out under N<sub>2</sub> flow in a Shimadzu TGA 50 analyzer equipped with a platinum cell. The samples were heated at a constant rate of 10 °C min<sup>-1</sup> from room temperature to 700 °C. Optical spectra were recorded from Shimadzu UV-2501PC (UV-vis) spectrophotometer in the absorbance mode. To investigate the FTIR and Raman spectra of

dehydrogenate product rGO, 10 mg HRGO was placed in Shimadzu TGA 50 analyzer equipped with a platinum cell and annealed for 2h at 450°C in presence of inert atmosphere argon.

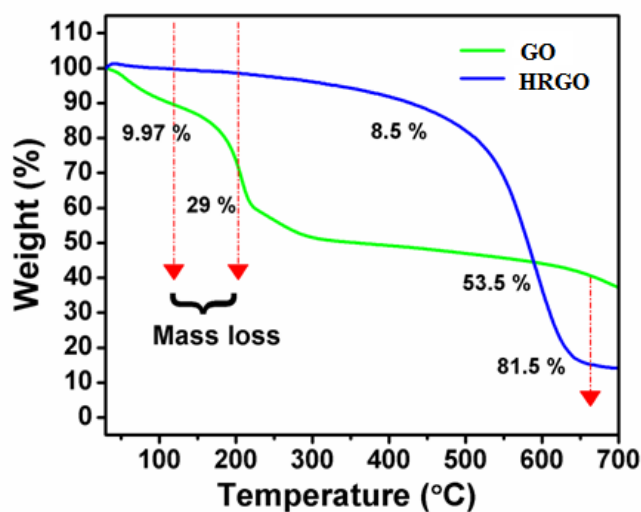


Figure S1 TGA of GO and HRGO.

Figure S1 (TGA plots) depicts the % weight change of GO, and HRGO in N<sub>2</sub> atmosphere. In GO, initial two weight losses 9.97% and 29% at 100°C and 200°C, respectively, were observed due to the removal of surface adsorbed water.<sup>2</sup> The final weight loss 53.5% at 600°C is due to the decomposition and pyrolysis of oxygen functionality at higher temperature. However, in HRGO the weight loss profile was totally different from GO. The weight losses of 3.5% at 200°C is less compared to GO. Moreover, a weight loss of 8.5 % was observed at 400 °C. The final weight loss (81.5% ) in HRGO was observed at 590°C.

<sup>2</sup> Z. J. Fan, W. Kai, J. Yan, T. Wei, L. J. Zhi, J. Feng, Y.M. Ren, L.P. Song, and F. Wei, *ACS Nano*, 2011, **5**, 191

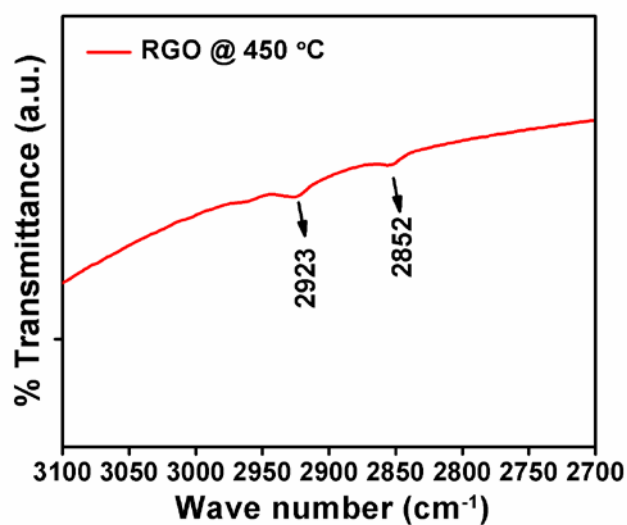


Fig.S2 FTIR spectrum of HRGO after annealing at 450°C.

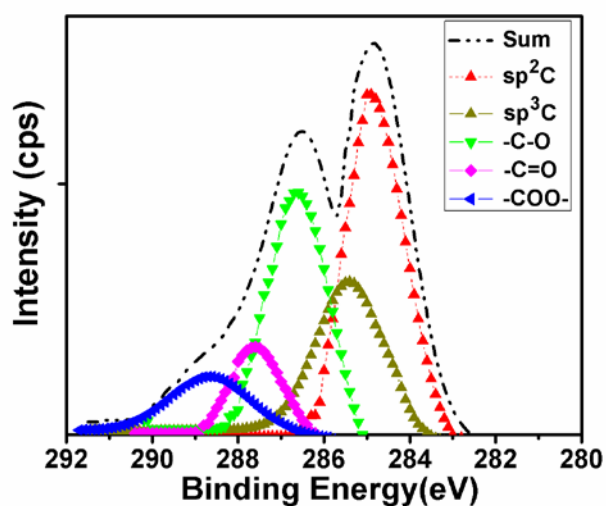


Figure S3 XPS spectra of GO.

Figure S3 displays C1s XPS of GO after the deconvolution of raw data containing five different peaks<sup>2</sup> related to sp<sup>2</sup>C, sp<sup>3</sup>C, -C-O, -C=O and -COO groups in the region of 280 to 292 eV and no peak was observed less than 284.6 eV.

