Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information for:

Highly conductive, flexible and scalable graphene hybrid thin films with controlled domain size as transparent electrodes

Keun-Young Shin and Jyongsik Jang*

World Class University (WCU) program of Chemical Convergence for Energy & Environment (C_2E_2), School of Chemical and Biological Engineering, College of Engineering, Seoul National University (SNU), Seoul 151-742, Korea.

[*] E-mail: jsjang@plaza.snu.ac.kr
Tel.: +82-2-880-7069
Fax: +82-2-888-1604

1. Experimental Section

Fabrication of ball-milled graphite.: The pristine graphite (5.0 g) was placed into a planetary ball-mill capsule (80 mL) containing three types of balls (diameter 1, 2 and 5 mm). For the effective ball milling process, the quantity ratio of three different ball types were *ca*. 18:4:1. Used materials for grinding bowls and balls were zirconium oxide. The capsule was then fixed in the planetary ball-mill machine, and agitated with 550 rpm. The resultant product was collected by sieving.

Synthesis of size-controlled and pristine GO sheets.: Size-controlled GO was synthesized from chemically exfoliation of ball-milled graphite using a modified Hummers method. Typically, ball-milled graphite (1.0 g) was added to 70 mL of H_2SO_4 (1M) in an ice bath, which was followed by the addition of $KMnO_4$ (3.0 g) and $NaNO_3$ (0.5 g). After stirring for 4 h, 70 mL of distilled water was slowly added and maintained at that temperature for 30 min. Subsequently, H_2O_2 solution was added to the solution until the color turned a brown indicating fully oxidizing state. Ball-milled graphite oxide was exfoliated to generate size-controlled GO nanosheets by sonication using an ultrasonic generator (42 kHz, 100W, Branson 3510, Branson Cleaning Equipment Co., Shelton, CT, USA) for 3 h. Finally, the mixture was separated by centrifugation, washed repeatedly with 5% HCl and distilled water, and dried in a vacuum oven at 40 ºC for 24 h. Pristine GO was prepared by chemically exfoliation of pristine (non-milled) graphite using an identical modified Hummers method.

Fabrication of pristine graphene and graphene hybrid thin film via screen printing and reduction process.: For the preparation of GO hybrid ink, size-controlled GO and pristine GO (non-milling) powders were mechanically mixed, and they were dispersed in water/ethanol solvent (1 mg/mL concentration, 30 mL) by sonication (30 min). The volume ratio of ethanol to water was 1.5:1. Pristine GO ink was obtained by dispersing the pristine GO powder in water/ethanol solvent using sonication (3 h). The viscosity and surface tension values of pristine and GO hybrid solutions were ranged from 2 to 10 mpa s and 65 to 75 mN m^{-1}, respectively. In order to match between surface energy of the PES film and surface tension of GO inks, PES film was treated with oxygen plasma (gas flow rate: 20 sccm, power: 100 W, time: 20 s) that caused the surface energy of the substrate to increase from 32.0 to 68.7 mN m^{-1}. The GO inks meeting the above conditions could be printed out precisely onto the substrate through mesh using only a scraper (6,000 rpm). The patterned architectures were designed by screen printing mesh. The printed pristine and GO hybrid thin film was properly cut, and located in vapor deposition chamber containing hydrazine solution (1mL, Sigma Aldrich). The chamber was sealed and placed in an oven at 90 °C for 1 h. The color of the pristine and GO hybrid thin film changed from brown to metallic gray by chemical reduction. Finally, pristine graphene and graphene hybrid thin films were fabricated via pressure-assisted reduction using hot press between stainless-steel plates at 180 °C for 5 min.

Characterization.: Scanning electron microscopy (SEM) images were acquired with JSM-6700F microscope (JEOL, Tokyo, Japan) at an acceleration voltage of 10 keV, and the Atomic force microscopy (AFM) topography was obtained by a Digital Instrument Nanoscope IIIA from veeco systems in tapping mode using silicon tips with a resonance frequency of of 320 KHz. X-ray photoelectron spectroscopy (XPS) spectra were recorded using Kratos Model AXIS-HS system, and Raman spectrum was obtained on a Jobin-Yvon T64000 spectrometer. Dynamic light scattering (DLS) measurements on the graphene solution were carried out using a Photal dynamic laser scattering spectrometer DLS-7000 (Otsuka Electronics Co. Ltd., Tokyo, Japan) with an argon laser with 488 nm. Plasma reactor was of the parallel electrode type with a 13.56 MHz radiofrequency generator. The viscosity was measured by rheometer (AR 2000 Advanced Rheometer, TA Instruments) and the surface energy was calculated by Owens-Wandt equation. Film transmittance was measured using a UV–visible spectrometer (Lamda-20; Perkin-Elmer, Waltham, MA, USA) at a resolution of 1 nm. The measurement of electrical resistances was performed with a Keithley 2400 sourcemeter at 25 °C by a four-probe method. The sheet resistance was measured at 10 different locations of graphene-based thin film and calculated as an average value.

