SUPPORTING INFORMATION

A CASE STUDY: EFFECT OF DEFECTS IN CVD-GROWN GRAPHENE ON GRAPHENE ENHANCED RAMAN SPECTROSCOPY

Jong-Chul Yoon[a], Pradheep Thiyagarajan[a], Hyo-Jin Ahn[a] and Ji-Hyun Jang[a*]

Interdisciplinary School of Energy and Low dimensional Carbon materials Center, UNIST, Ulsan 689-798, Republic of Korea. Email : _clau@unist.ac.kr_

EXPERIMENTAL PROCEDURE

GRAPHENE GROWTH AND TRANSFER PROCESS

Graphene growth on copper foil (Alfa Aeasr, 99.9999%) was performed by chemical vapor deposition (CVD) at 1000 ºC. First 100sccm of H_2 was passed over the foil while increasing the temperature to remove impurities on its surface. Then a continuous flow of 100sccm of CH_4 gas was passed through the quartz tube for 5min, without turning off the H_2, to grow the graphene. After growth, the temperature in the quartz tube rapidly decreased to room temperature. The graphene transfer processes were as follows. For PMMA-graphene, the graphene/Cu film was coated using a PMMA solution dissolved in toluene and then dried at 100 ºC in an ambient air for 10min. For the preparation of TRT-graphene, the tape was attached to the graphene/Cu film and pressure was then applied to remove air between the tape and sample. For both PMMA- and TRT-graphene, the Cu foil was removed from the sample by etching for 2hrs in an ammonium persulfate solution. After removing the Cu foil, both samples were floated for 1hr on D.I. water to wash the etchant solution from the samples and dried using N_2 gas. Finally the prepared sample was transferred onto the desired substrate.

R6G DYE ADSORPTION ON THE GRAPHENE SUBSTRATE

R6G as a probe molecule was dissolved in a DI water. The concentration of R6G in solution was 10^{-5} M (mol L^{-1}). The molecule was adsorbed by soaking the sample in the prepared solution for 1hr followed by washing three times to remove any residue.

GERS MEASUREMENT

To confirm the GERS effects of the prepared substrate, combined AFM-Raman microscopy (WITec) was used to check the signal enhancement of R6G dye. R6G was dissolved in DI water with a concentration of 1 mM to obtain a stock solution and then diluted to obtain the required concentration. The substrate was dipped into the dye solution where it remained for 60 min to stabilize deposition. After adsorption, the substrate was rinsed by DI water. For the Raman measurements, the power was adjusted to 0.2 mW and integration time was set to be 10 s.
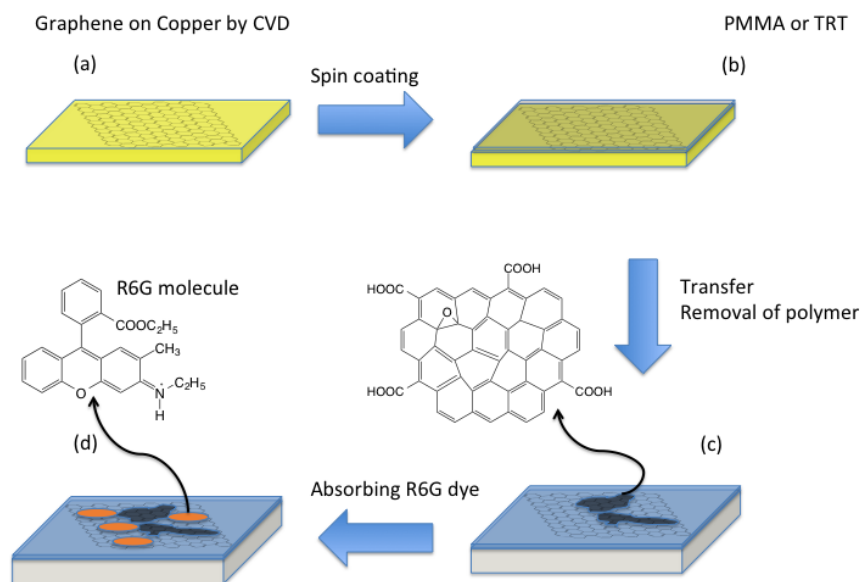

