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Single Sheets of Graphene for Fabricating Fibers with Enhanced Mechanical Properties

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Supplementary Information

Materials and Methods

Graphene Synthesis

Graphene was grown on copper foil (25 µm thick, Alfa Aesar, item No.46365) using a CVD method previously reported.[1] First, copper foil was electropolished similar to the previously reported electropolishing method.[2] In brief, copper foil is electrolyzed at 8 V with the current limit of 0.45 A for 30 – 45 s in phosphoric acid solution (500 ml of deionized water, 250 ml of phosphoric acid, 250 ml ethanol, 50 ml isopropyl alcohol, and 5 g of urea). Copper foil was used for both anode and cathode electrode, but only polished anode copper foil was used for graphene growth. After the electropolishing treatment, copper foil was thoroughly rinsed with deionized water, blow dried with nitrogen gas, and placed on a quartz boat. The quartz boat with the copper foil was then inserted into the centre of a 1-inch-diameter fused quartz tube furnace. The tube was pump down to the base pressure ~50 mTorr and back filled with H_2 (10 standard cubic centimetres per minutes (sccm)). The tube pressure with H_2 flow was maintained at ~500 mTorr. The furnace temperature was ramped to 1050 °C and annealed for 1 h. CH_4 (2 sccm, P_{total} ~750 mTorr) was introduced after the annealing step for 30 min (growth), and the furnace was cooled rapidly to room temperature with the same gas flow. Figure 1 summarizes the CVD growth process. Graphene samples were stored in a clean glass petri dish until the transfer.

Raman Spectroscopy of CVD Grown Graphene

CVD grown graphene was transferred on to a silicon wafer using a wet transfer technique and characterized via Raman spectroscopy. Micro-Raman spectra were obtained using Horiba scientific XploRA PLUS with Olympus Microscope BX41 with 100X (NA:0.9, WD:0.21mm) objectives. 473nm (20-25mW) continues wave laser with 10 % density filter and 1800 gr/mm grating were used. Slit and pin hole size was 100 µm and 300 µm, respectively. Laser power and acquisition time settings were adjusted to prevent the oxidation of graphene from the laser induced heating effect. Typical Raman spectrum of graphene is shown in Figure 2. The negligible D peak intensity, low intensity ratio between the G peak and the 2D peak (I_G/I_{2D}), and narrow linewidth of the 2D peak suggest that the CVD graphene used in this study is mostly single layer and have low defect density.[3-4]

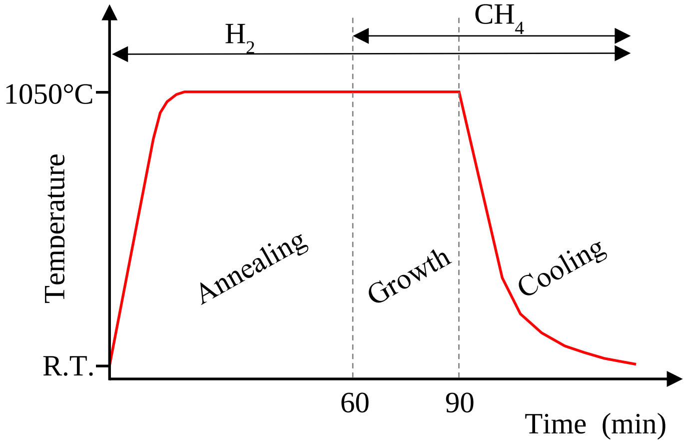

Figure S1. The CVD growth of graphene. Furnace temperature was set to 1050 °C. Annealing and growth period was 60 min and 30 min, respectively. H_2 and CH_4 flow rate was set to 10 sccm and 2 sccm, respectively. The quartz tube had base pressure of ~50 mTorr after evacuation, ~500 mTorr with H_2, and ~750 mTorr with H_2+CH_4.