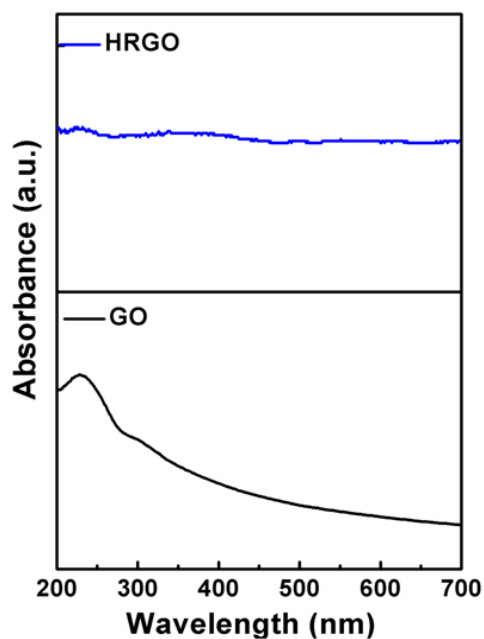


Figure S4 UV-Vis spectra of GO and HRGO.

Figure S4 shows the GO possess two characteristic absorption bands at 230 nm and 300 nm (in water medium), they were corresponding to (i)  $\pi \rightarrow \pi^*$  transitions of aromatic C=C bonds and (ii)  $n \rightarrow \pi^*$  transitions of C=O bonds as peak and shoulder, respectively.<sup>2</sup> While in HRGO no apparent peak was observed, unlike GO and suggests the removal of alkenes and carbonyl functionalities.

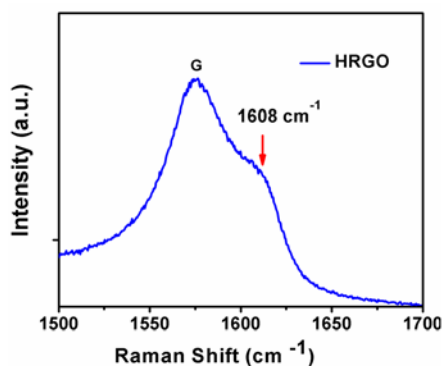


Figure S5 Magnified Raman spectra of HRGO in the region of 1500 to 1700  $\text{cm}^{-1}$ .

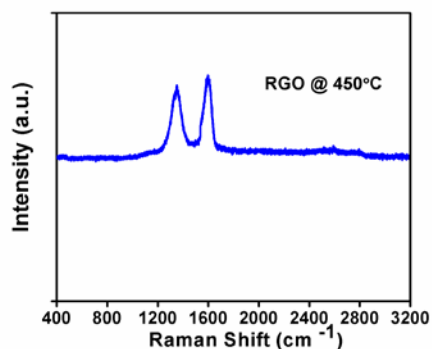


Fig.S6 Raman spectrum of HRGO after annealing at 450°C.

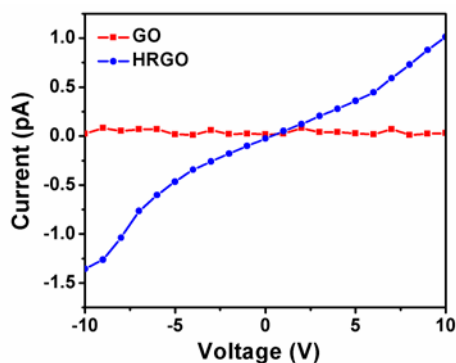


Figure S7 I-V characteristic of GO and HRGO at 300K.

Figure S7 illustrates the current- voltage (*I-V*) characteristics of GO and HRGO samples at 300K. Results show that GO possess negligible current ( $10^{-4}$  nA) while sweeping voltage from -10 to +10 V and behaves like an insulator. Whereas, the displayed current in HRGO was 2 orders higher than GO.

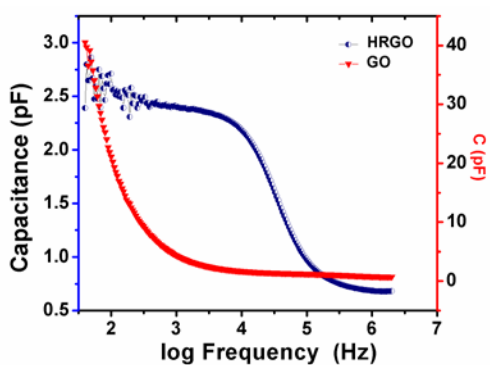


Figure S8 Capacitance measurement of GO and HRGO at 300K.

Figure S8 shows the Frequency vs capacitance characteristics of GO and HRGO. The capacitance measurement also reveals a clear difference in their behaviour. While GO displayed an exponential

decrease in capacitance with increase in frequency from 10 to 1000Hz, HRGO showed a steady capacitance up to 10KHz. This type of capacitive behaviour can be used for various energy storage device applications.<sup>3</sup>

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<sup>3</sup> D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P. L. Taberna and P. Simon, *Nature Nanotech.*, 2010, **5**, 651.