Supporting information for

Friction and conductance imaging of sp^2- and sp^3-hybridized subdomains on single-layer graphene oxide

*Hyunsoo Lee[a,b+], Narae Son[c+], Hu Young Jeong[d], Tae Gun Kim[e], Gyeong Sook Bang[c], Jong Yun Kim[c], Gi Woong Shim[c], Kalyan C. Goddeti[a,b], Jong Hun Kim[a,b], Nam Dong Kim[f], Hyun-Joon Shin[f], Wondong Kim[g], Sehun Kim[h], Sung-Yool Choi[*c], and Jeong Young Park [*a,b]*

[a]Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 305-701, Korea

[b]Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

[c]Department of Electrical Engineering and Graphene Research Center, KAIST, 291 Daehak-ro, Daejeon, Korea

[d]UNIST Central Research Facilities (UCRF), UNIST, 100 Banyeon-ri, Eonyang-eup, Ulsan, Korea

[e]Korea University of Science and Technology (UST), 206 Gajeong-ro, Daejeon 305-350, Korea

[f]Pohang Accelerator Laboratory, Pohang 790-834, Korea

[g]Center for Nanometrology, Korea Research Institute of Standards and Science (KRISS), 267 Gajeong-ro, Yuseong-gu, Daejeon 305-340, Korea

[h]Department of Chemistry and Molecular-Level Interface Research Center, KAIST, 291 Daehak-ro, Daejeon, Korea

*To whom correspondence should be addressed. E-mail: jeongypark@kaist.ac.kr

1. UV–Vis spectra

Fig. S1 shows a UV–Vis spectrum of GO dissolved in water, exhibiting two absorption peaks in the visible and near-infrared range. The maximum absorption at 229 nm corresponds to $\pi \rightarrow \pi^*$ transitions of aromatic C–C bonds, and the shoulder at 300 nm originates from $n \rightarrow \pi^*$ transitions of C–O bonds.[1]

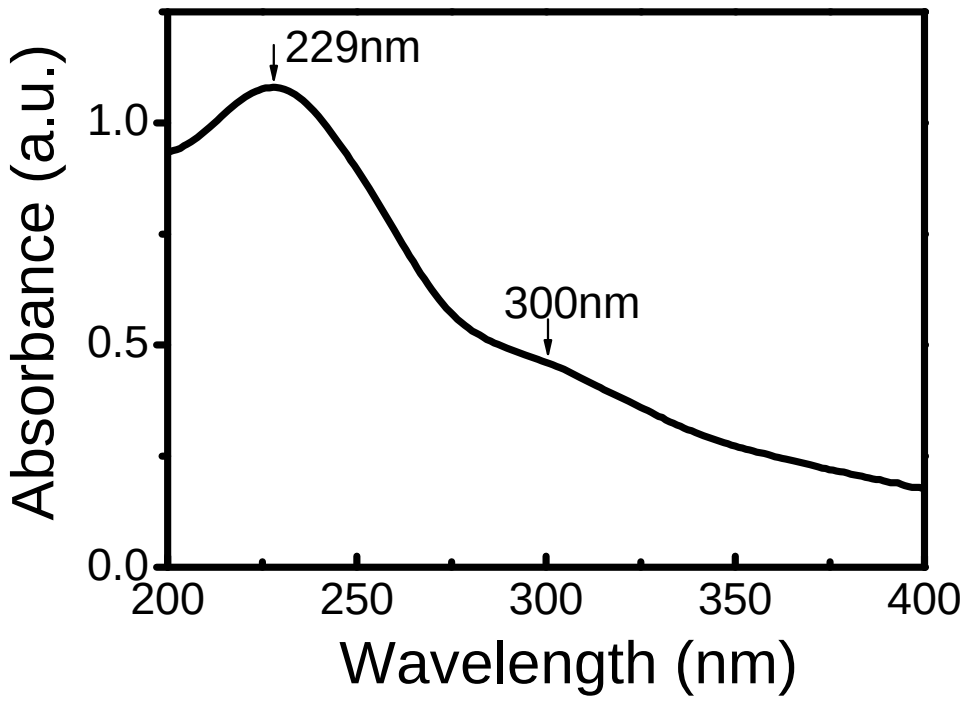

Fig. S1. UV–Vis absorbance spectrum of the GO solution in water.

