Electronic Supplementary Information for

A high-performance supercapacitor-battery hybrid energy storage device based on graphene-enhanced electrode materials with ultrahigh energy density

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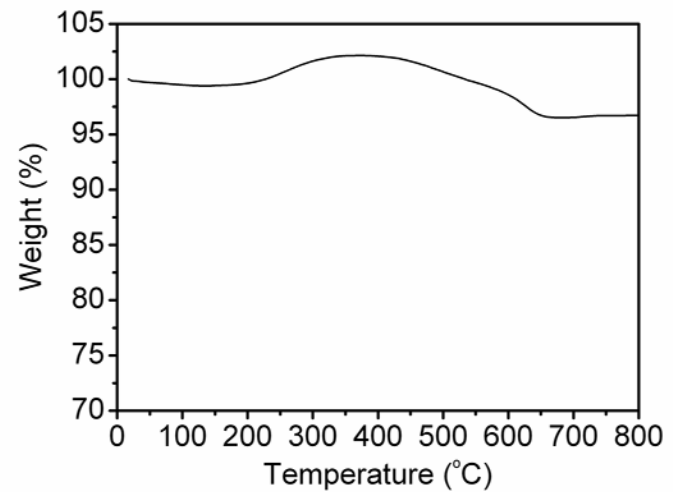

Fig. S1 Thermogravimetric analysis (TGA) curve of Fe_3O_4/G composite, measured from 20 to 800 °C at a heating rate of 10 °C/min in air. According to the TGA result, the weight percentage of graphene is 3.3 wt % in the Fe_3O_4/G composite.

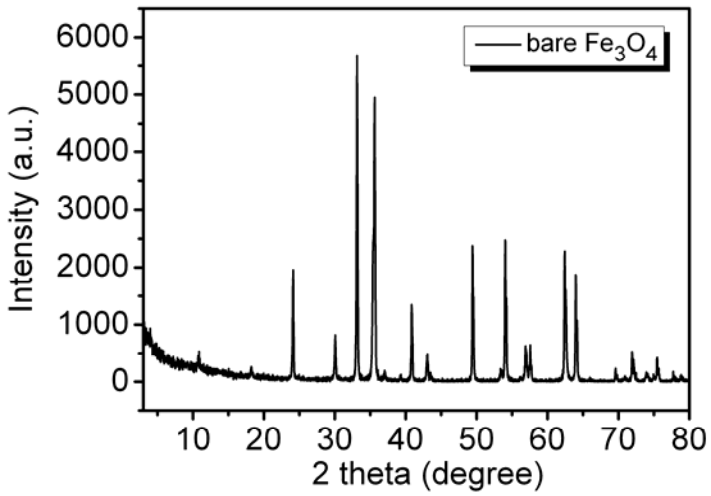

Fig. S2 XRD profile of as-prepared Fe_3O_4 in the same condition. It shows that the product is a mixture of Fe_3O_4 and Fe_2O_3, indicating that the Fe_3O_4 is more inclined to form the stable Fe_2O_3 during the processing without graphene.

