Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

The Unique Photoemission from Single-Layer Graphene on SiO_2 Layer by Substrate Charging Effect

Hyunseob Lim[a], *Hyun Jae Song*[a], *Minhyeok Son*[a], *Jae Yoon Baik*[b], *Hyun-Joon Shin*[b,*] *and Hee Cheul Choi*[a,*]

[a]Department of Chemistry and Division of Advanced Materials Science, [b]Pohang Accelerator Laboratory and Department of Physics, Pohang University of Science and Technology (POSTECH), San 31, Hyoja-Dong, Nam-Gu, Pohang, Korea, 790-784.

To whom correspondence should be addressed.

Email: choihc@postech.edu, shj001@postech.ac.kr

Detail measurement process of SPEM imaging and SR-XPS experiments

For the acquisition of SPEM images, X-ray was exposed for 150 ms with a step size of 0.5 μm (measuring time was 120 ms and waiting time for the next step was 30 ms). During the SR-XPS measurements, each spectrum was obtained from a fixed position of the sample. The energy step was 0.05 eV and the energy scan range was 22 eV to obtain the C1s spectral range. Total spectral acquisition time was then ~ 40 s [(Δ22 eV)/(Δ0.05 eV/step) x (100 ms/step)], which was much longer than that for SPEM measurements. This resulted in effectively much greater charging shift in the SR-XPS mode than those of images.

Detail quantitative analysis of C and G peak in SR-XPS

For a quantitative analysis, the area intensity of C and G peak was plotted in Figure 3(d). It shows that the intensity of G peak is directly proportional to the number of graphene layer, whereas the intensity of C peak is almost unchanged regardless of the number of layer. Generally, the population of emitted photoelectron from atoms under the surface is exponentially decreased according to the depth from the surface, as the intensity of G peak can be described by Eq. S(1) (I_n: intensity of photoelectron from n-layer graphene, I_1: intensity of photoelectron from single-layer graphene, d_x: depth from top layer to x-th layer, λ_p: probing depth).

$$I_n = \sum_{x=1}^{n} I_1 \exp[-d_x / \lambda_p] \qquad \text{S(1)}$$

In the case of graphene, d_x is much smaller for a few layer of graphene ($d_2 \approx 3.8$ Å, $d_3 \approx 7.6$ Å) than probing depth (λ_p = ~ few nanometer). Hence, the intensity of photoelectron of C from n-layer graphene (I_n) becomes proportional to the number of layer (n), which agrees well with our results. Meanwhile, the area intensity of amorphous C peak does not change as the number of graphene layer increases, which makes a correct sense considering the overall amount of naturally involved amorphous carbon like adsorbed carbon dioxide should be constant.

Fig. S1. SR-XPS spectra obtained from single- (**I**), bi- (**II**), and tri- (**III**) layer graphenes in Figure 1(a).

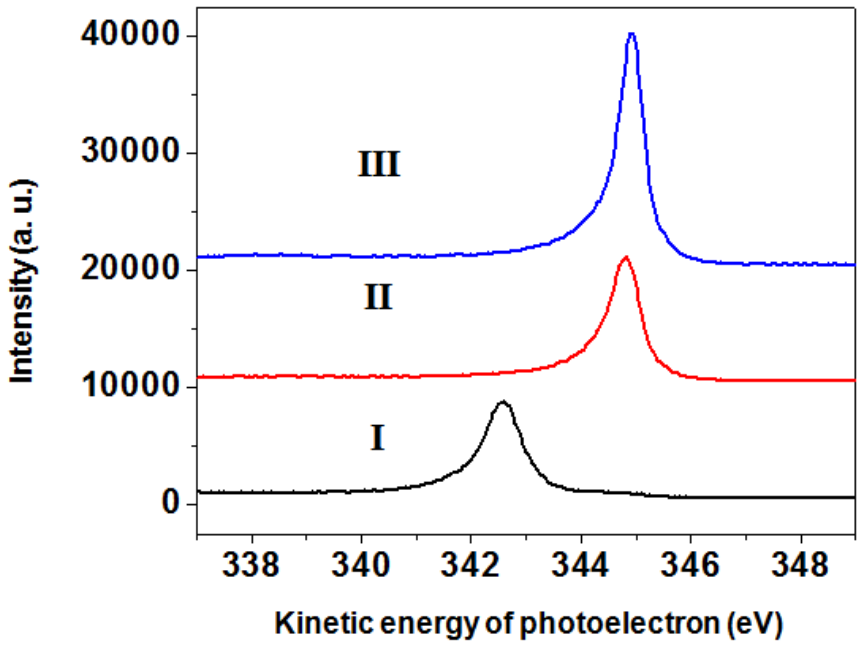

Table S1. SR-XPS peak positions, KE difference of G and C peak, and full-width at half-maximum (FWHM) values of G peaks for single-, bi- and tri-layer graphene.

	Single-layer	**Bi-layer**	**Tri-layer**
KE (G)	342.6 eV	344.8 eV	344.85 eV
KE (C)	342.3 eV	344.2 eV	344.2 eV
KE (G – C)	0.3 eV	0.6 eV	0.65 eV
FWHM (G)	623 meV	519 meV	481 meV

Scheme S1. Schematic view of distinct charging effect for SLG and BLG. Positives charges generated on (a) SLG and (b) BLG layers upon X-ray irradiation. (c) Positive charges on SLG are compensated well by the electrons provided from SLG through in-plane screening effect, while positive charges on SiO_2 are still present. (d) Positive charges developed on BLG and SiO_2 are compensated well by both in-plane screening effect and inter-graphene layer screening effect.