2. Raman spectra

To characterize the structural information for GO (e.g., crystal size and disorder level), micro-Raman spectra (Fig. S2) were obtained using a 514.5 nm laser. The spectra exhibited three main characteristic peaks: G band (~1603 cm^{-1}), D band (~1347 cm^{-1}), and 2D band (~2700 cm^{-1}). The relative intensity ratio of the D and G peaks (I_D/I_G) was about 0.975. The feature at ~2920 cm^{-1} is associated with a D + G combination mode induced by disorder.

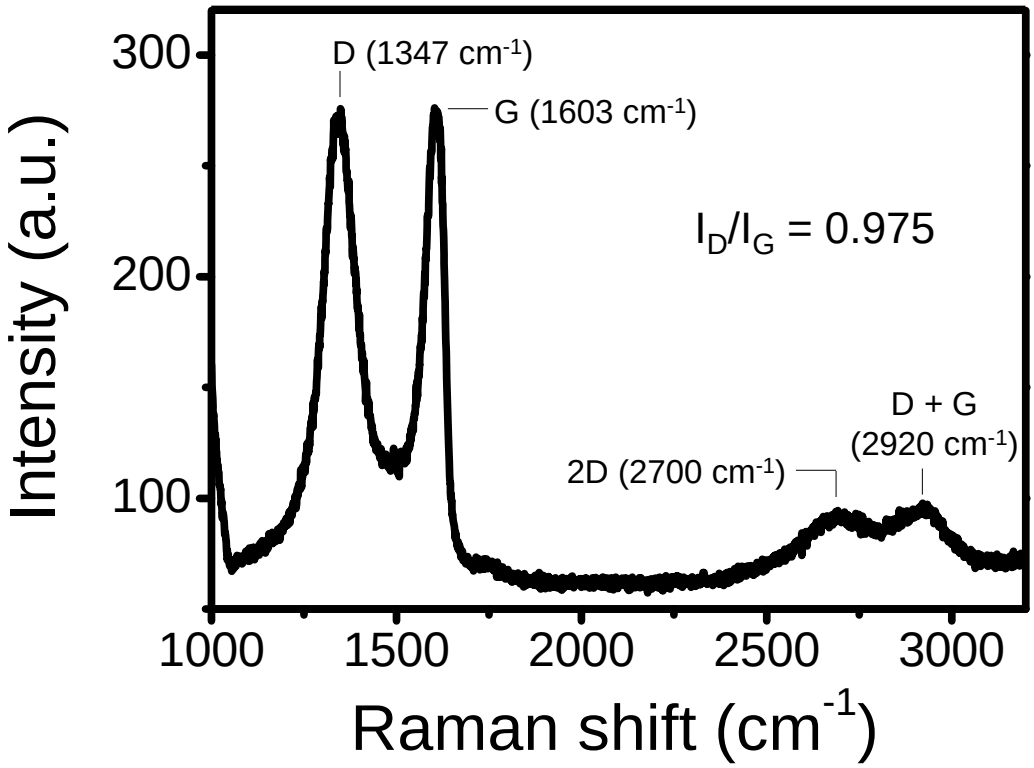

Fig. S2**.** Raman spectrum of single-layer GO recorded using a 514.5 nm laser and calibrated using the 521 cm^{-1} Si peak as reference.

3. Fourier transform infrared spectra (FT-IR)

FT-IR was used to verify the presence of functional groups in GO. We observed dominant peaks at 3423, 1733, 1619, 1360, 1222 and 1051 cm^{-1}. The peak at 1619 cm^{-1} corresponds to C–C bonds associated with skeletal vibrations of the graphitic sp^2 domains. The other peaks are all attributed to oxygen functional groups: The peak at 3423 cm^{-1} corresponds to stretching vibrations from O–H bonds of hydroxyl groups or adsorbed water. The peak at 1733 cm^{-1} is attributed to C=O bonds in carboxylic acid and carbonyl groups. The peaks at 1360, 1222, and 1051 cm^{-1} correspond to C–O bonds in carboxylic acid, epoxide, and alkoxy groups, respectively.