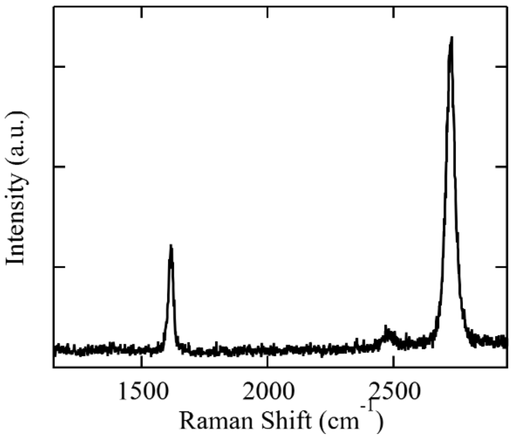

Figure S2. The Raman spectrum of graphene on SiO_2/Si wafer.

Graphene Transfer on Si Wafer

In a typical transfer, as grown graphene on top of Cu foil was spin coated with 5 wt% PMMA solution (PMMA, Aldrich, MW 996000 in anisole, Sigma-Aldrich, 99%). After the PMMA was coated on top of the graphene layer, the Cu foil was etched in etchant solution, 1 M of iron chloride in 10 % w/w hydrochloric acid ($FeCl_3$, Sigma-Aldrich, 97%, in HCl, Fisher Scientific, 37.1%) for 30 min. Then, the PMMA/graphene film was scooped out with a clean glass slide and transferred into multiple water baths to rinse off the etchant. After thorough rinsing, the PMMA/graphene film was scooped on a SiO_2(300nm)/Si wafer (University Wafer, 300 nm wet thermal oxide, P type/Boron) and spin dried at 5000 rpm for 5 min. The PMMA layer was removed by placing the sample in an acetone bath for 1 h. The graphene surface was rinsed with isopropanol and gently blow dried with N_2.

Fabrication of Graphene Fiber

Graphene fiber was assembled by folding flat sheet of graphene on a glass slide. In a typical assembly, graphene/Cu was spin coated with 3-5 wt% PMMA solution and Cu foil was etched as

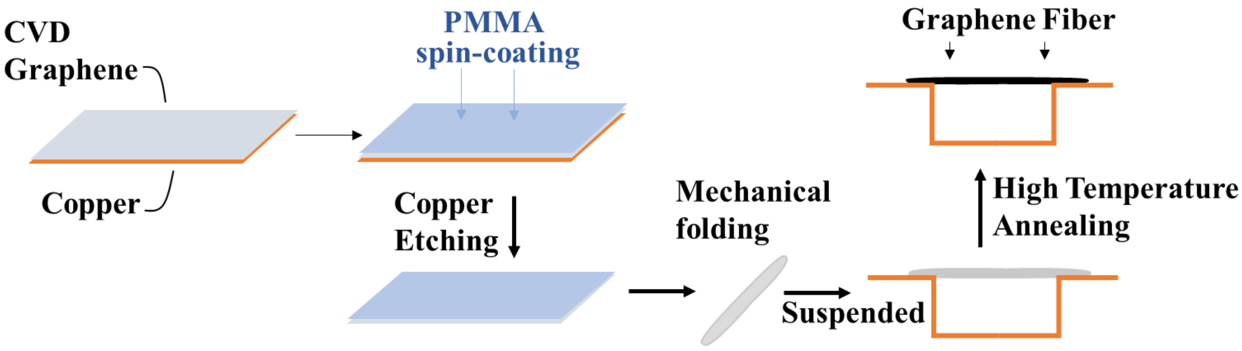

Figure S3. Fabrication scheme of graphene fibers. Single sheets of CVD graphene are used to fabricate graphene fibers through steps of copper etching, mechanical folding, and thermal decomposition/removal of the supporting organic film.

described above. The PMMA/graphene film was rinsed in water bath and placed on a clean glass plate. Then the film was pushed horizontally with clean glass slides to form a folded structure. All glass plate and slides were thoroughly cleaned and treated with UV/O_3 (PSD Pro Series UV-Ozone System, Novascan) for 1 hr to increase the wetting property before use. The schematic drawing of folding process is shown in Figure 1.

