Supplementary Information for:

Flexible and transparent graphene films as acoustic actuator electrodes using inkjet printing

Keun-Young Shin, Jin-Young Hong 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

Materials: The graphite flakes used in the majority of experiments were purchased from Sigma-Aldrich (Product Number 332461). GO was printed using a commercial office inkjet printer (Canon Pixima IP1300). The printer was equipped with a piezo-based print-head (dispenser system) with an inner diameter of 50 μm. The driving voltage applied to the piezo was 24 V and the dot spacing, which was the center-to-center distance between two adjacent droplets, was *ca.* 70 μm. Poly (vinylidene fluoride) (PVDF, Fils Co., Ltd) with 60 μm thickness was used as a substrate for inkjet printing.

Synthesis of GO dispersion for inkjet printing: GO was synthesized from natural graphite by a modified Hummers and Offeman method as presented originally by Kovtyukhova and colleagues. Synthesized purified GO suspensions were exfoliated in water by sonication for 1.5 h to avoid the nozzle blockage. The obtained brown dispersion was then washed for 4 cycles of centrifugation at 5,000 r.p.m. to remove any unexfoliated GO.

Modification of inkjet printer: The ink cartridge (printer head) was disassembled and washed several times by ethanol and distilled water after removing all inks. The exfoliated GO in distilled water (0.1 wt%) was injected into the modified cartridge as an alternative ink. Subsequently, the completely sealed ink cartridge was placed in the printer body and prepared to use for further experiments.

The fabrication of PVDF thin film acoustic actuator using the graphene electrodes by inkjet printing and hydrazine VDP process: For fabricating of graphene onto the PVDF film, low-temperature oxygen plasma treatment was performed in order to modify the surface energy of PVDF substrate (gas flow rate: 20 sccm, power: 100 W, time: 120 s at 5℃). The 10 x 10 cm rectangular architectures were designed by computer software in advance (Microsoft PowerPoint 2003), and GO ink printed on both sides of the PVDF film by inkjet printing repeatedly for several times. Subsequently, the printed GO film was properly cut and located in 90 °C VDP chamber containing hydrazine and ammonia solution for 30 min under vacuum. The graphene were immediately formed at low temperature. Then, the graphene electrodes of acoustic actuator were connected by Cu tape to the amplifier and sound source, which was used to reduce the electrode contact resistance. The transducers were excited to produce sound by a 50 V_{rms} white noise signal. The range of frequency response was from 40 Hz to 20 kHz (audible frequency range) and measured at 1 m distance from the film along the centerline axis. As a commercial thin film speaker, PEDOT:PSS-based acoustic actuator had the 85 % transmittance and 10 x 10 cm rectangular size. For ANC application, a soft substrate (3M VHB4910 acrylic form tape, Young's modulus = 105 kPa) was attached to graphene-based PVDF thin film in order to make an ANC actuator.

Characterization: TEM image was taken with a JEOL 6700F and the XPS spectra was recorded using Kratos Model AXIS-HS system. The AFM topography was obtained by a

Digital Instrument Nanoscope IIIA from veeco systems in tapping mode using silicon tips with a resonance frequency of 320 KHz. Plasma reactor was the parallel electrode type with a 13.56 MHz radio-frequency generator. The viscosity was measured by rheometer (AR 2000 Advanced Rheometer, TA Instruments) and the surface energy was calculated by Owens-Wandt equation after measuring the contact angle of distilled water droplet on the film surfaces. The measurement of electrical resistances was obtained with a Keithley 2400 sourcemeter at 25 °C by a four-probe method. The surface sheet resistance was measured at 5 different locations of graphene film and calculated as an average value. For the acoustic actuator characteristics, Brtiel and Kjaer 2012 audio analyzer was carried out (40 kHz to 20 kHz).