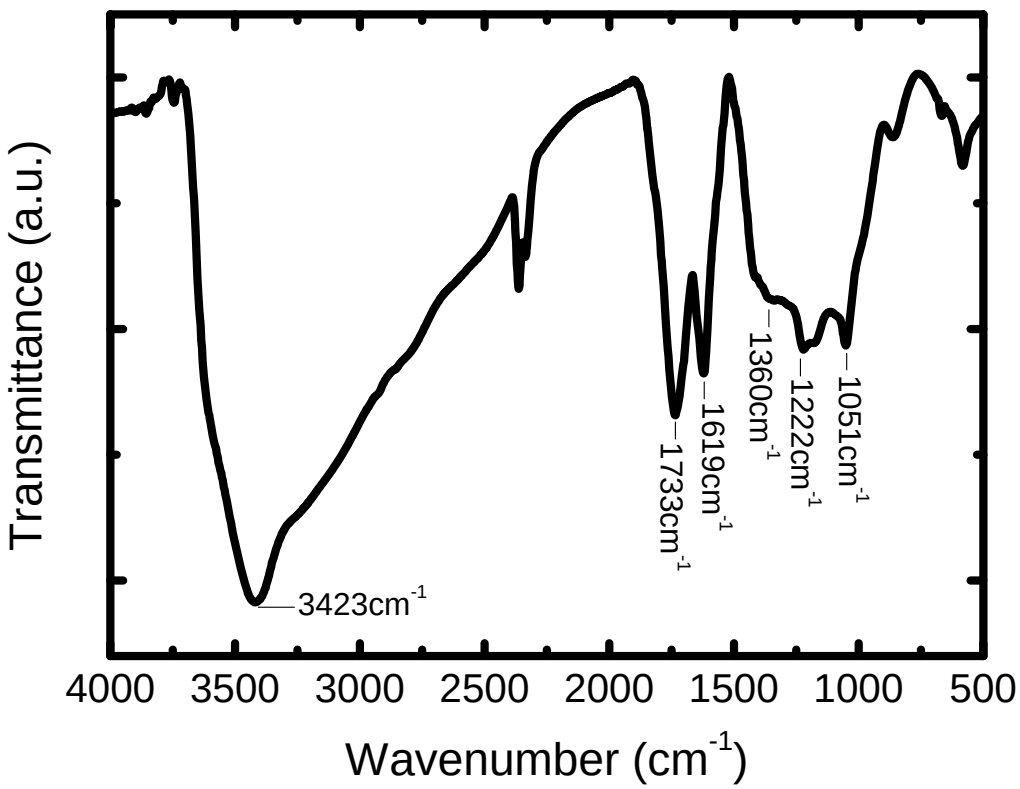

Fig. S3. FT-IR spectrum of GO.

4. X-ray photoelectron spectroscopy (XPS)

XPS was employed to analyze the components of the oxygen functional groups of GO. Fig. S4a shows a wide-scan spectrum characterized by two main peaks: O1s and C1s. The intensity ratio of O/C was about 1.84. The C1s core-level spectrum revealed three major peaks, which are assigned to sp^2 and sp^3 C–C bonds at 284.8 eV; C–O bonds of epoxy groups at 286.9 eV; and carboxylic groups at 288.7 eV in Fig. S4b.[2-5]

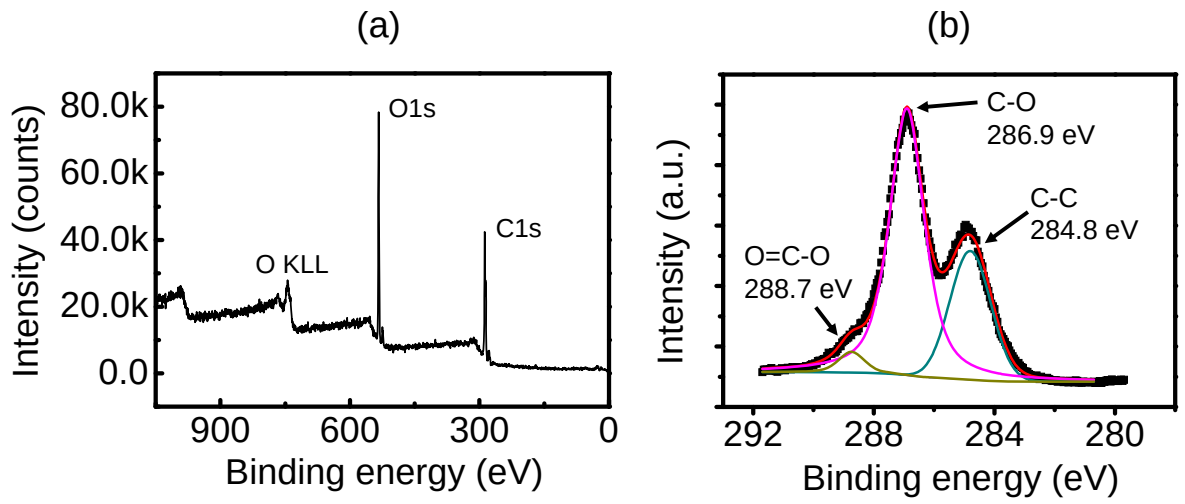

Fig. S4. XPS spectra of GO: (a) wide-scan spectrum and (b) C1s spectrum.