Figure S1. Schematic diagram of the overall process. (a) Graphene grown on a copper foil, (b) polymer(PMMA or TRT)(gray)/graphene/copper substrate, (c) graphene with residues (black) after removing the polymer that was used to transfer, (d) R6G dye molecules (blue) adsorbed on the surface of graphene at positions either where carboxyl groups are present or epoxy groups are not present.
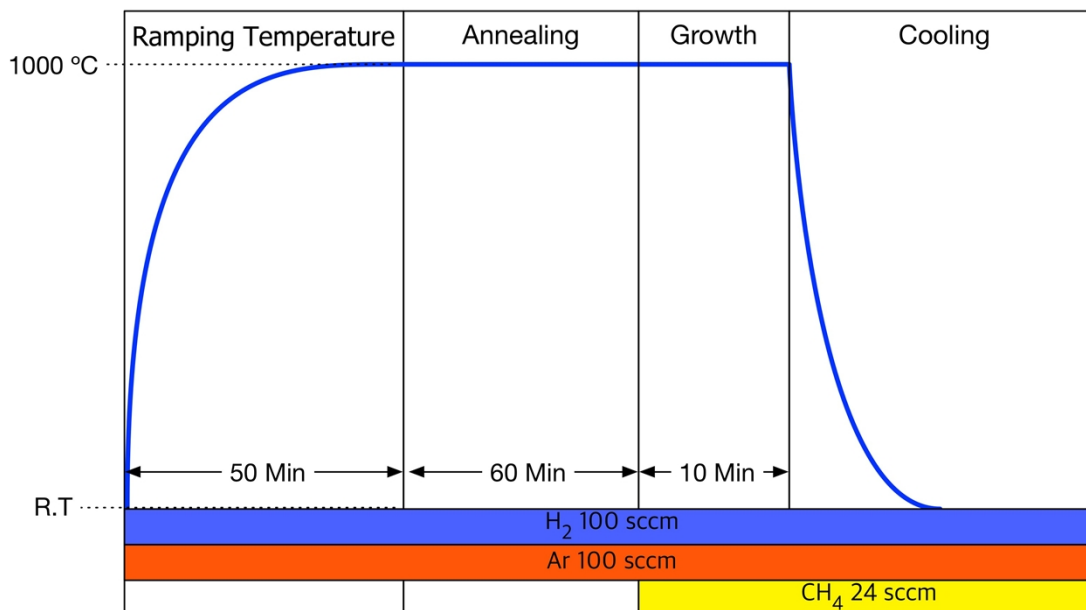
Ramping Temperature | Annealing | Growth | Cooling

1000 °C

50 Min → ← 60 Min → ← 10 Min →

R.T

H₂ 100 sccm

Ar 100 sccm

CH₄ 24 sccm

Figure S2. Schematic of the process cycle for the growth of graphene on the surface of Cu by CVD

Table S1. A table of comparison of Raman intensity of PMMA-graphene and TRT-graphene at 610 and 1645 cm^{-1}.

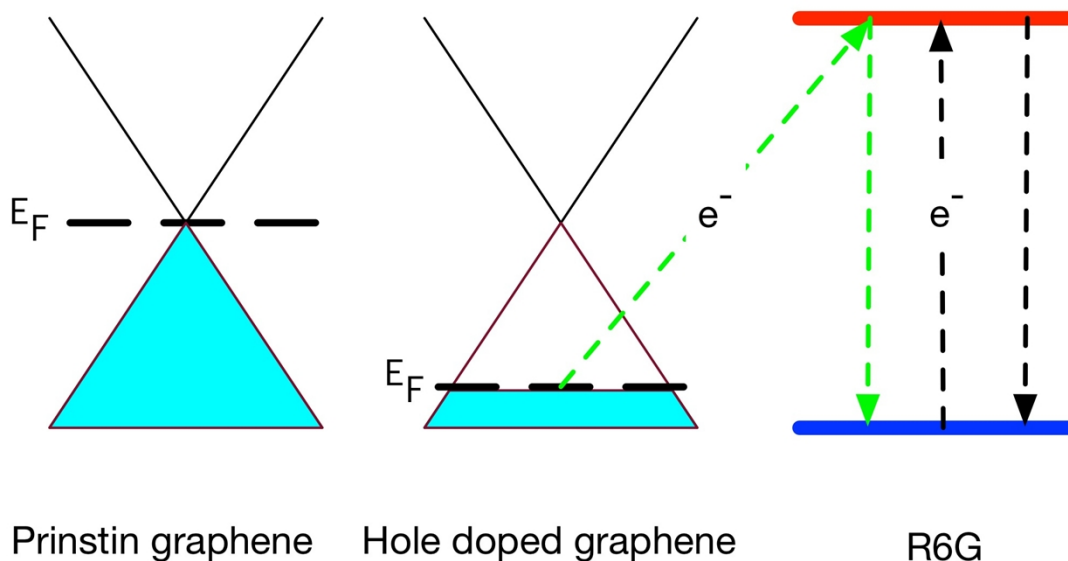| Position	610 cm^{-1}		1645 cm^{-1}	
Methods	TRT	PMMA	TRT	PMMA
Higher intensity	2532.35	3895.05	1758.47	7142
Baseline	1607.05	1708	816.35	1859.41
Height	925.3	2187.05	942.12	5282.59
I$_{PMMA/TRT}$	2.3636		5.6071	

