Supporting Information for

Mechanically Robust 3D Graphene Macroassembly with High Surface Area

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Experimental Details

Materials Synthesis. In a typical reaction, graphene oxide (GO) was suspended in deionized water and thoroughly dispersed using a VWR Scientific Model 75T Aquasonic (sonic power ~ 90 W, frequency ~ 40 kHz). The concentration of GO in the reaction mixture was 1-2 wt%. To determine the optimal conditions for GO dispersion, a range of sonication times (4 to 24 hrs) was evaluated. Once the GO (6 ml) was dispersed, concentrated ammonium hydroxide (1 ml) was added to the dispersion. The sol-gel mixture was then transferred to glass molds, sealed and cured in an oven at 85°C for 12-72 h. The resulting gels were then removed from the molds and washed with deionized water to remove reaction byproducts and excess ammonium hydroxide. Then the gels were washed in acetone to remove all the water from the pores of the gel network. The wet gels were subsequently dried with supercritical CO_2 to yield the reduced GO assemblies. These aerogels were thermally reduced via pyrolysis at 1050°C under a N_2 atmosphere for 3 h. The 3D graphene macroassemblies were isolated as black cylindrical monoliths.

Characterization. The ^{13}C and ^{1}H solid-state single pulse magic angle spinning (SP/MAS) MAS NMR spectra were collected using a Bruker HXY probe configured for 4 mm (o.d.) rotors. Samples were contained in 4 mm ZrO_2 rotors and spun at a MAS rate of 12 kHz. ^{13}C SP/MAS NMR spectra were collected using a 6 μs pulse ($\nu_1 = 41.6$ kHz) with a 20 s pulse delay for a total of 6 000 acquisitions. ^{1}H SP/MAS NMR spectra were collected using the DEPTH pulse sequence [1] in order to suppress broad background signals from the probe head. We used an 8 μs 90° pulse (ν_1 = 31.3 kHz) followed by two 16 μs 180° pulses for the DEPTH sequence. ^{1}H spectra were collected using a 2 s pulse delay for 64 and 512 acquisitions for the uncalcined and calcined macroassemblies, respectively. Experiments on rotor blanks show that this procedure is sufficient to suppress all background signals from the probe. In all cases, spectra were referenced with respect to an external sample of tetramethylsilane (δ_C, δ_H = 0 ppm).Field-emission scanning electron microscopy (SEM) characterization was performed on a JEOL 7401-F at 5-10 keV (20mA) in secondary electron imaging mode with a working distance of 2-8 mm. Surface area determination and pore volume and size analysis were performed by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods using an ASAP 2000 Surface Area Analyzer (Micromeritics Instrument Corporation). [2] Samples of approximately 0.1 g were heated to 150°C under vacuum (10^{-5} Torr) for at least 24 hours to remove all adsorbed species. X-ray diffraction (XRD) measurements were performed on a Bruker AXS D8 ADVANCE X-ray diffractometer equipped with a LynxEye 1-dimensional linear Si strip detector. The samples were scanned from 5 to 75° 2θ. The step scan parameters were 0.02° steps and 2 s counting time per step with a 0.499° divergence slit and a 0.499° antiscatter slit. The X-ray source was Ni-filtered Cu radiation from a sealed tube operated at 40 kV and 40 mA. Phases in the samples were identified by comparison of observed peaks to those in the International Centre for Diffraction Data (ICDD PDF2009) powder diffraction database, and also peaks listed in reference articles. Goniometer alignment was ensured using a Bruker-supplied Al_2O_3 standard.

Monoliths were machined with a 6-mm-diameter cylindrical endmill rotating at a speed of $2x10^4$ revolutions per minute, yielding macroscopically flat surfaces needed for mechanical characterization by indentation. The samples were indented in the load-controlled mode in an MTS XP nanoindenter with a flat punch diamond tip with an effective diameter of 62 microns. Representative indentation stress (σ) and strain (ε) were defined as $\sigma=4P/(\pi D^2)$ (i.e., the average contact pressure) and $\varepsilon=4h/(\pi D)\approx h/D$ (i.e., the proportionality coefficient between σ and the reduced modulus in the elastic regime). [3] Here, P is the load, D is the indenter tip diameter, and h is the indenter displacement. Both loading and unloading rates were kept constant to maintain an indentation strain rate of 10^{-3} s^{-1}. [3] Elastic properties are characterized by the Young's modulus, which was calculated based on the initial slope of the unloading curve according to the Oliver-Pharr method [4] for maximum loads below those resulting in failure events. In Oliver-Pharr calculations, we assumed Poisson's ratios of diamond and aerogels of 0.07 and 0.2, respectively, and the Young's modulus of diamond of 1141 GPa. [3] Several (>10) measurements of the Young's modulus, failure stress, and failure strain were made on different sample locations, and results were averaged. The error bars given are standard deviations.