2. Preparation of Graphene Thin Films on PVDF Substrate

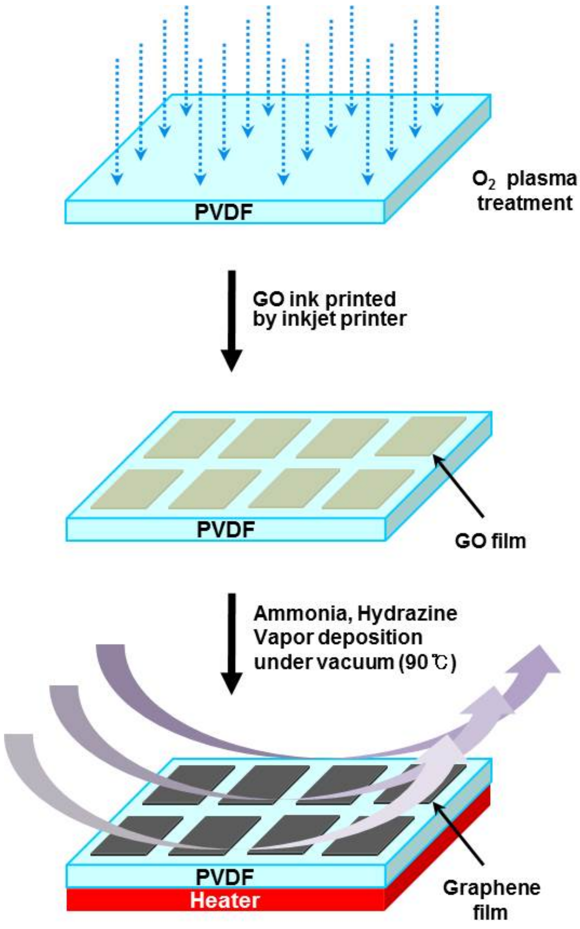

Fig. S1 The fabrication of graphene electrodes on PVDF film by inkjet printing and vapor deposition process. The reduction process was performed by mild-thermal annealing at 90°C with hydrazine and ammonia vapor. The PVDF film was treated with oxygen plasma at low temperature (5℃) to increase surface energy of the substrate (gas flow rate: 20 sccm, power: 100 W, time: 120 s and print resolution: 4800 x 1200 dpi).

The overall procedure for fabrication of the graphene film onto the PVDF substrate by inkjet printing is illustrated in Fig. S1. In general, ideal ink for inkjet printing is required to have viscosity between 1 and 20 mPa s and to match surface tension of the ink with surface energy of the substrate. Under our experimental condition, exfoliated GO aqueous solution had excellent dispersibility due to its hydrophilic property. The viscosity value of GO aqueous solution was measured to be *ca.* 2.2 mpa·s that was applicable to be used as an ink for inkjet printing without any other additives. In addition, in order to match between surface energy of a substrate and surface tension of GO ink (75.2 mNm^{-1}), PVDF film was treated with oxygen plasma that caused the surface energy of the substrate to increase from 25.0 mNm^{-1} to 58.7 mNm^{-1}. The GO-based ink meeting the above conditions could be printed out precisely onto the substrate via loading GO solution into modified ink cartridge. Inherently, GO is electrically insulating because of its structural defects and oxidized GO domains. Therefore, an additional reduction step is needed to make it electrically active. In our study, this reduction process was performed using the hydrazine vapor deposition (VDP) and mild thermal annealing under vacuum conditions (*ca.* 10^{-3} torr). As a result, graphene thin film could be efficiently synthesized in the large area (10 x 10 cm rectangular size).

3. The AFM and TEM Images of Exfoliated GO

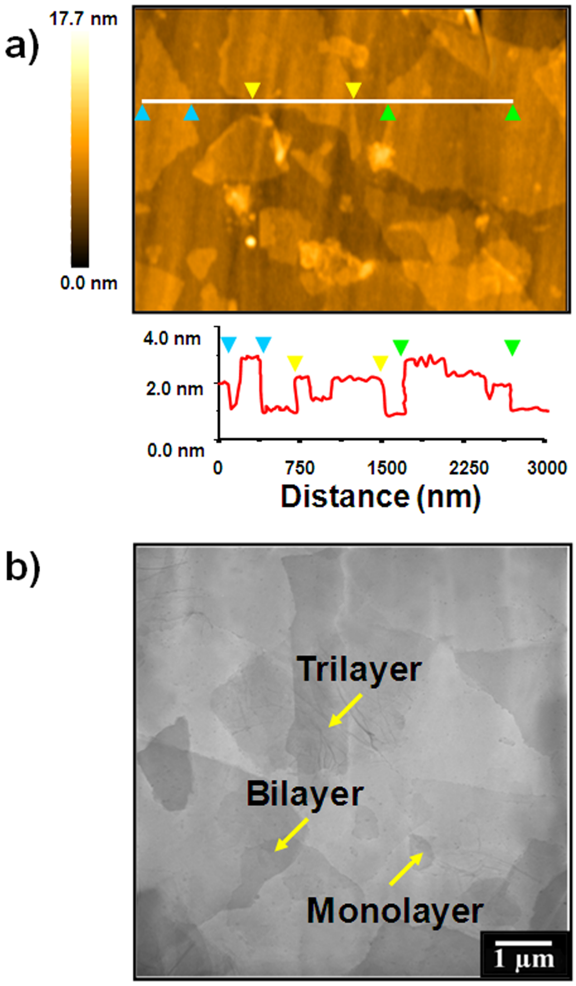

Fig. S2 Representative a) AFM and b) TEM image of the exfoliated GO as a conductive ink for inkjet printing. For the TEM sample preparation, GO solution was cast onto copper grid, and the AFM topography of the GO solution deposited on Si wafer.

The GO was first prepared from natural graphite by a modified Hummers and Offeman method. Synthesized GO based on aqueous solution can be easily exfoliated as individual GO sheets by sonication, since the functional groups such as hydroxyl, epoxy in the basal plane and carboxyl, carbonyl at the sheet edges make GO sheets hydrophilic and diminish the interaction energy between the graphene layers.