5. Height profile of GO on SiO_2/Si

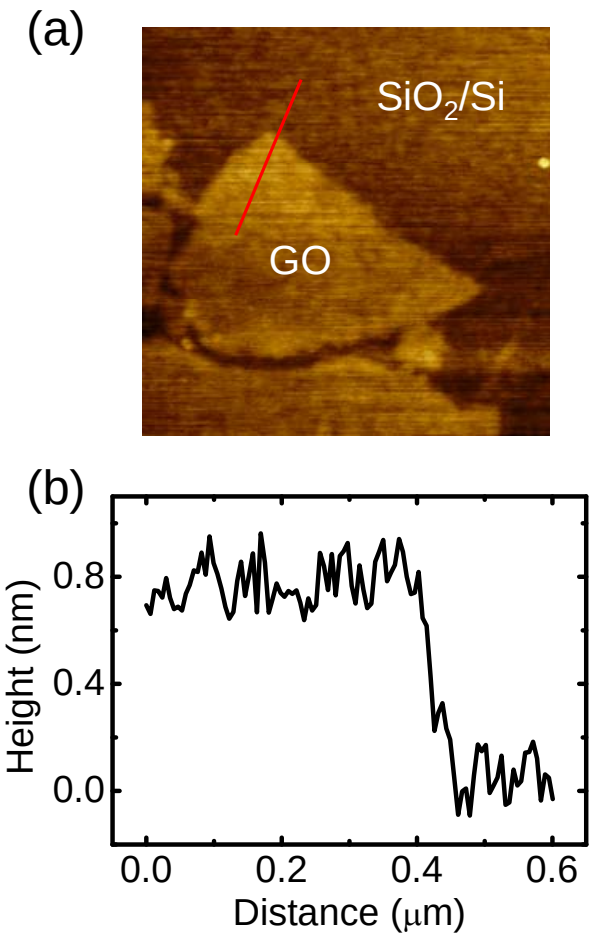

Fig. S5. (a) Topography and (b) cross-section profile (along the red solid line in (a)) of the GO sheet on SiO_2/*n*-Si. The average height of the GO sheet is about 0.8 nm.

6. Friction loop of the GO sheet on SiO_2/Si

Fig. S6 shows the friction loop for the data in Fig. 3. The regions with sp^2- and sp^3-rich phases, and SiO_2 substrate are clearly distinguished. The sp^2-rich phase does not exactly correspond with the pristine graphene. The GO sheet can have higher friction than that of the SiO_2 substrate due to a high concentration of –OH groups, creating a reactive, polar surface with a higher density of silanol groups on the GO sheet.[6, 7]

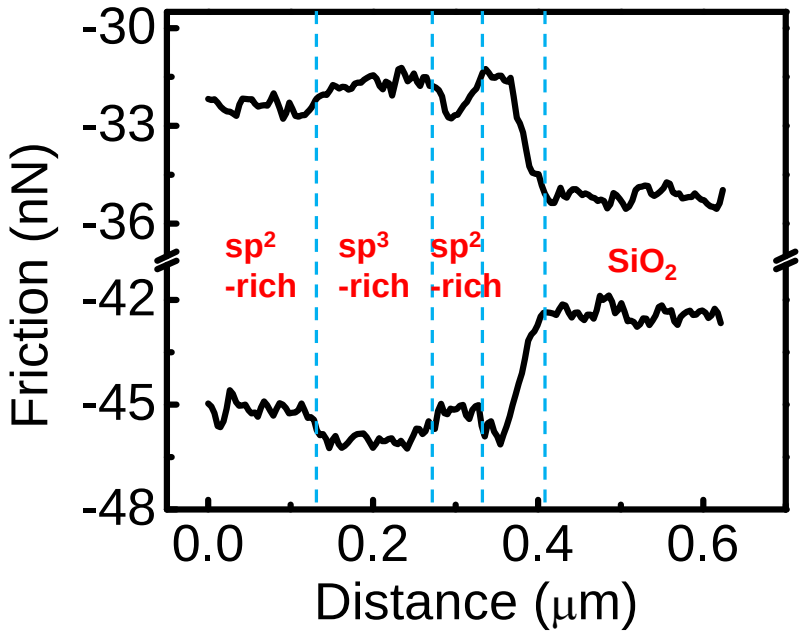

Fig. S6. Friction loop of the GO sheet on SiO_2/Si substrate.