Figure S3. A schematic of the effect of the Fermi level of graphene on charge transfer: Hole-doped graphene can supply electrons to the LUMO of R6G by laser excitation due to a similar energy gap to the energy of the laser.
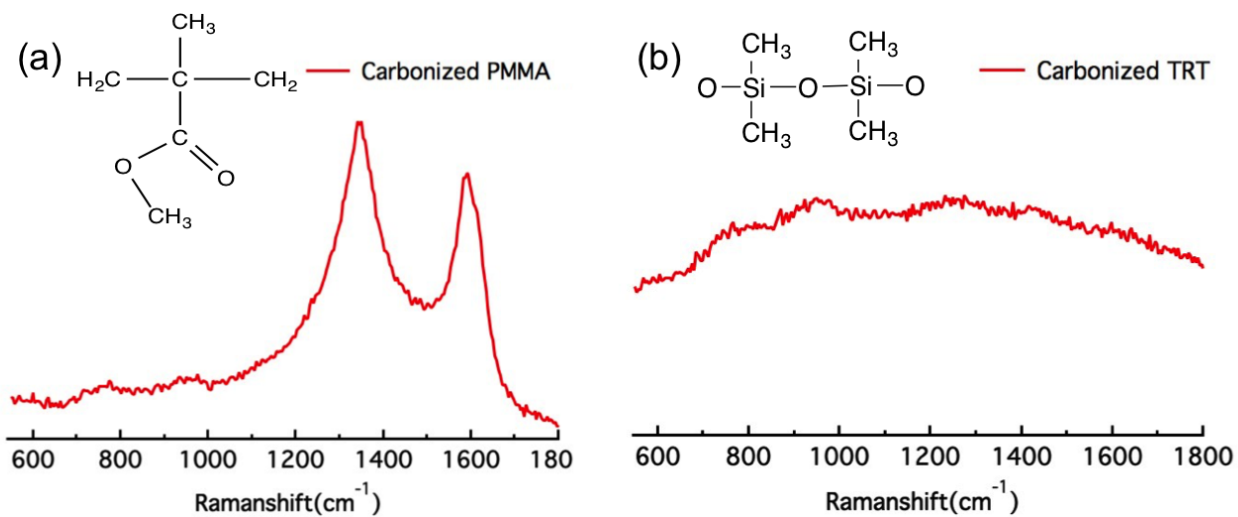

Figure S4. Raman spectroscopy of R6G dyes (10^{-5}M) on carbonized PMMA (a) and carbonized thermal release tape (b). Both samples do not show enhanced Raman scattering effects without graphene.
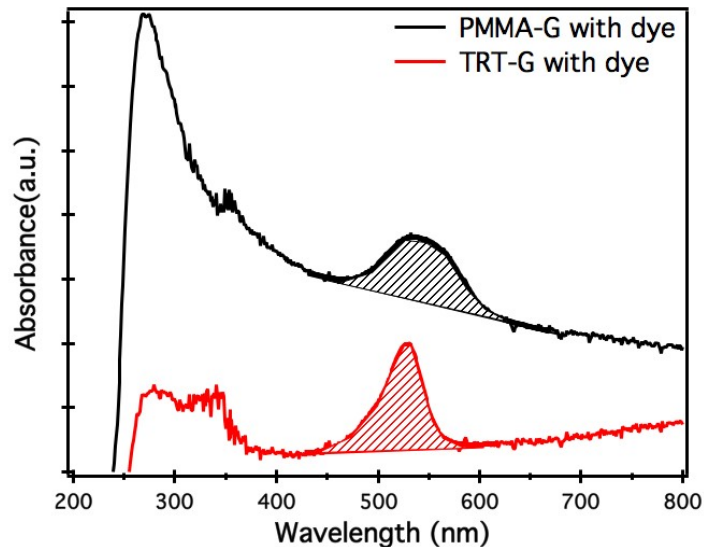
Figure S5. The absorption spectra of PMMA-G (black) and TRT-G (red) after attaching R6G molecules. The area of an absorption peak (a deviant crease line) is calculated by integration using a software.

	Area
PMMA-G	0.27361
TRT-G	0.37749

Table S2. The value of the area of each sample in the UV-absorption spectra.

When the EF value is calculated, the uniform and monolayer deposition of dyes per unit area of the substrate is assumed. Unfortunately, we were not able to directly measure the concentration of R6G on PMMA-G and TRT-G because R6G did not fully cover the unit area of each graphene at low concentration of dyes (10^{-5}M) by a simple soaking/washing method we inevitably used. Further there might be some inhomogeneity in the deposition of dye molecules. In this regard, we are not convinced that the exact number of R6G on graphene can be calculated. However we can predict relative concentration of R6G by comparing the peak area of each graphene transferred by two methods in the UV absorption spectra. The area of dyes/TRT-G is 1.38 times larger than that of dyes/PMMA-G in the UV spectra. If we assume that the number of dye molecules is proportional to the area of a peaks in the absorption spectra, we can calculate the relative ratio of EF by a following equation.

$$EF_{PMMA/TRT} = \frac{I_{SERS-P} \times N_{SERS-T}}{N_{SERS-P} \times I_{SERS-T}}$$

Where I_{SERS-P} and N_{SERS-P} are the peak intensity of Raman spectra and the number of dye molecules on the surface of PMMA-G, respectively. I_{SERS-T} and N_{SERS-T} are the peak intensity of Raman spectra and the number of dye molecules on the surface of TRT-G. Therefore the relative ratio of EF ($EF_{PMMA/TRT}$) is 8.28, when considering the relative density of dye molecules.