Supplementary Information for:

A strategy for fabricating single layer graphene sheets based on a layer-by-layer self-assembly

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1. Experimental Section

Materials: Anionic poly(styrenesulfonate); PSS (M_w = 70,000) and cationic polyallylamine; PAA (M_w = 70,000) were used as received from Aldrich. Iron (III) chloride (Aldrich, reagent grade, 97%) as a metallic dopant was used without further purification. Quartz substrate (3.0 cm × 3.0 cm, thickness of 1000 μm) was purchased from JMC Glass, manufactured in Korea.

Fabrication of PSS/PAA multi-layer using layer-by-layer (LbL) self-assembly: Quartz substrate was cleaned by ultrasonication with a hot mixture of H_2SO_4/H_2O_2 (7:3) for 3 h. The quartz substrate was heated in a mixture of $H_2O/H_2O_2/NH_3$ (5:1:1) at 80 ˚C for 1 h, and then subsequently dried by N_2 gas purging. After that, the substrate is negatively charged and used for the polyelectrolyte deposition starting with the cationic PAA. The concentration of PAA and PSS solutions used for all the in this experiments was 1 mg mL^{-1}. The deposition steps were carried out as follows: At first step, aqueous $FeCl_3$ solution (7 M) was added into the PSS solution and allowed to equilibrate. The volume ratios of aqueous $FeCl_3$ solution to PSS solution was 2.0×10^{-2}. Afterwards, a few drops of polyelectrolyte solution were placed on the substrate and then the substrate was rotated with a spinner at 3000 rpm for 45 sec. After the deposition of each polyelectrolyte layer, the substrates were thoroughly rinsed with plenty of deionized water. The spinning time and the speed for the washing step were identical to those for the layer deposition.

Carbonization of PSS/PAA multi-layer: The prepared PAA/PSS multilayer on a quartz substrate was placed in a furnace under N_2 atmosphere. The sample was heated to 1000 ˚C at a heating rate of 3 ˚C min^{-1}, held at 1000 ˚C for 5 h, and then cooled to room temperature.

Graphene nanosheets characterization: The PSS/PAA multi-layer film was acquired using a PWM32 spinner (Headway Research, Inc.). Photographs of transmission electron microscopy (TEM) were obtained with a JEOL EM-2000 EX II microscope. In the sample preparation, the graphene nanosheets dispersed in water were cast onto copper grid. AFM topography analysis was carried out with a Digital Instruments Nanoscope IIIA from Veeco Systems in tapping mode using silicon tips with a resonance frequency of 320 kHz. Raman spectra were recorded using a Bruker FRA 106/S FT-Raman spectrometer with 1064 nm laser excitation (a spectral resolution of 1 cm^{-1}). The peak positions obtained from the Raman spectrometer have a margin of error of ± 0.05 cm^{-1}. For Raman spectroscopy analysis, the as-prepared graphene nanosheets were dried in a vacuum oven for 12 h at room temperature and were examined under ambient conditions without any pre-treatment.

Investigation of opto-electronic properties: The graphene nanosheet films were measured for optical transparency with Ultraviolet-visible (UV-vis) sepectroscopy. The UV-vis spectra were taken with a Perkin-Elmer Lamda 20 spectrometer at a resolution of 1 nm. Current-voltage (I–V) measurements were conducted using a Wonatech WBCS 3000 potentiostat at room temperature. The samples were coated onto the interdigitated microelectrodes, and the data were collected at a scan rate of 50 mV s^{-1}. The electrical conductivity was measured by the four-probe method using a Keithley 2400 sourcemeter at room temperature.