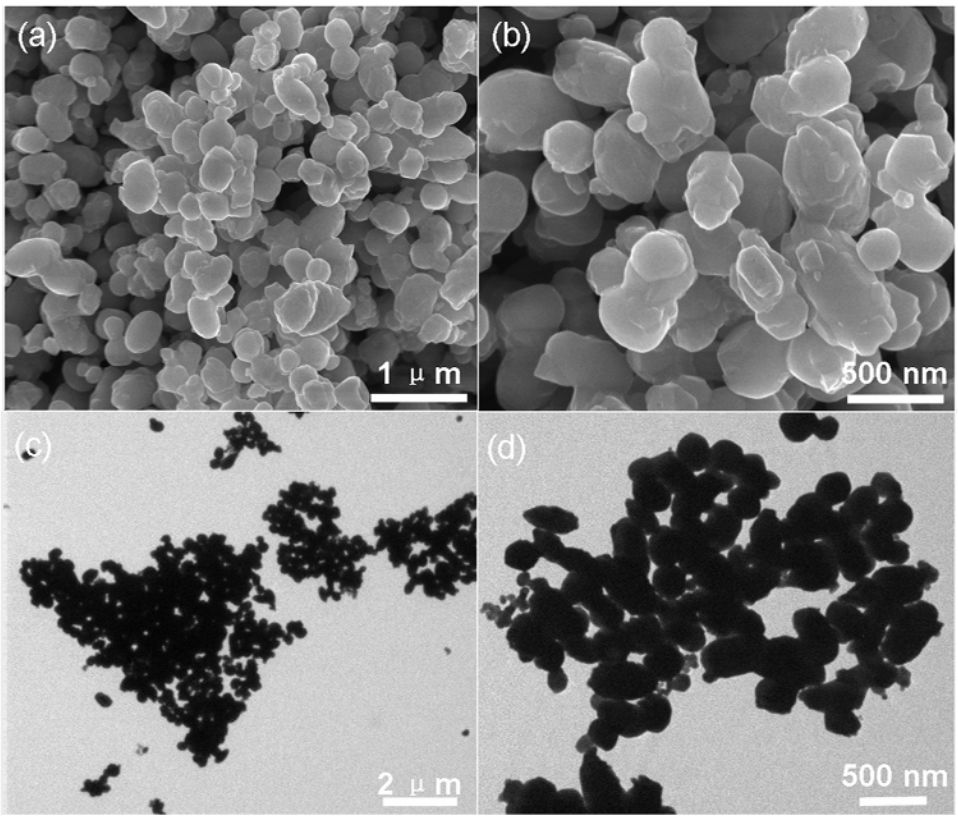

Fig. S3 SEM (a, b) and TEM (c, d) images of as-prepared Fe_3O_4 in the same condition. It can be clearly seen that compared to Fe_3O_4/G composite, the bare Fe_3O_4 have larger particle sizes of about 200-500 nm with severe agglomeration.

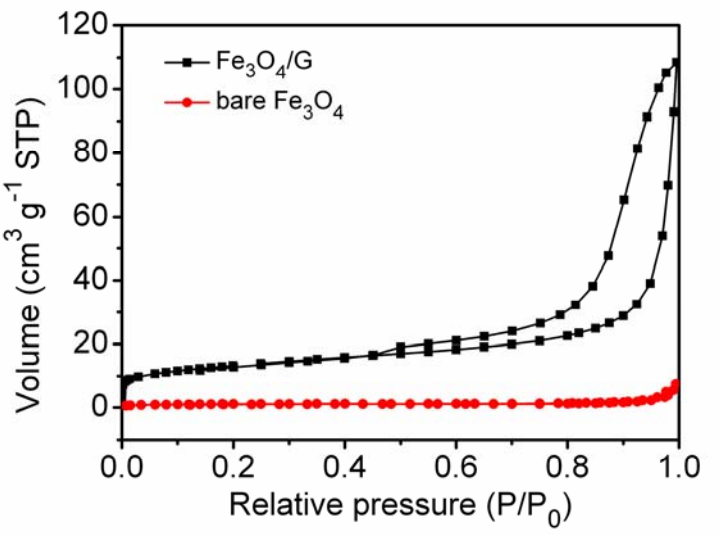

Fig. S4 N_2 adsorption/desorption isotherms of Fe_3O_4/G nanocomposite and bare Fe_3O_4. The results indicate that the Fe_3O_4/G nanocomposite is more porous mainly with mesopores and the surface area is much higher than that of bare Fe_3O_4.