7. Magnified friction image of GO

Fig. S7 shows a friction image with small scans on a mixture of hydroxyl and carboxyl groups, and epoxy bridges within the 2-dimensional carbon layer, which includes both sp^2- and sp^3-rich domains. The contrast of friction is clearly shown in Fig. S9b.

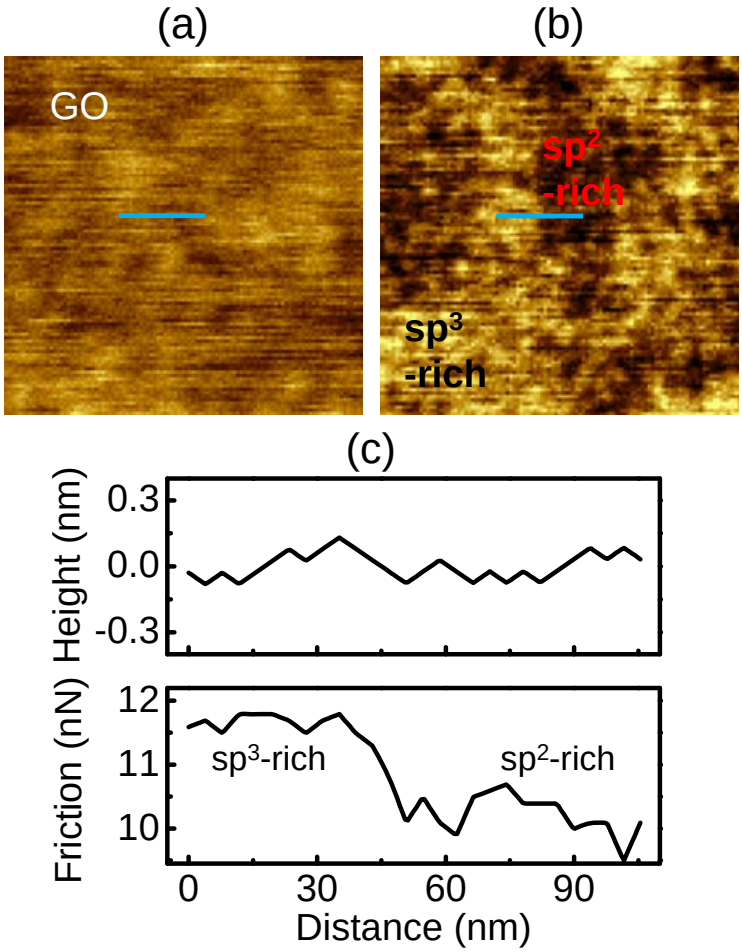

Fig. S7. (a) Topography (400 × 400 nm^2) and (b) friction mapping of the GO surface taken using C-AFM. (c) Line profiles of the height and friction along the blue lines in (a) and (b).

8. Statistical difference of friction

Fig. S8 shows a histogram showing the statistical difference for friction from multiple GO flakes. It clearly shows two main peaks for the friction on sp^2- and sp^3-rich regions.