2. Schematic illustration for size-controlled graphite

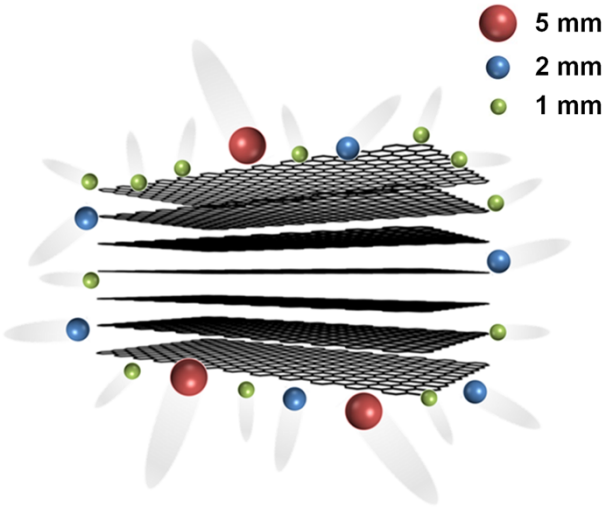

Fig. S1 Schematic illustration for size-controlled graphite via mechanochemical process using three types of ball (1, 2, and 5 mm).

3. SEM images for size-controlled graphite

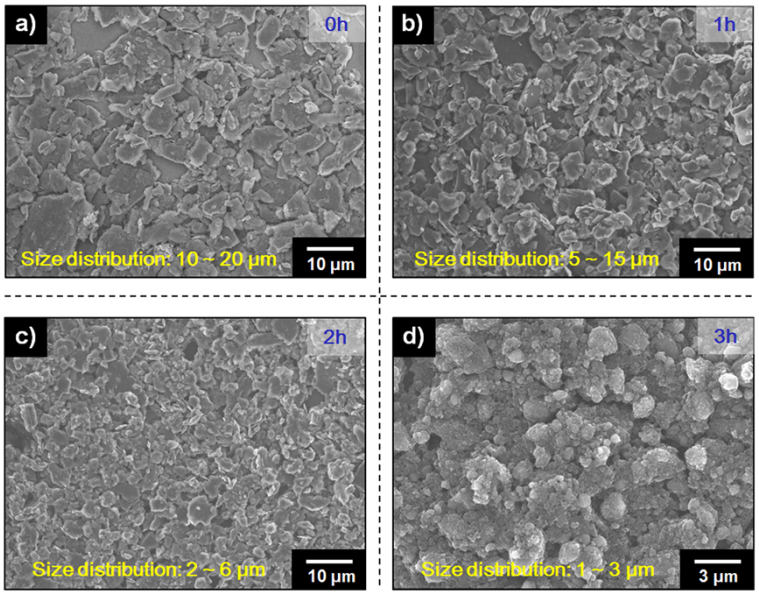

Fig. S2 Representative SEM images of size-controlled graphite as a function of ball milling time.

4. AFM images of size-controlled GO

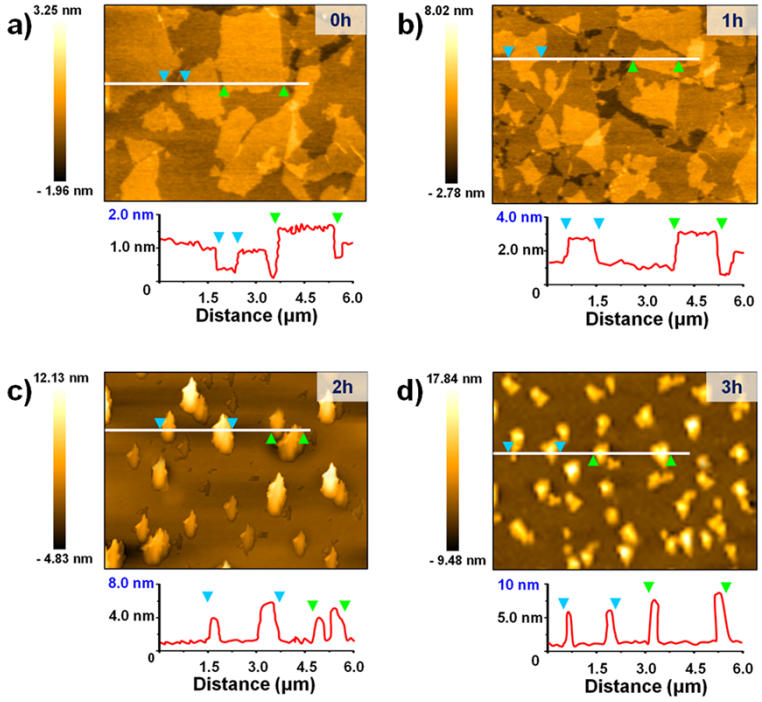

Fig. S3 Representative AFM images of size-controlled GO according to ball milling time. For the AFM sample preparation, the GO solution was deposited on Si wafer.