The bright-field TEM and AFM images display the exfoliated GO, which is composed of a few micron-sized monolayer (<1.5 nm thickness), bilayer (2~3 nm thickness) and multilayer (> 3nm thickness) graphene (Fig S2). In addition, large objects with thickness of more than a few layers were rarely observed by electron microscopy. It demonstrates that the GO can be readily exfoliated to form monolayer and few-layer graphene, dispersing in a stable aqueous solution.

4. XPS spectra

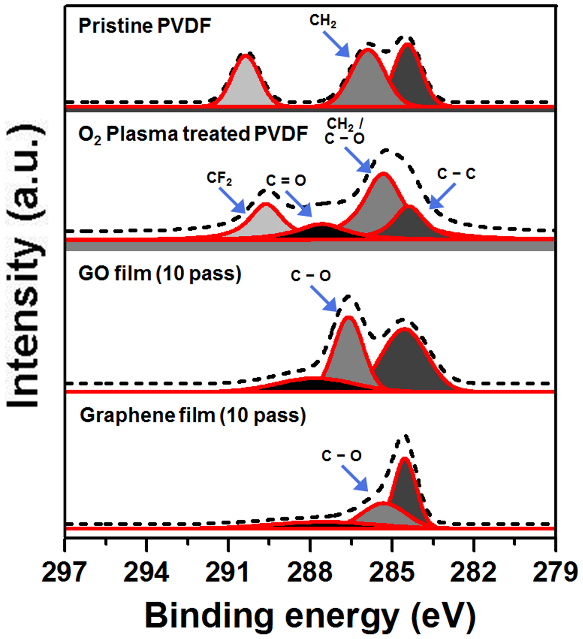

Fig. S3 Comparison of deconvoluted XPS spectrum of pristine PVDF, O_2 plasma treated PVDF films, exfoliated GO by inkjet printing for 10 passes and graphene thin films resulted from the reduction procedure onto the PVDF substrate in the C1s region.

To confirm the successful reduction from printed GO to graphene film onto the PVDF substrate, X-ray photoelectron spectroscopy (XPS) analysis for four different films (pristine PVDF, O_2 plasma modified PVDF, GO film on PVDF substrate and graphene film on PVDF substrate) are conducted. For pristine PVDF film, each main peak of CF_2, CH_2 and C–C bonding appeared at 290.8, 286.2 and 284.5 eV. After the low-temperature O_2 plasma treatment on the PVDF film, the intensity of the CF_2 peak decreased. On the contrary, the C–O component (286.3 eV) from epoxy and hydroxyl groups and the C=O bond (288.5 eV) from carboxy and carbonyl groups had emerged. It could be originated from the defluorination and oxidation of carbon radical occurred on the PVDF surface. When the GO ink was printed out by repeat printing for 10 passes, it was apparent that the CF_2 peak of pristine PVDF film was disappeared. It meant that the PVDF substrate had negligible effect on XPS intensity of GO film. Furthermore, as a result of reduction process for graphene film, the ratio of the $I_{C\text{–}O}/I_{C\text{–}C}$ decreased from 1.19 (GO) to 0.29 (graphene).

5. Raman Spectra

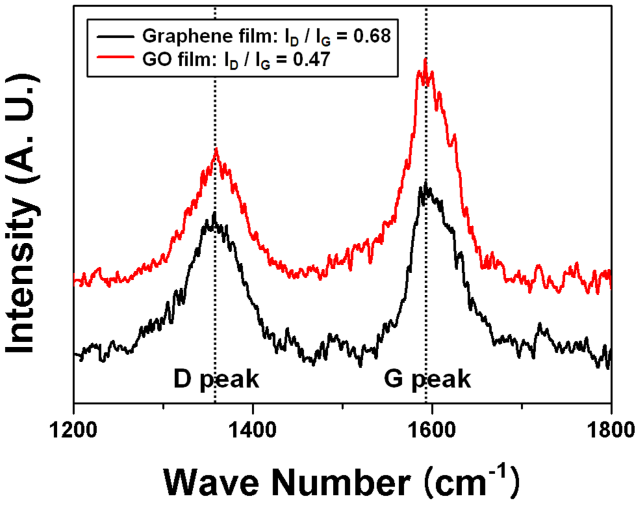

Fig. S4 The Raman spectra of GO and graphene film on the PVDF substrate showing G and D peaks.

The Raman spectrum of GO and graphene film on the PVDF substrate is exhibited in Fig. S4. It is well-known that the G peak (around at 1,586 cm^{-1}) indicates graphite carbon structure, whereas the D peak (around at 1,355 cm^{-1}) means typical defects ascribed to the structural edge effects, such as epoxides covalently bonded to the basal plane. The intensity ratio of I_D/I_G for GO film was 0.47. Furthermore, the Raman spectrum of the graphene film also contained both G and D bands. However, with an increased I_D/I_G intensity ratio (0.68) compared to that in GO. This change suggested a decrease in the average size of the sp^2 domains upon reduction of the exfoliated GO. Judging from these data, it was evident that the printed GO was successfully reduced to graphene film by the hydrazine vapor as a reducing agent at a mild-temperature.