

UV/Ozone-Oxidized Large-Scale Graphene Platform with Large Chemical Enhancement in Surface-Enhanced Raman Scattering

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Synthesis of graphene by CVD method and its Raman spectrum

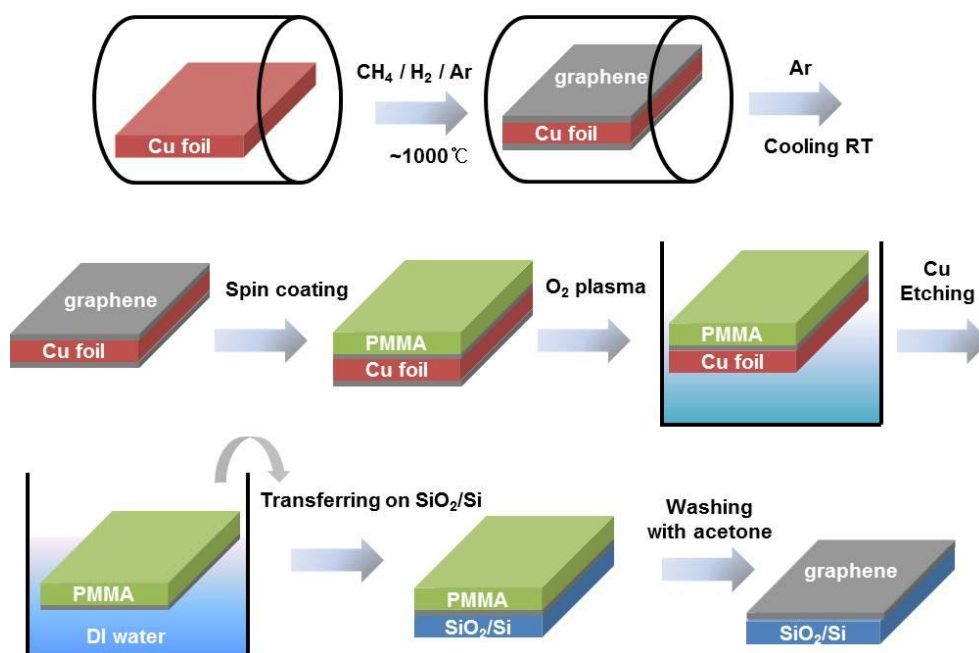


Figure S1. CVD-based graphene growth.

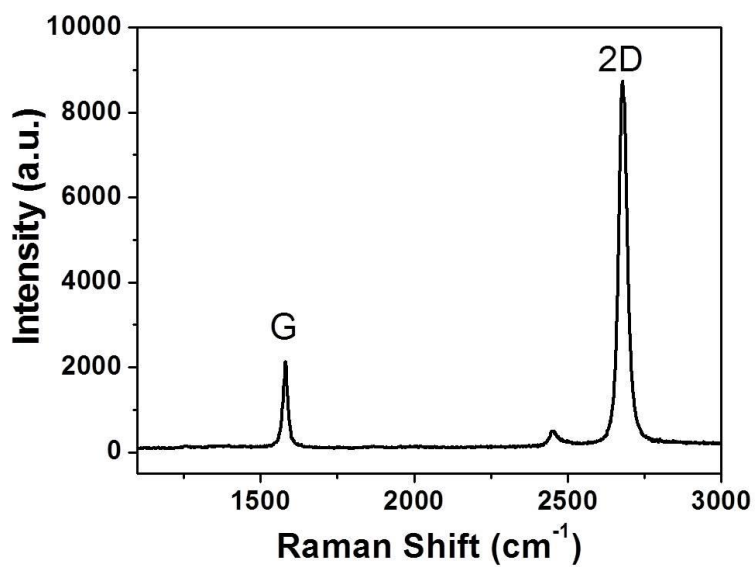


Figure S2. Raman spectrum of the CVD-grown single-layered graphene.

Device fabrication for transport measurement

Electrical measurements were performed on the fabricated devices by using heavily doped p-type Si wafers as the gate electrodes and a silicon dioxide (SiO_2) with 150-nm thickness (capacitance = 20 nFcm^{-2}) as the gate dielectric layer (Figure S3a). The 30-nm-thick gold source and drain electrodes were structured in top-contact transistors with a channel length of $9 \mu\text{m}$ and a width of $1 \mu\text{m}$. A 5-nm-thick titanium layer was used for the adhesion of the gold electrodes. The graphene layer was transferred onto the substrate and located between source and drain electrodes as a channel layer. Current-gate voltage curves of the graphene measured at $V_{sd} = 10 \text{ mV}$ with various ozone exposure time are shown in Figure S3b, c.