2. Raman Spectra

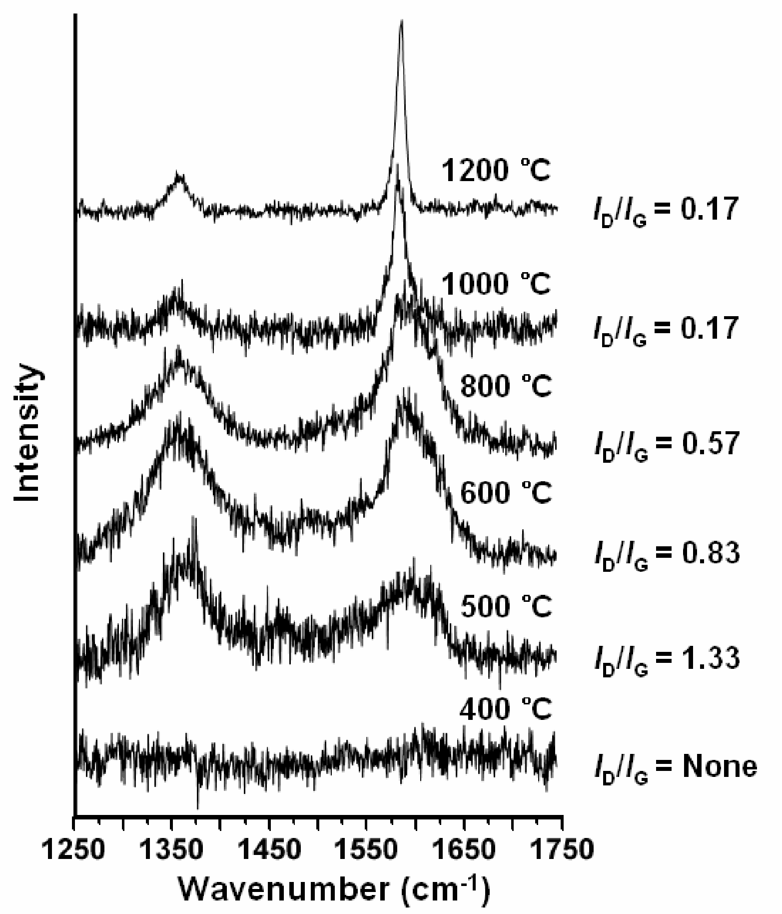

Fig. S1 Raman spectra of resulting as-carbonized PSS/PAA multi-layers under various carbonization temperatures.

Fig. S1 demonstrates the Raman spectra of as-carbonized PSS/PAA multi-layers under various reaction temperatures. Under our experimental condition, the samples represented a weak and broad band from 1250 to 1750 cm^{-1}. Interestingly, no carbon structures were found at 400 °C. Above 500°C, the Raman spectra indicated two strong wide bands near 1582 and

1357 cm^{-1}. The peak located near 1582 cm^{-1} is due lo the graphitic structure, whereas that the peak near 1357 cm^{-1} is originated from disordered structure in the carbon. With increasing reaction temperature, the intensity of the disordered structure (D peak) decreases, which indicates that the randomly and disorderly formed carbon structures are removed during heat-treatment. In addition, it is known that an increase in degree of carbon crystallinity is reflected by an increase in the intensity of the G mode, as well as a decrease in its bandwidth. The D mode intensity of the carbonized PSS/PAA multi-layers increased remarkably and narrowed its bandwidth above 1000 °C, indicating that the amount of amorphous carbon structure in the as-carbonized PSS/PAA multi-layers is very small. Consequently, the Raman results reflected that the I_D/I_G ratio decreased with increasing reaction temperature. This relatively small ratio of I_D/I_G ($I_D/I_G \approx 0.17$) indicated that the as-prepared graphene nanosheets had a low defect level in the atomic carbon structure.

3. The XPS Survey Scan Spectrum

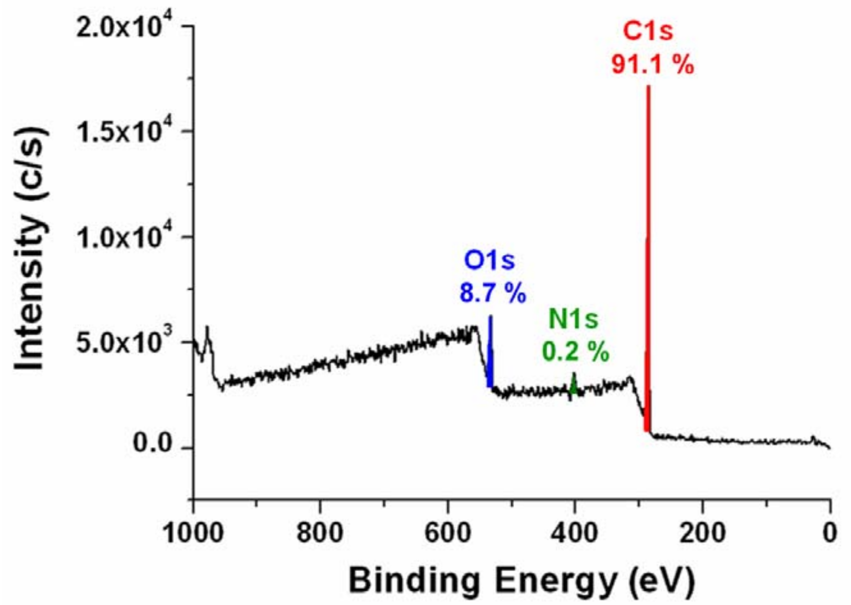

Fig. S2 Survey XPS of as-synthesized graphene nanosheets.