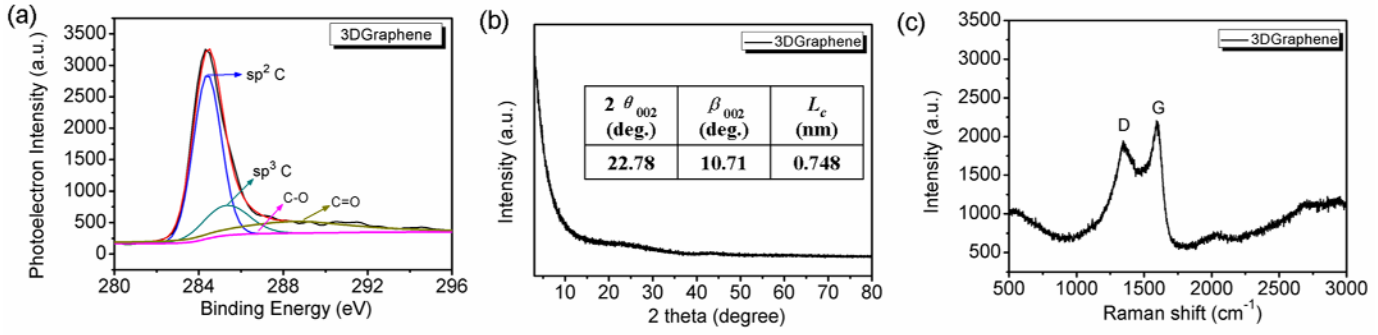

Fig. S5 (a) XPS spectra of C1s and their deconvolution for the material 3DGraphene. The primary C1s XPS peak mainly appears at a binding energy of 284.4 eV, assigned to sp^2-bonded carbon. Meanwhile, there are other much weaker peaks that can be identified as sp^3-bonded carbon at 285.3 eV, C-O at 286.8 eV, and C=O at 288.5 eV respectively.[1] (b) XRD profile of 3DGraphene and its lattice parameters. The average graphene domains height (*Lc*) can be approximately determined to be ~0.748 nm (calculated by the Scherrer's equation,[2] indicating a much disordered porous structure with mainly single-layered graphene sheets. (c) Raman spectrum of 3DGraphene material. Lorentzian fitting was examined to obtain the positions and widths of the D and G bands. The size of graphene sheets (L_a, nm) can be estimated by equation L_a (nm) = $(560/E^4)(I_D/ I_G)^{-1}$,[3] where E is the laser energy in nanometers (λ = 514.5 nm, 2.41 eV), and I_D and I_G are the intensities of the D and G bands, respectively. The approximate dimensional size of the graphene nanosheets is ~6.6 nm.

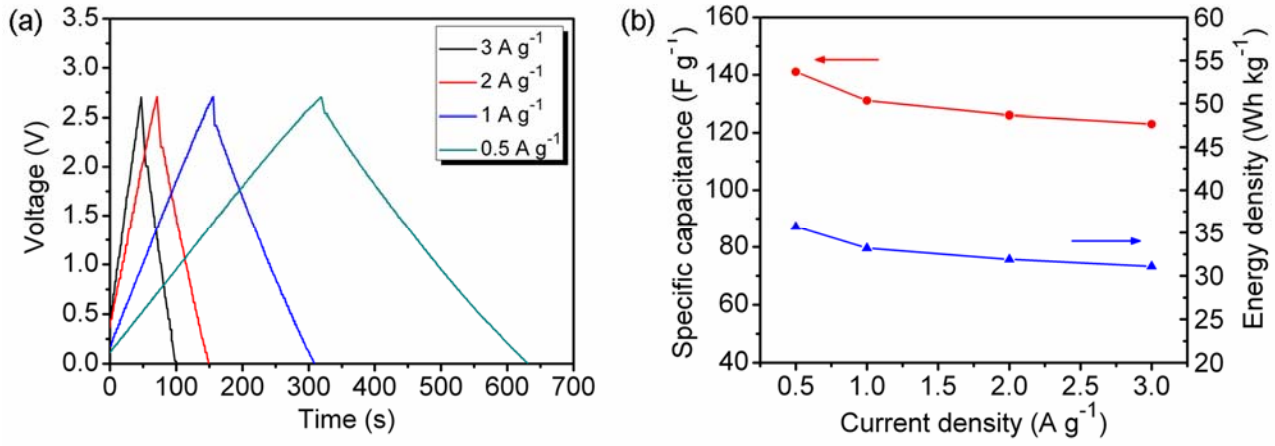

Fig. S6 (a) Galvanostatic charge/discharge curves of SUAC-based supercapacitor at current densities of 0.5-3 A g^{-1} in the voltage range of 0-2.7 V. (b) Specific capacitances and energy densities of SUAC-based supercapacitor at different densities. The SUAC product showed lower specific capacitance of 126-141 F g^{-1} and energy density of 31.1-35.7 Wh kg^{-1} at current densities of 0.5-3 A g^{-1}. All these values were calculated based on the mass of single electrode activate material.