Electrical conductivity was measured using the four-probe method with metal electrodes attached to the ends of cylindrical samples. The amount of current transmitted through the sample during measurement was 100 mA, and the voltage drop along the sample was measured over distances of 3 to 6 mm. Seven or more measurements were taken on each sample, and results were averaged. Bulk densities of the samples were determined from the physical dimensions and mass of each sample. Cyclic voltammetry was performed on a Biologic VSP electrochemical workstation with a 30 ga Pt wire counter electrode coiled around a Radiometer Analytical double-junction standard calomel reference electrode (SCE). The mass of the 3D graphene monolith used for the electrode was 1.54 mg. Ohmic drop was compensated with the ZIR technique at 100 kHz and the capacitance, F, was determined through integrating over either positive or negative current responses and then dividing by the potential range, V, of 1.1 V. Energy density was calculated according to

$$\frac{1}{2}\frac{FV^2}{kg*3600\frac{s}{hr}}$$

Power density was calculated according to

$$\frac{1}{2}\frac{FV^2}{kg*t}$$

where *t* is the time of charge or discharge.

Supporting Results

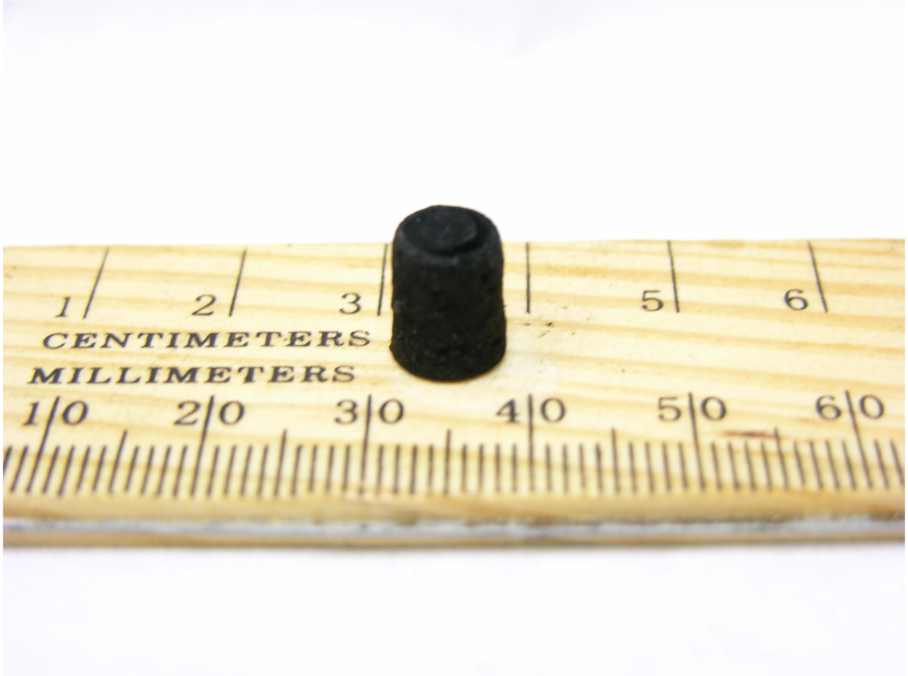

Figure S1. Optical image of 3D graphene monolith.