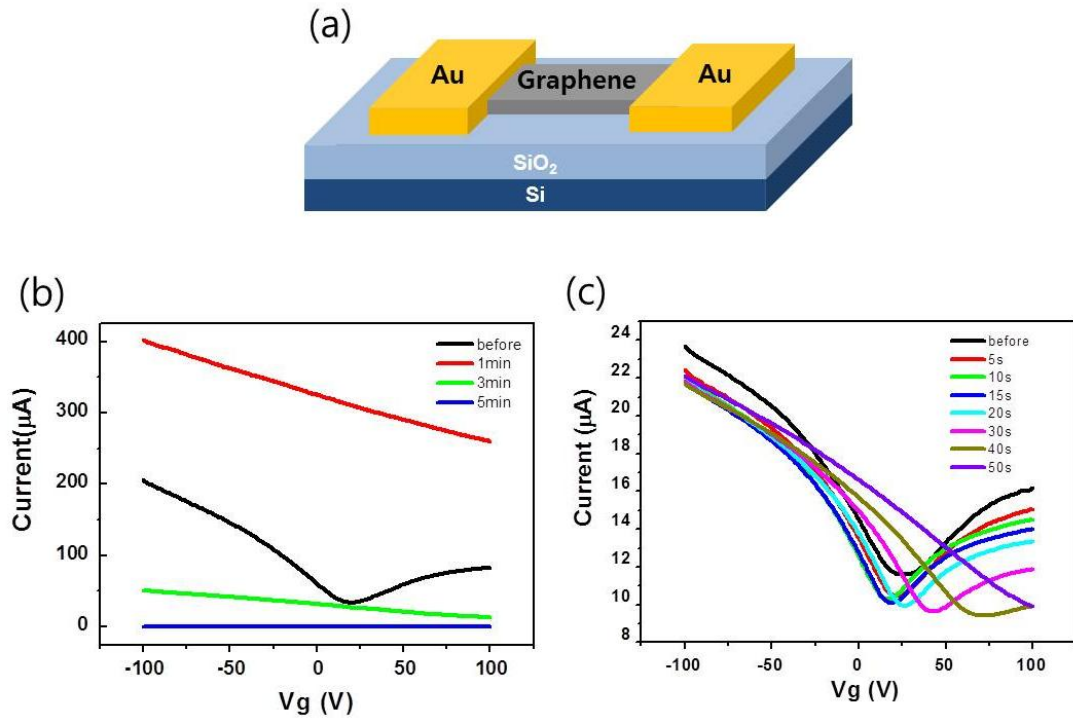


Figure S3. (a) Schematic diagram of the device for graphene-FET. Current-gate voltage curves of the graphene while varying UV irradiation time were measured on the long-term UV irradiation (b) and short-term UV irradiation (c).

Raman spectrum and SERS spectra of the RhB molecules

Figure S3 shows the Raman spectra of 10^{-2} M RhB solution and the RhB molecules on graphene with various RhB concentrations (from 10^{-3} to 10^{-10} M). To obtain the Raman spectrum of the pure RhB molecules in the solution, 10 μ l of RhB solution (10^{-2} M) was prepared in a sample chamber (SecureSealTM, GRACE BIO-LABS). The 514-nm excitation was used for the Raman measurement, and we found that the Raman intensity of the finger print bands of RhB molecules was increased as the concentration of RhB increases. We estimated an approximate saturation point is $\sim 10^{-5}$ M of the RhB solution.¹