5. XPS spectrum of size-controlled GO and graphene

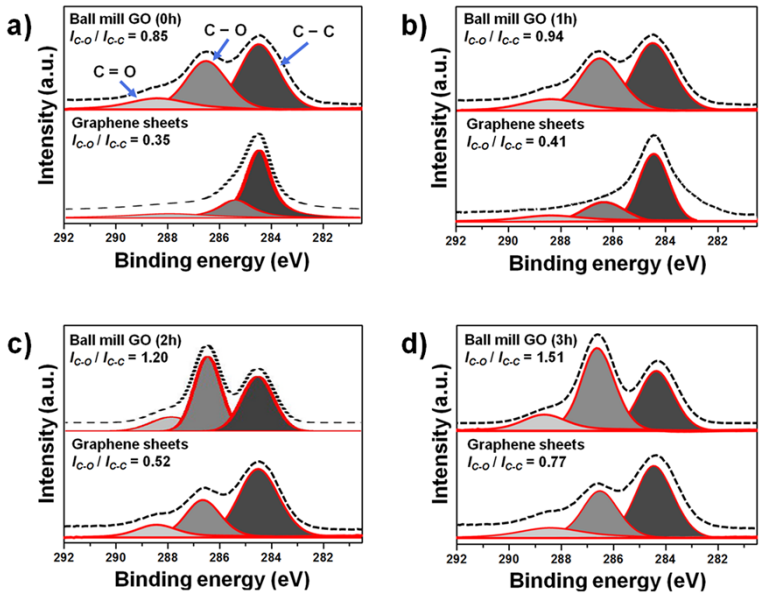

Fig. S4 Comparison of deconvoluted XPS spectrum of size-controlled GO and graphene thin films as a function of ball milling time in the C1s region. Fit lines are labeled as: C − C, C − O, and C = O bonds.

6. Raman spectra of size-controlled graphene

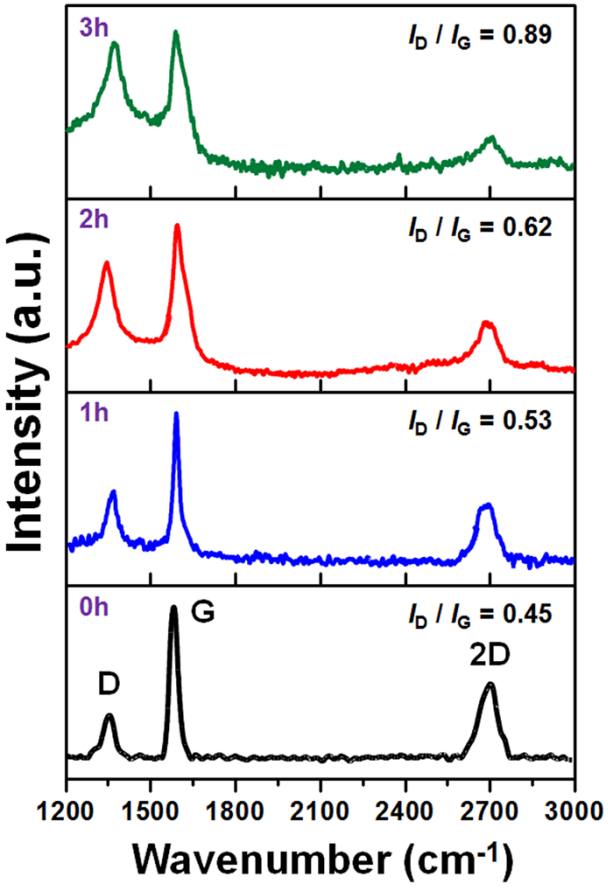

Fig. S5 Raman spectra of size-controlled graphene thin films according to ball milling time showing D, G, and 2D peaks.

7. Stoke's law

The Stoke's law is a formula for determining the rate of sedimentation, and it depicts that a motion of particle existed in viscous liquid reaches at constant state with a uniform velocity or sedimentation rate. The equation that describes Stokes' law is as follows:

$$V_g = d^2(\rho_p - \rho_l) / 18\eta \times G$$

where V_g is the sedimentation velocity, d is the particle diameter, ρ_p is the particle density, ρ_l is the liquid density, η is the viscosity of liquid, and G is the gravitational acceleration. The density was measured by a pycnometer, and the viscosity was calculated by rheometer (AR 2000 Advanced Rheometer, TA Instruments).