The XPS survey scan is an effective way to determine the presence of N, O and C elements on the surface of a material, as well as the atomic percentage of the elements detected. Fig. S2 depicts a survey scan of graphene nanosheets with the relative atomic percentages of carbon (91.1 %), oxygen (8.7 %), and nitrogen (0.2 %), respectively. Judging from these data, the PAA/PSS multi-layers prepared by LbL method were successfully transformed into graphene nanosheets.

4. Preparation of Graphene Nanosheets Films on PET Substrate

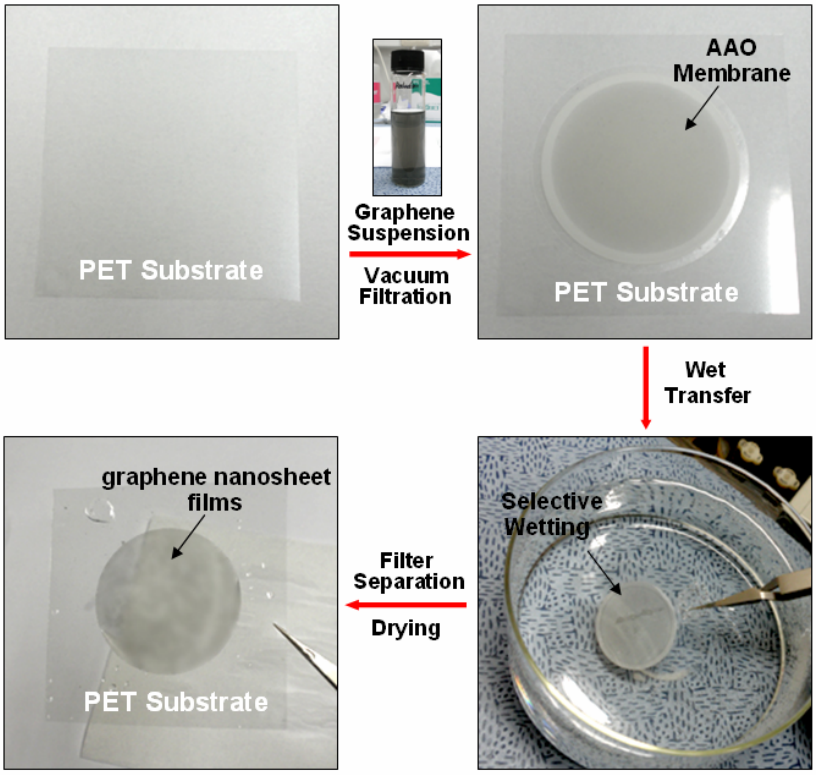

Fig. S3 Schematic diagram of the filtration-wet transfer process. A uniform flexible graphene nanosheet film was obtained by vacuum filtration using an AAO membrane and transferred to a PET film.

First of all, the as-carbonized PSS/PAA multi-layer was exfoliated in water by sonication for 120 min (Branson 1510E-MT bath sonicator) and followed by centrifugation at 500 rpm for 60 min to achieve exfoliated graphene nanosheets. However, these prepared graphene nanosheets still had some oxygen-containing functional groups and this partially oxidized graphene should be restore π-conjugated electronic structure by reduction procedure. A partially oxidized graphene suspension was subsequently reduced to graphene suspension in the presence of hydrazine solution and ammonium hydroxide solution. Finally, a uniform flexible graphene film was obtained by vacuum filtration of this dilute graphene suspension using an anodic aluminum oxide (AAO) membrane (Whatman International Ltd.) and wet-transferred to a PET film. The film thickness was controlled by the volume of suspension filtered and hence the deposited graphene mass (Figure S2).