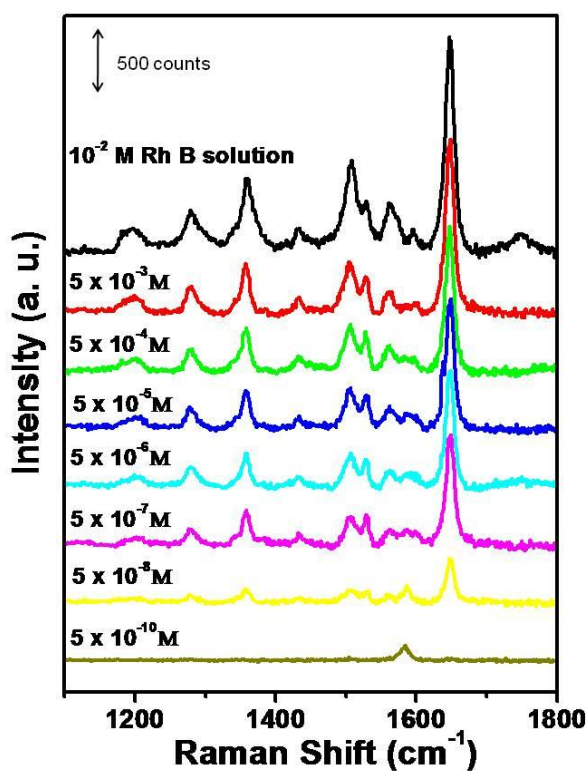


Figure S4. Raman spectrum of 10^{-2} M RhB aqueous solution (black line) and the SERS spectra of RhB molecules on graphene with various concentrations (from 10^{-3} to 10^{-10} M).

The Raman spectra of R6G and CV molecules

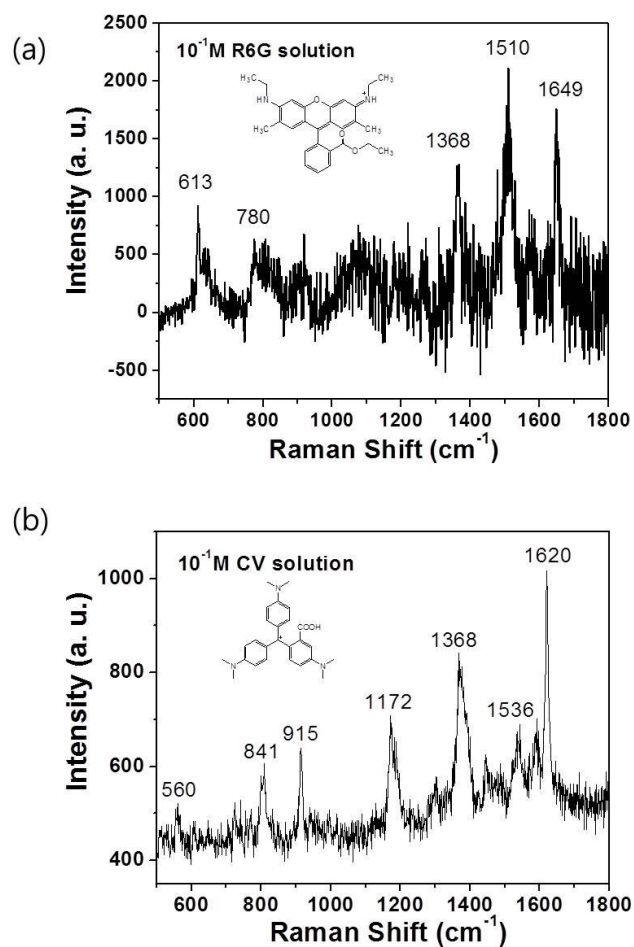


Figure S5. The Raman spectra of R6G (a) and CV (b). Methanol and water were used as solvents for R6G and CV, respectively.

Calculation of the SERS enhancement factors (EFs)

To determine the EF values, we compared the SERS intensity of RhB molecules on the graphene surface (I_{SERS}) to the Raman intensity of the pure RhB solution (50 mM). The EFs were calculated using the following equation,²

$$EF = \frac{I_{\text{SERS}} N_{\text{solution}}}{I_{\text{Solution}} N_{\text{SERS}}}$$

where N_{solution} and N_{SERS} are the numbers of RhB molecules that contribute to the Raman intensity in aqueous solution, as shown in Figure S4, and SERS on the graphene surface, respectively. The laser spot size is 2 μm . To define the focal volume of the RhB solution, assuming it as a cylinder, the height (h) was calculated by following equation,

$$\frac{h}{2r} = \frac{3.28\eta}{NA}$$

where r is the radius (1 μm), η is the refractive index of water medium (1.33),³ and NA is the numerical aperture of the objective lens (50 \times , $NA=0.5$). In the calculation of EFs, we assume that RhB molecules were adsorbed as a monolayer and fully covered on the active substrate with a maximum number of molecules.^{4,5} Thus, there is a chance that the calculated EFs is underestimated.

The EFs were calculated *via* the SERS intensities in Figure S6 and listed in Table S1. As the ozone exposure time is increased, EF is gradually increased with slight peak shifts. The results also suggest that the interactions between the molecule and the substrate occurred before and after ozone treatment.