To remove PMMA, folded PMMA/graphene was heated beyond the thermal decomposition temperature of PMMA (390 °C).[5-6] First, PMMA/graphene was suspended on a copper foil and placed in a quartz tube. Once the tube was evacuated (P ~ 50 mTorr), PMMA/graphene was heated to 420 °C for 30 min in Ar (P > 1 Torr). The system was cooled to room temperature, and graphene fiber was stored in a plastic petri dish until further testing.

Characterization Methods

Graphene fibers were characterized by field-emission Scanning Electron Microscopy (SEM) using a Zeiss Sigma 500 VP SEM. Conductive silver paste (Silver Conductive Adhesive

503, Electron Microscopy Sciences) was added over the non-conductive epoxy or crystal bond adhesives to eliminate charging during the SEM imaging of graphene fibers.

Tensile Test Setup

Tensile measurements were collected using a custom-made tensile testing setup, shown schematically in Figure 4. The setup employed a cantilever beam of known stiffness (882 N/m) coupled with a capacitive displacement sensor (Physic Instrumente, D-510.010) to measure applied force with an accuracy of +/- 25 μN. A newly fabricated graphene fiber, which still anchored to the copper substrate where it was annealed, had one end of it raised into a droplet of epoxy (Devcon No. 14250) on the tip of the cantilever via a three-axis stage (Aerotech MPS75SL-V)—the epoxy was allowed 45 min to 1 hour to harden before testing. Sequential measurements on the same mounted graphene fiber were performed by lowering the newly broken end of the graphene fiber into a pool of crystalbond mounting adhesive (Ted Pella 509-3) (heated to 150°C, past its softening point). Ideally the samples would be aligned perfectly vertically, parallel to the loading axis. In the case of the experiments done, this was generally not the case, further angle details are provided in the results.

The experimental setup was positioned on a vibration isolation table (Kinetic systems minus K) in ambient conditions (22 ˚C and 20-30% relative humidity).

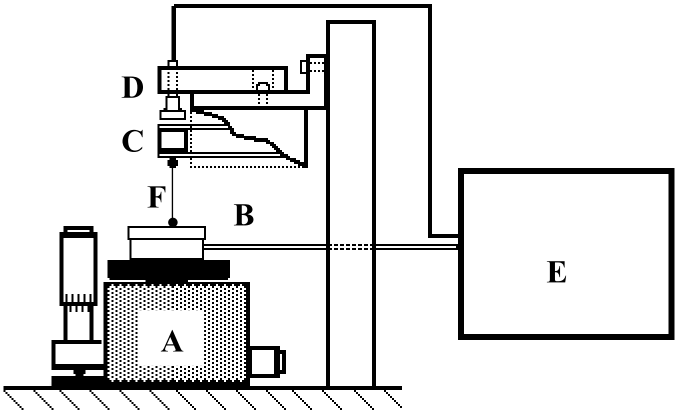

Figure S4. **(A)**Testing setup for contact tests depicting the three-axis motor-driven stage; **(B)** the piezoelectric actuator; **(C)** the cantilever with bead of epoxy; **(D)** the capacitive sensor; **(E)** and the corresponding controls; **(F)** graphene fiber mounted with beads of adhesives.

Uniaxial Tensile Test Procedure

Once the graphene fiber was mounted, as indicated above, and adhesives had hardened, the three-axis motorized stage was lowered. This movement created a tensile load on the sample which was registered by the cantilever beam/capacitive sensor. The loading occurs at rates (r_p) varying between 0.1 – 2 µm/s until fracture, with data sampling at (1000 data points/sec). The displacement of the stage was recorded along with the displacement and corresponding force of the cantilever beam. The stage was lowered until fracture was observed. The broken samples were preserved for later SEM imaging. After fracture, another test was carried out on the graphene fiber still attached to the epoxy on the cantilever beam. The broken end was then lowered into liquid crystalbond adhesive on the stage. Again, the crystalbond was allowed to harden completely before applying any load to the sample. After each fracture, the new, shorter sample was reattached to a new pool of crystal bond adhesive on the stage, allowed to harden, and then pulled until fracture. This process was repeated until the sample was too short to test again.