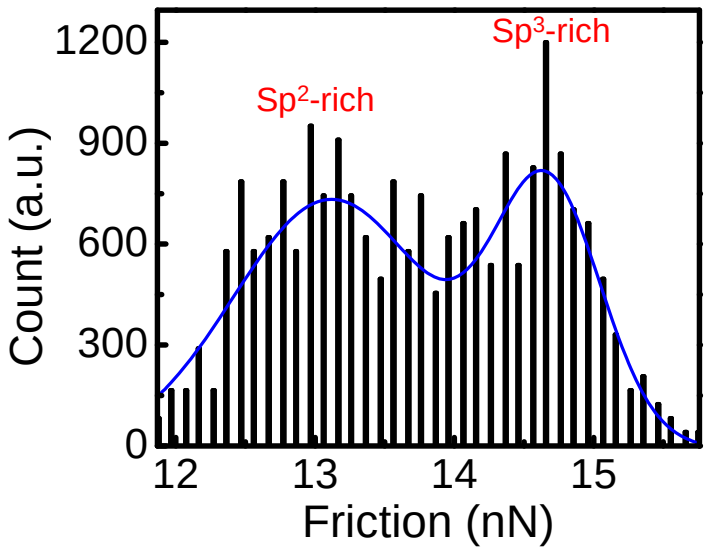

Fig. S8. Histogram of the friction on GO flakes with a Gaussian-fitted blue line.

9. Energy levels of a sample junction

Fig. S9 show the energy levels of a sample junction that includes Pt from the C-AFM tip, single-layer GO, SiO_2, and *n*-Si (100).

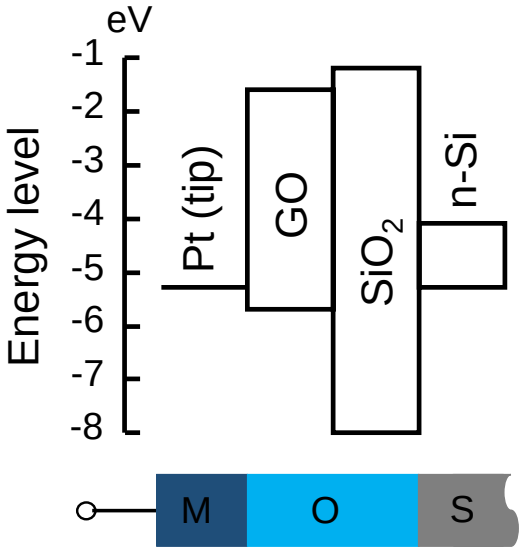

Fig. S9. The energy levels of the elements composing the metal–oxide–semiconductor (MOS) structure.

10. SEM images of AFM tip

Fig. S10 shows scanning electron microscopy (SEM, Magellan400) images of the Pt-coated tip before and after the AFM measurements. The tip size and shape before and after the AFM measurements did not change, within the error of measurement; the curvature radius remained at 50 nm $\pm$ 10.

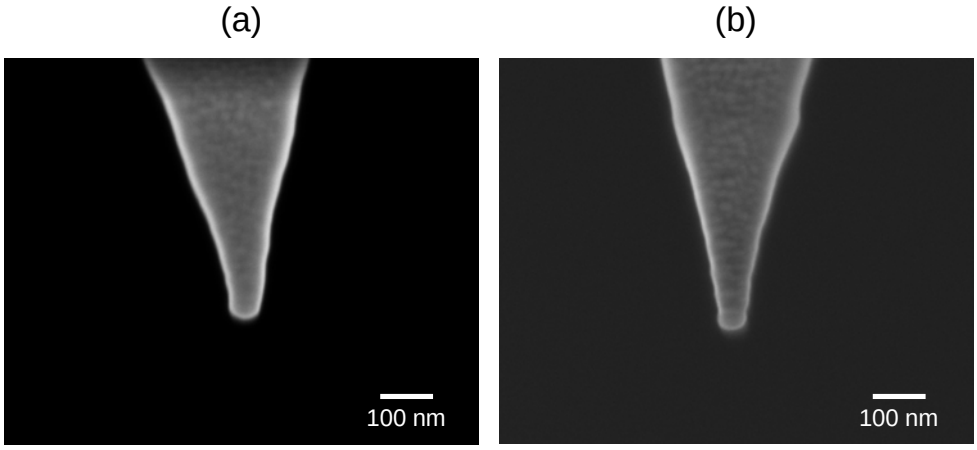

Fig. S10. SEM images of the Pt-coated tip (a) before and (b) after AFM measurements on the GO sheet.

11. Scanning transmission X-ray microscopy (STXM)

Fig. S11 shows STXM images and C K-edge spectra of the GO sheet on lacey carbon at a photon energy of 304.6 eV. The A and B regions show the free-standing GO sheet, and the C region shows the GO sheet on lacey carbon. The π^*/σ^* ratio in the A region is higher (0.66) than in the B (0.41) and C (0.59) regions. The peak of I_3 (288.5 eV) in the C region, which originated from the π^*(C=O) states of COOH, is relatively low. Therefore, the lacey carbon shows a distinct ratio of π^*/σ^*, compared with the A and B regions.

