Supporting Information

Electron beam "ballooned" carbon sphere derived from graphene oxide by a hydrazine assisted hydrothermal method

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Experimental details

Graphene oxide (GO) making: GO used in this work was synthesized by modified hummer method and described in brief as follows: The concentrated 7.5 mL H_2SO_4 in a 100 mL beaker was heated up to 80 °C. $K_2S_2O_8$ (2.5 g) and P_2O_5 (2.5 g) were added in sequence with continuous stirring until the reactants were completely dissolved. Graphite powder (5 g) was then added to above mixture. The resulting mixture was kept at 80 °C for 6 hours, after which the mixture was diluted with distilled water, filtered and washed to remove all soluble substances, and the corresponding

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pretreated graphite was transferred to a drying dish and left overnight under ambient conditions. Another 115 mL H_2SO_4 was put into a 500 mL Erlenmeyer flask and then cooled in an ice bath. The pretreated graphite and 15 g $KMnO_4$ were added slowly in sequence and allowed to dissolve completely. The mixture was then allowed to react at 35 °C for 2 hours, after that, 230 mL distilled water was slowly added. After stirring for 15 min, another 700 mL of distilled water was added to the mixture, thereafter 12.5 mL of 30% H_2O_2 was added to the mixture. The mixture was allowed to stand for at least 12 hours then the clear supernatant was decanted. The remaining mixture was washed with 1.1 L 1:10 HCl solution followed by distilled water. Finally, it was purified by dialysis for at least one week to remove any remaining salt impurities for the following experiments.

Preparation of self-assembled carbon spheres: As synthesized GO was firstly suspended in distilled water (1 mg mL^{-1}) with ultrasound for 2 h, then the GO aqueous suspension was centrifuged at 5000 rpm for 5 min to remove any residual unexfoliated graphite oxide. The as-prepared GO aqueous suspension (1 mg L^{-1}) was directly mixed with 50 % hydrazine hydrate aqueous solution with a volume ration of 1:1. After being homogenized by stirring for several minutes, a total of 30 mL GO/hydrazine hydrate mixed aqueous suspension was transferred to a 40 mL Teflon-lined autoclave and heated at 160 ^{o}C for 10 h to generate pristine carbon spheres. Then the self-assembled pristine carbon spheres were collected by filtration, washed with distilled water for several times, and then redispersed in distilled water

with mild sonication. For the control experiment, 50% hydrazine hydrate was simply replaced by 0.5 M $NaBH_4$ aqueous solution, and other procedures were same. The annealing of the carbon spheres was carried out in an electric oven at 200 ^{o}C for 2 h in air atmosphere.

Characterization instruments: The electron beam irradiation of the self-assembled carbon spheres were performed using a transmission electron microscopy (TEM, Tecnai G2 F30, FEI) and a focused ion beam scanning electron microscope (FIB-SEM, FEI HELIOS Nanolab 600i). X-ray photoelectron spectroscopy measurement was performed using an X-ray photoelectron spectrometer (XPS, K-Alpha, Thermofisher Scienticfic Company) with monochromated Al Kα radiation (*hv* = 1486.6 eV). All XPS spectra were corrected using the C1s line at 284.6 eV. Curve fitting and background subtraction were accomplished using Thermo Avantage software. Raman spectra were collected with a LabRAM XploRA laser Raman spectrometer (HORIBA Jobin Yvon CO. Ltd) using a 532 nm laser with an incident power of 0.15 mW. Thermogravimetric analysis (TGA) was conducted on a STA 449C thermalgravimetric analyzer from 35 to 800 °C at a heating rate of 10 °C min^{-1} in argon flow.

Supplementary Figures

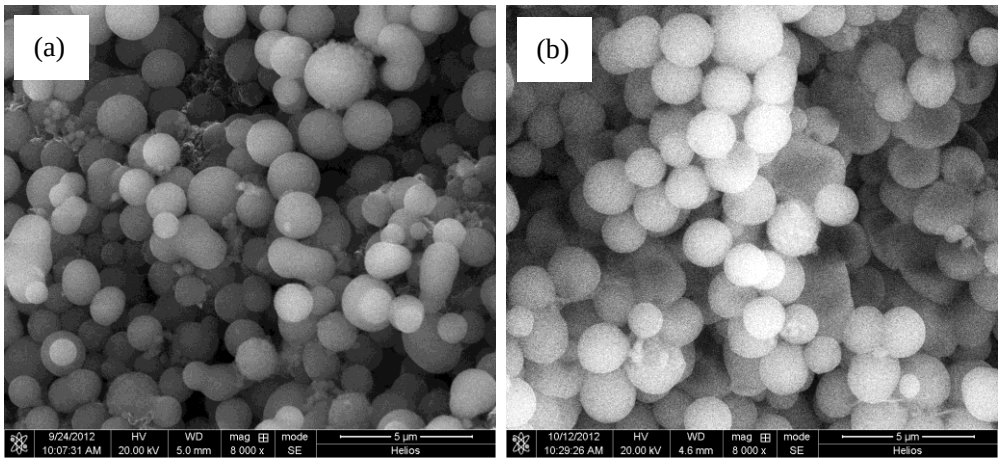

Figure S1 SEM images of pristine carbon spheres obtained from different reductants. (a) Hydrazine hydrate, (b) Sodium borohydride.

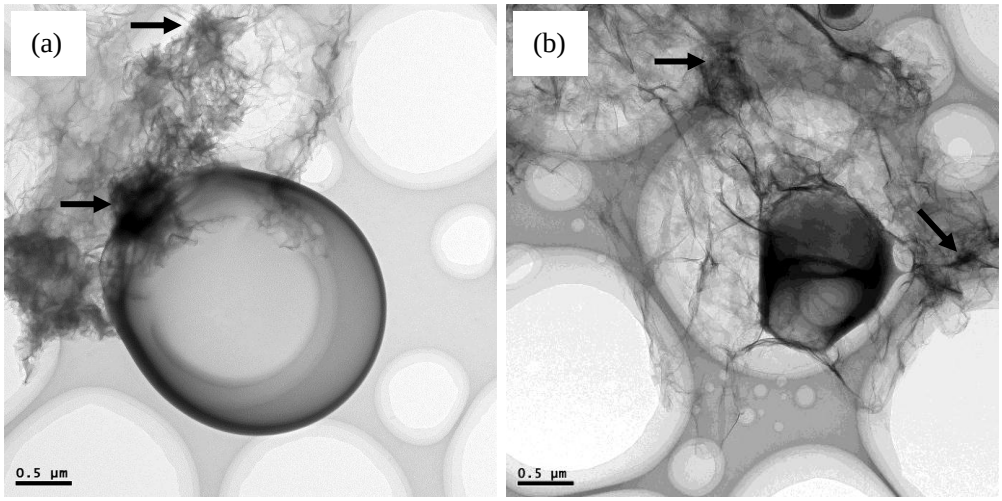

Figure S2 (a) TEM image of a ballooned carbon sphere with enfolded r-GO aggregates (marked by arrow); (b) TEM image of a broken carbon sphere which was surrounded by graphene aggregates.