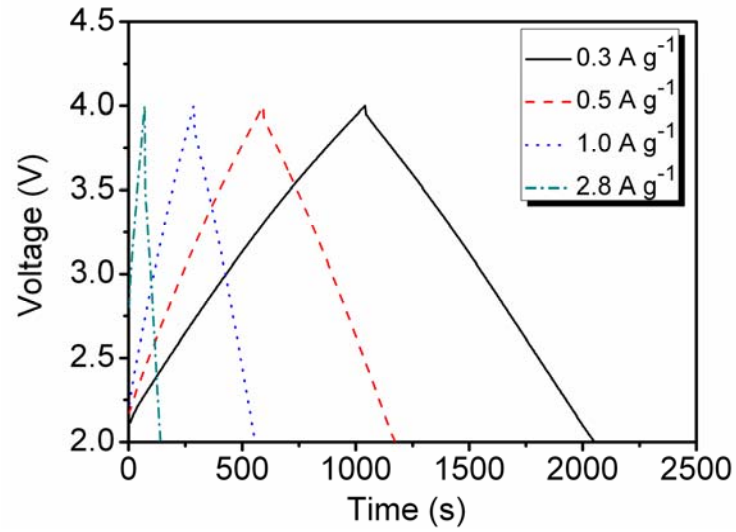

Fig. S7 Galvanostatic charge/discharge curves of 3DGraphene-based half cell (vs. Li/Li^+) at different current densities in the voltage range of 2.0-4.0 V.

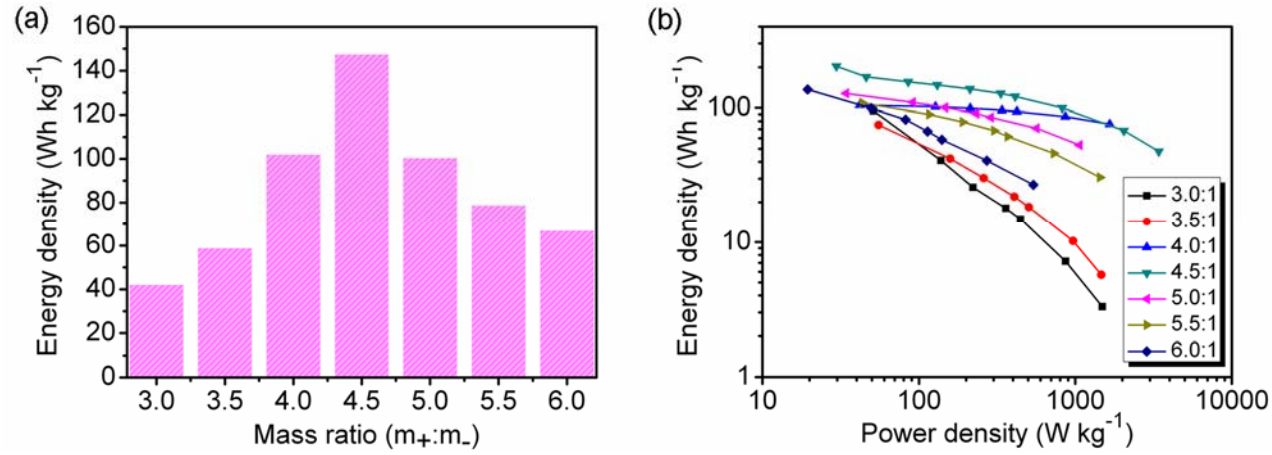

Fig. S8 (a) Energy density of Fe_3O_4/G//3DGraphene hybrid devices with different mass ratios of positive *vs.* negative materials. The power density is ~ 150 $W \cdot kg^{-1}$ based on the total mass of both electrodes for the optimized ratio of 4.5:1, and the voltage range is 1.0−4.0 V. (b) Ragone plots (power density vs. energy density) of Fe_3O_4/G//3DGraphene hybrid devices with different mass ratios of positive against negative materials in the voltage range of 1.0−4.0 V. At the mass ratio of 3DGraphene: Fe_3O_4/G = 4.5:1, the hybrid cell achieves the highest energy density of 147 Wh kg^{-1} under the same power density (~ 150 W kg^{-1}), and the tendency remains almost the same with increasing the charging/discharging rate, thus the optimized mass ratio of 4.5:1 is selected in the work.

References

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3 L. G. Cancado, K. Takai, T. Enoki, M. Endo, Y. A. Kim, H. Mizusaki, A. Jorio, L. N. Coelho, R. Magalhães-Paniago and M. A. Pimenta, *Appl. Phys. Lett.*, 2006, **88**, 163106.