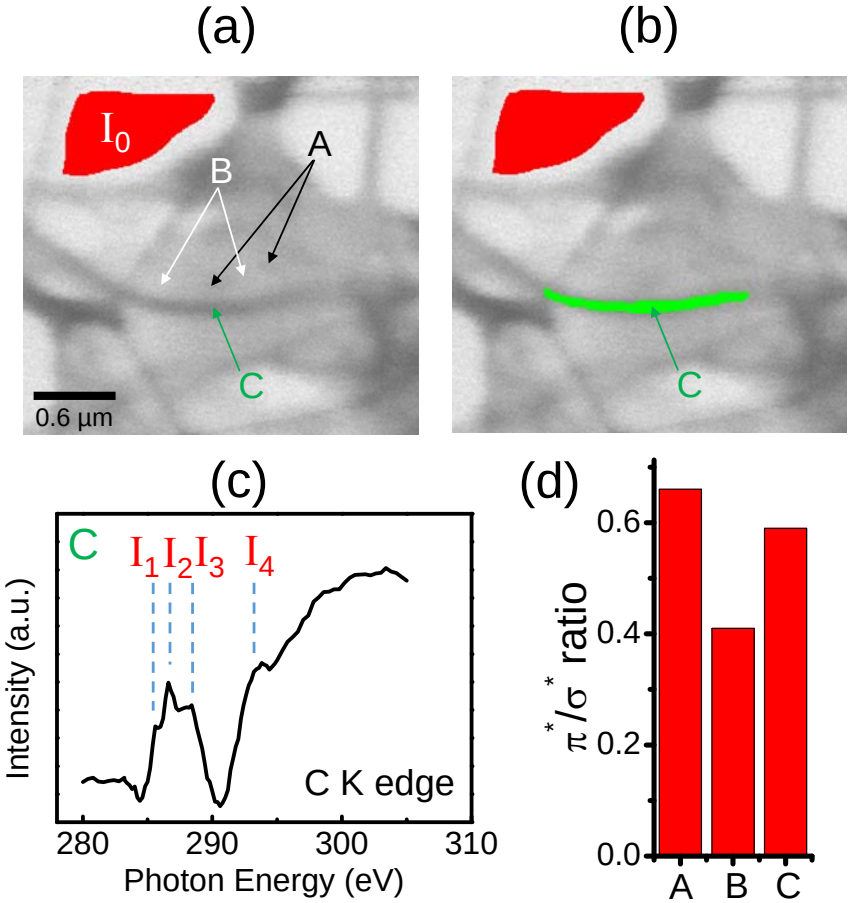

Fig. S11. STXM images (a) before and (b) after marking the C region. The I_0 region is marked by red in an empty area for reference. (c) C K-edge spectra of the C region in (b). I_1 and I_4 are the unoccupied π^* and σ^* states, respectively, and I_2 and I_3 originate from π^*(C-O-C) with the π^*(C-OH) and π^*(C=O) states of COOH, respectively. (d) Bar graph of the π^*/σ^* ratio at different positions. A, B, and C are the bright and dark regions in the free-standing GO sheet, and the lacey-carbon-supported GO sheet, respectively.

References

1. J. I. Paredes, S. Villar-Rodil, A. Martínez-Alonso and J. M. D. Tascón, *Langmuir*, 2008, **24**, 10560-10564.
2. K. J. Kim, H. Lee, J. H. Choi, Y. S. Youn, J. Choi, H. Lee, T. H. Kang, M. C. Jung, H. J. Shin, H. J. Lee, S. Kim and B. Kim, *Adv. Mater*, 2008, **20**, 3589-3591.
3. P. Wang, Y. Zhai, D. Wang and S. Dong, *Nanoscale*, 2011, **3**, 1640-1645.
4. O. C. Compton, B. Jain, D. A. Dikin, A. Abouimrane, K. Amine and S. T. Nguyen, *ACS Nano*, 2011, **5**, 4380-4391.
5. J. Chen, S. Liu, W. Feng, G. Zhang and F. Yang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5664-5669.
6. L.-F. Wang, T.-B. Ma, Y.-Z. Hu and H. Wang, *Phys. Rev. B*, 2012, **86**, 125436.
7. J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei and P. E. Sheehan, *Nano Lett.*, 2008, **8**, 3137-3140.