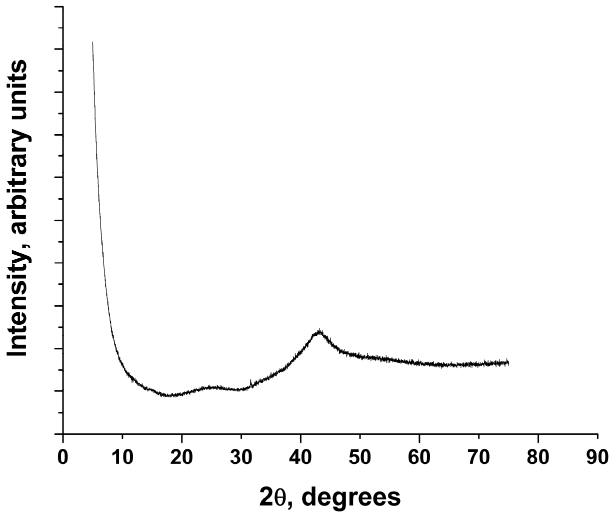

Figure S2. XRD pattern for 3D graphene.

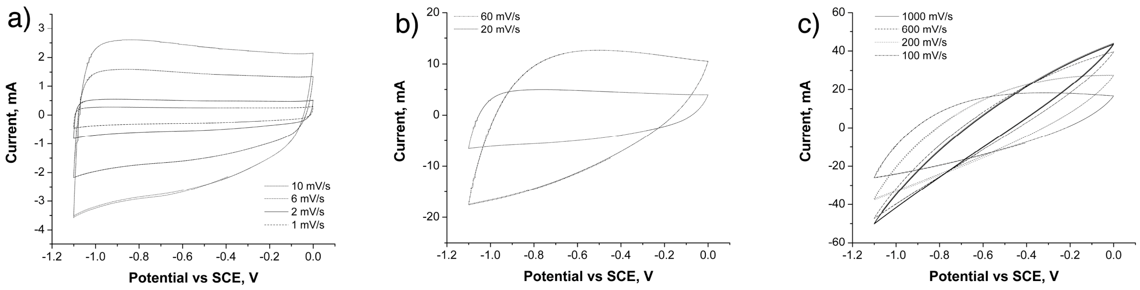

Figure S3. Cyclic voltammetry plot for scan rates a) 1-10, b) 20, 60, and c) 100-1000 mV/s in 5M KOH.

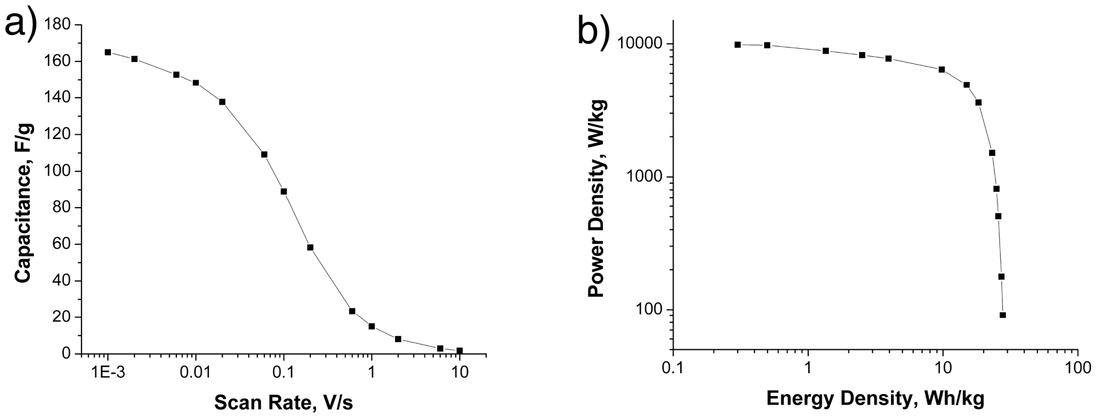

Figure S4. a) Capacitance vs scan rate and b) power density vs energy density for the 3D graphene macroassembly in 5M KOH.

References

[1] D.G. Cory, W.M. Ritchey, *Journal of Magnetic Resonance* **80**, 128, 1988.

[2] Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic: London, 1982.

[3] S. O. Kucheyev, A. V. Hamza, J. H. Satcher Jr, and M. A. Worsley, *Acta Materialia* ***57***, 3472, 2009.

[4] W. C. Oliver and G. M. Pharr, *Journal of Materials Research* **7**, 1564, 1992.