5. XPS Spectra of Partially Oxidized Graphene and Graphene

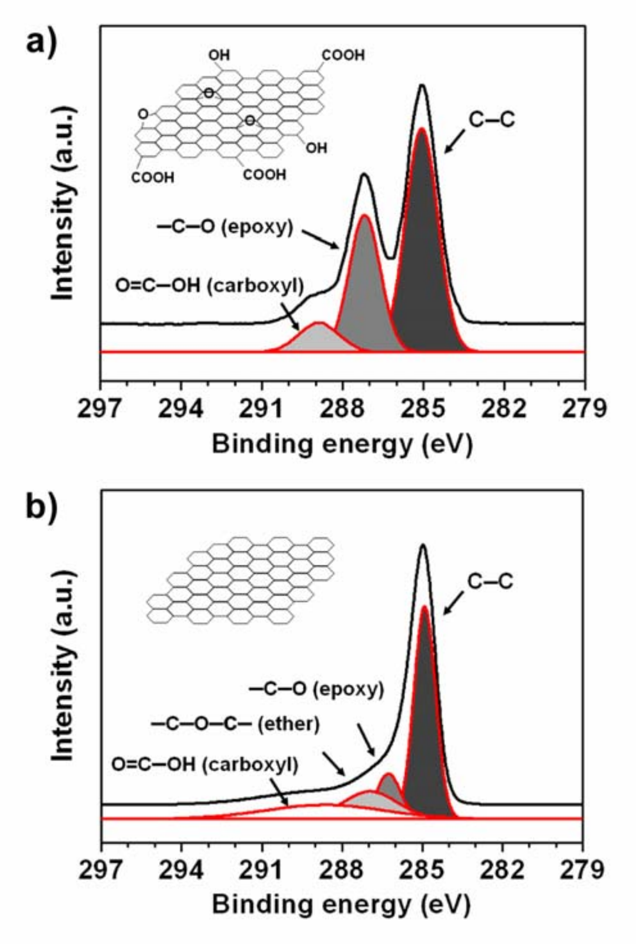

Fig. S4 Deconvoluted XPS spectrum of (a) partially oxidized graphene and (b) graphene resulted from the reduction procedure in the C1s region.

The X-ray photoelectron spectroscopy (XPS) analysis was conducted to confirm the successful reduction from partially oxidized graphene to graphene. The deconvoluted C1s XPS spectrums of partially oxidized graphene and graphene by reduction procedure are presented in Fig. S4. Generally, the C1s signal of oxidized graphene mainly consists of three components, which are C=C/C−C in aromatic rings (285.0 eV), C−O (286.5 eV) and O=C−OH (288.5 eV) peaks. While the C−O component comes from epoxy and hydroxyl groups, the O=C−OH bond originates from carboxyl groups. The XPS spectrum result was that ratio of the $I_{\mathrm{C-O}}/I_{\mathrm{C-C}}$ decreased from 0.61 (partially oxidized graphene) to 0.21 (graphene). Taking these results into account, it is concluded that the partially oxidized graphene can be transformed into graphene by reduction procedure.

6. Thermogravimetric Analysis

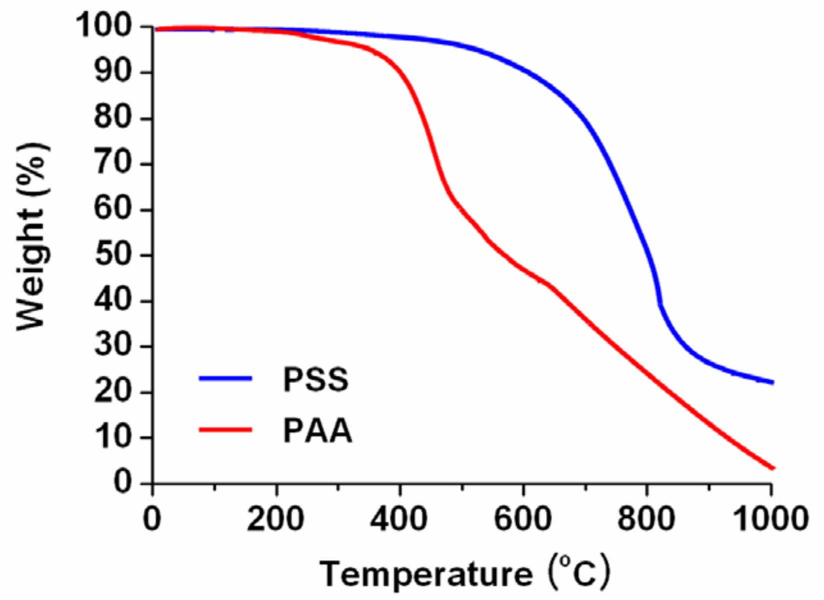

Figure S5 Thermogravimetric analysis of PSS and PAA.

The influence of the PAA layer on the formation of graphene nanosheets can be presumed by thermogravimetric (TG) analysis using similar conditions as performed in the carbonization process. In Fig. S5, it is possible to observe the weight loss starting around around 200°C for PAA. After 200 °C, mass loss of the PAA occurs very rapidly. Whereas, the degradation rate for PSS is very low in comparison to the PAA. TGA data for PSS, it is observed that the degradation starts about 400 °C. A weight loss about 400 °C is observed in PSS that may be due to removing of sulfonic group of the PSS. Finally, the residual weight at 1000 °C (final temperature of carbonization) is almost zero (0.15 %), while the residual weight of the PSS at 1000 °C is more than 20%. The comparison of PAA and PSS TGA data confirms that the PSS has more thermal stability compared to the PAA.

During the carbonization process, The PSS layer with high thermal stability is suitable for forming graphene nanosheets as a carbon source for the formation of graphene nanosheets. In addition, thermal degradation of PAA layer allows neighboring graphene nanosheets to support each other from its initial growth phase and thus effectively prevent them from growing into randomly oriented graphene nanosheets on quartz substrates.