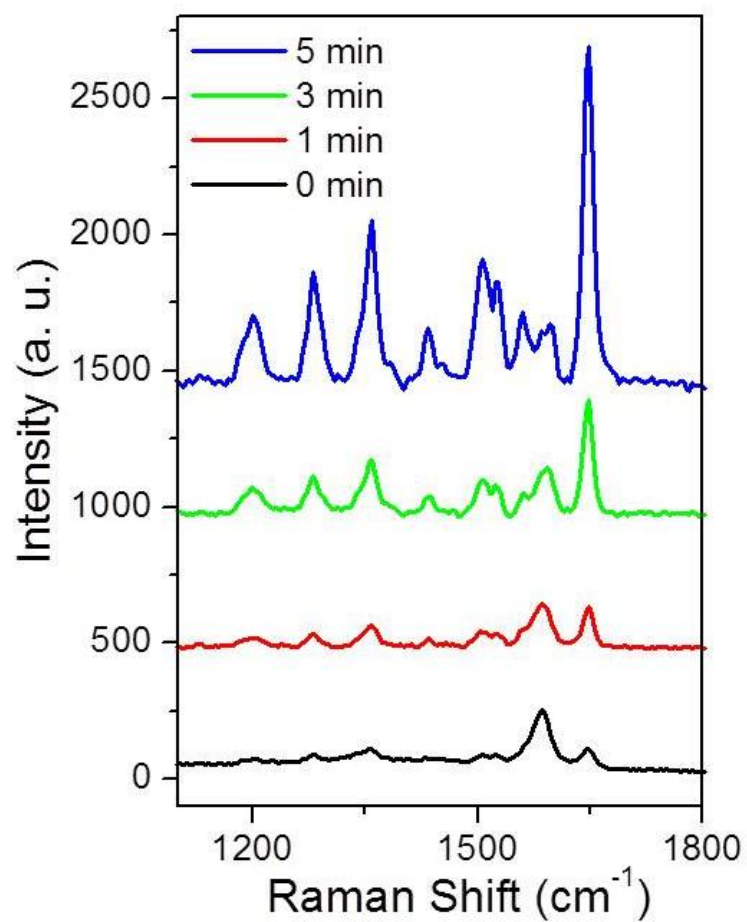


Figure S6. (a) The Raman spectra of the RhB molecules on UV/ozone-oxidized graphene substrates with different ozone-treatment time.

XPS spectra of the graphene with and without adsorbed RhB molecules

Figure S7 shows change in the nitrogen content of graphene while varying the UV/ozone treatment time. To determine the amount of the adsorbed RhB molecules on the oxidized graphene surface, we compared the XPS spectra of the graphene before and after RhB adsorption (Figure S8). After 5 min-ozone treatment, the graphene substrate was immersed in the 10^{-5} M RhB solution for 30 min and washed with deionized water. We could not observe the significant signal increase of N1s peak in the spectrum before RhB adsorption. We also found that the N1s peak was absent in the pristine graphene (data not shown). In our experiment, the amount of the adsorbed N on the oxidized graphene that could be originated from the air during the process seems to be negligible. As a result, we assumed that the signal of N is based on the adsorbed RhB molecules and carried out the monitoring of the nitrogen content in various UV/ozone treatment conditions, as shown in Figure S7

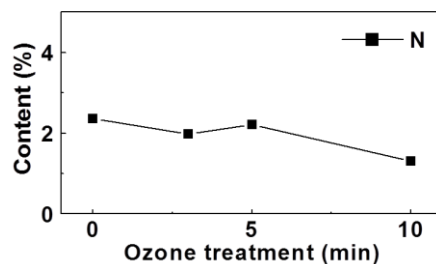


Figure S7. Change in the content of nitrogen of graphene while increasing ozone treatment time.

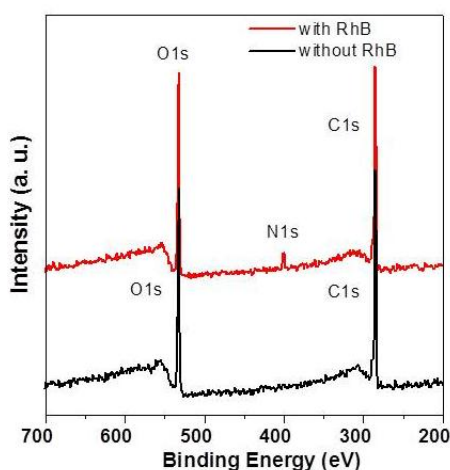


Figure S8. XPS spectra of the ozone-oxidized graphene with and without the adsorbed RhB molecules.