Data Collection

Data was collected on the stage displacement and the force exerted on the sample with respect to time by using a National Instruments DAQ unit (NI USB-6009) and the LabView development environment. Video and pictures were taken for each test with a digital microscope (Dinolite AM4515ZTL). This setup allowed for strain data to be extracted from the video and total mechanical failure to be observed. Such data was gathered several times for each sample over the course of multiple tensile tests.

The mounted graphene fibers were typically set at an angle (0-45° to vertical) due to restrictions in fabrication and mounting. Any load in the fiber where the sample is straight will be along the axis of the fiber. If it doesn't break at the bends in the sample, then the entire load is supported along the axis of the fiber. Since we are only measuring vertical deflection (force), the value we are getting should be an underestimate of the real force experienced by the fiber, which will also cause some horizontal deflection. Additionally, the fibers were usually slightly bent or kinked along their axis. Therefore, displacements measured during testing are affected by both the angle of setting and bends/kinks along the fiber axis. Force-Time plots was used (over F-ΔD plot) to help display the data due to these issues. Stress-strain curves were generated by measuring distances between reference points on the graphene fiber at instantaneous moments during the test by digital imaging.

Rolled Graphene Fibers

For comparison to the accordion-like folding pattern, rolled graphene fibers were prepared. Rolled graphene fibers were fabricated similar to a method previously reported.[7] These rolled fibers were annealed at 420ºC to decompose/remove PMMA and then mounted on the tensile puller until breakage to expose the cross section of the fibers. An example of SEM collected from a broken rolled fiber is shown below. These SEM images revealed that upon annealing, bubbled structures appear on the fiber surface and large hollow cavities appeared within the fiber. These structures are a result of decomposed PMMA becoming trapped between the rolled graphene layers during annealing.

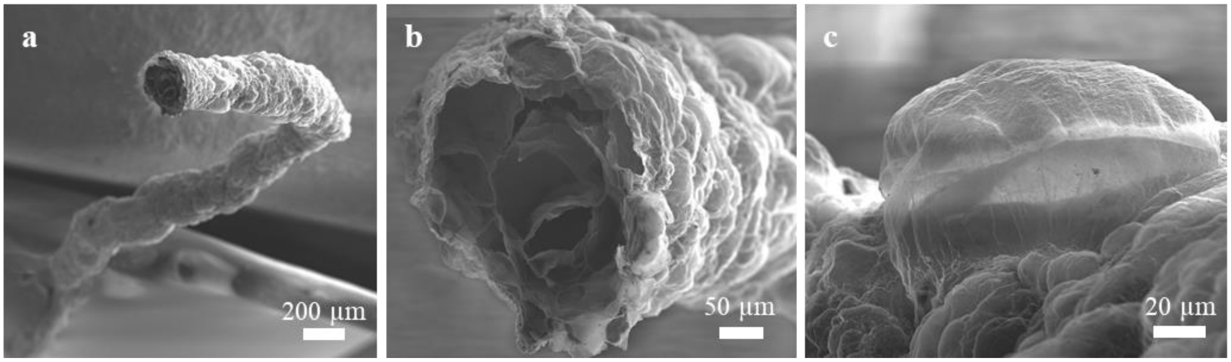

Figure S5. SEM of rolled graphene fibers after thermal annealing. Annealed graphene fibers prepared through a rolling-pattern (a) exhibit hollow cavities within the fiber (b) and large bubbled structures on their surface (c). These structures are a result of decomposed PMMA being trapped within graphene the sheets structure upon thermal annealing.

These hollow/bubble structures are not observed on the accordion-like prepared fibers, because the PMMA in the accordion-fibers is not confined within the graphene folds and can therefore be decomposed/removed without being trapped during annealing.