The distribution of RhB molecules on the graphene surface

To observe the distribution of the adsorbed RhB molecules on the graphene surface before and after ozone treatment, we obtained the fluorescence images (Zeiss, Germany). The graphene substrate, ozone-treated in the half of the area, was immersed in the 10^{-5} M RhB aqueous solution for 30 min, washed with deionized water and dried with an air gun. The RhB emission fluorescence images on graphene were obtained for the two regions – masked and ozone-treated areas, respectively (Figure S9). Although it is difficult to observe the perfectly-uniform distribution of the fluorescence emission, caused by the fluorescence quenching effect by graphene,⁶ the images show that RhB molecules are adsorbed almost equally to two different regions – the ozone-treated and masked areas.

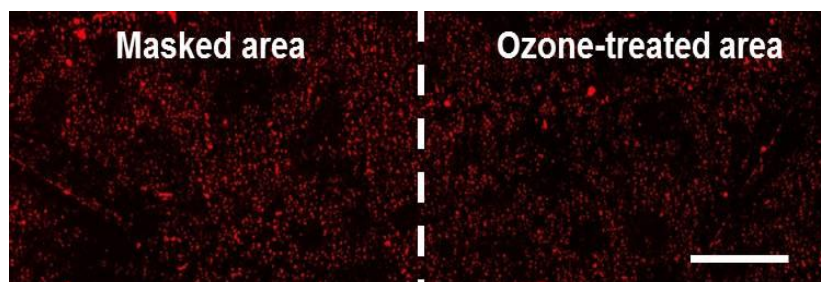


Figure S9. Fluorescence microscopic images of RhB molecules for the masked and ozone-treated areas, respectively. The scale bar is 100 μm .

Table S1. The SERS spectra and enhancement factors obtained on graphene surface as an active substrate for RhB molecules, adsorbed during immersion in the RhB solution (10^{-5} M) with the ozone exposure time of 0, 1, 3 or 5 min using the 514 nm-excitation of ~1 mW. These values were compared with the Raman spectra of RhB solution (50 mM).

SERS spectra										Raman spectra	
mode	5min		3min		1min		0min			mode	counts
	counts	EF	counts	EF	counts	EF	counts	EF			
1648	1231	10449	411	3489	145	1231	72	611		1647	18602
1560	205	9385	83	3800	58	2655	45	2060		1563	3449
1507	433	10661	132	3250	63	1551	26	640		1508	6413
1433	186	16444	60	5305	29	2564	11	973		1434	1786
1357	592	17406	403	11870	392	11546	34	1001		1360	5361
1281	379	20976	127	7029	52	2878	26	1439		1279	2853
1208	257	26265	91	9300	25	2555	17	1737		1200	1545

References

- (1) Joo, S. W.; Han, S. W.; Kim, K. Adsorption of 1,4-Benzenedithiol on Gold and Silver Surfaces: Surface-Enhanced Raman Scattering Study. *J. Colloid Interface Sci.* **2001**, *240*, 391–399.
- (2) Fang, Y.; Seong, N.-H.; Dlott, D. D. Measurement of the Distribution of Site Enhancements in Surface-Enhanced Raman Scattering. *Science* **2008**, *321*, 388–392.
- (3) Pawley, J. B. *Handbook of Biological Confocal Microscopy*; Plenum Press: New York, 1995.
- (4) Cho, S. H.; Han, H. S.; Jang, D. J.; Kim, K.; Kim, M. S. Raman Spectroscopic Study of 1,4-Benzenedithiol Adsorbed on Silver. *J. Phys. Chem.* **1995**, *99*, 10594–10599.
- (5) Camargo, P. H. C.; Cobley, C. M.; Rycenga, M.; Xia, Y. Measuring the Surface-enhanced Raman Scattering Enhancement Factors of Hot Spots formed between an Individual Ag Nanowire and a Single Ag Nanocube, *Nanotechnology* **2009**, *20*, 434020.
- (6) Kim, J. M.; Cote, L. J.; Kim, F.; Huang, J. Visualizing Graphene Based Sheets by Fluorescence Quenching Microscopy *J. Am. Chem. Soc.* **2010**, *132*, 260–267.