Surface Morphology of Fibers after Uniaxial Tension

SEM images were collected of graphene fibers before (Figure 1 A/B) and after (Figure 1 C/D; Figure S6) tensile tension to compare surface morphology. An overall reduction in folds/wrinkles was observed, with an increased alignment of folds/wrinkles along the tension axis.

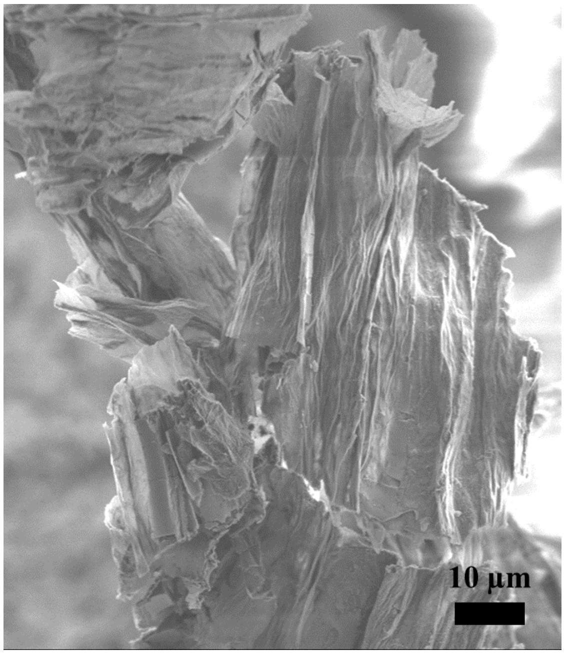

Figure S6. SEM of Graphene Fiber Fracture after Uniaxial Tension. The surface morphology of an accordion-folded graphene fiber after uniaxial tension and breaking.

References

[1] Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S., Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. Science (2009) 324, 1312-1314. https://doi.org/10.1126/science.1171245

[2] Chen, S. S.; Ji, H. X.; Chou, H.; Li, Q. Y.; Li, H. Y.; Suk, J. W.; Piner, R.; Liao, L.; Cai, W. W.; Ruoff, R. S., Millimeter-Size Single-Crystal Graphene by Suppressing Evaporative Loss of Cu During Low Pressure Chemical Vapor Deposition. Adv. Mater. (2013) 25, 2062-2065. https://doi.org/10.1002/adma.201204000

[3] Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K., Raman spectrum of graphene and graphene layers. Physical Review Letters (2006) 97. https://doi.org/10.1103/PhysRevLett.97.187401

[4] Graf, D.; Molitor, F.; Ensslin, K.; Stampfer, C.; Jungen, A.; Hierold, C.; Wirtz, L., Spatially resolved raman spectroscopy of single- and few-layer graphene. Nano Lett. (2007) 7, 238-242. https://doi.org/10.1021/nl061702a

[5] Witkowski, A.; Stec, A. A.; Hull, T. R., Thermal Decomposition of Polymeric Materials. In *SFPE Handbook of Fire Protection Engineering*, Hurley, M. J.; Gottuk, D.; Hall, J. R.; Harada, K.; Kuligowski, E.; Puchovsky, M.; Torero, J.; Watts, J. M.; Wieczorek, C., Eds. Springer New York: New York, NY, 2016; pp 167-254.

[6] Ferriol, M.; Gentilhomme, A.; Cochez, M.; Oget, N.; Mieloszynski, J. L., Thermal degradation of poly(methyl methacrylate) (PMMA): modelling of DTG and TG curves. Polymer Degradation and Stability (2003) 79, 271-281. https://doi.org/https://doi.org/10.1016/S0141-3910(02)00291-4

[7] Liu, P.; Jin, Z.; Katsukis, G.; Drahushuk, L. W.; Shimizu, S.; Shih, C.-J.; Wetzel, E. D.; Taggart-Scarff, J. K.; Qing, B.; Van Vliet, K. J.; Li, R.; Wardle, B. L.; Strano, M. S., Layered and scrolled nanocomposites with aligned semi-infinite graphene inclusions at the platelet limit. Science (2016) 353, 364-367. https://doi.org/10.1126/science.aaf4362