Supporting information

Nanoscale Chemical Characterization of Functionalized Graphene by Heterodyne AFM-IR and Chemical Force Microscopy

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Experimental methods

Sample preparation

GO on Si: An aqueous suspension of graphene oxide (GO) solution purchased from Fujifilm Wako co. ltd. (product #: ACN0578) was diluted 10 times with MilliQ water. The diluted solution was then spin-coated onto a cleaned Si substrate at 1500 rpm. Finally, the sample was blow dried with N_2 gas.

Amino-functionalized AFM probe: A cleaned Si cantilever (OMCL-AC200TS-R3, Olympus) was placed in a plastic container and 20 μL of 3-aminopropyltriethoxysilane (Wako) was added to initiate the silane coupling reaction. The reaction was carried out for 1.5 h at 25 ^{o}C. Finally, the functionalized probe was washed with excess MilliQ water and dried with N_2 gas.

Measurements/Analysis

Both CFM and AFM-IR measurements were performed with a commercial AFM-IR system (Dimension IconIR, Bruker). All measurements were performed at 25 ^{o}C with humidity below RH1%.

CFM: The Peak-Force Quantitative Nanomechanical Mapping (PFQNM) mode was used for CFM measurements. Tip-view Si cantilevers (OMCL-AC200TS-R3, Olympus) with and without amino functionalization were used. Spring constant and deflection sensitivity were calibrated on a sapphire substrate. Occasionally during the measurements, soft X-ray was applied to neutralize static electricity. The force curve was recorded at each pixel, the adhesion force (=minimum force) in the approach curve was calculated with linear baseline correction, and finally the adhesion map was reconstructed. The details of the measurement conditions are as follows: Set point = 15 nN, Peak force amplitude = 100 nm, Peak force frequency = 1 kHz, Scan rate = 0.2-0.5 Hz, Pixel number = 256 pts.

AFM-IR: The AFM-IR measurements were performed in the tapping AFM-IR mode (=heterodyne AFM-IR mode). All measurements were performed with the same commercial gold-coated cantilever (PR-UM-TnIR-D, Bruker). The output of a quantum cascade laser (QCL) (Daylight, MIRCat) was pulsed at the frequency f_m, where $f_m = f_1 - f_0$. Here, f_0 and f_1 are the frequencies of the first and second resonances of the cantilever. In the measurements, f_1 is used to drive the cantilever and the difference frequency at f_0, generated by frequency mixing, was measured as an IR signal. The laser polarization was set to p-polarized (= parallel to the long axis of the probe). During IR imaging, a phase-locked loop (PLL) circuit was used to compensate for the resonance frequency shift caused by the contact resonance effect. The details of the measurement conditions are as follows: [Point measurement] Pixel resolution = 1 cm^{-1}, Accumulation time = 120 s, Average = 10 times. [IR imaging] Pixel number = 192-256, Scan rate = 0.6-1.5 Hz.

XPS: X-ray photoelectron spectroscopy (XPS) measurements were performed using a commercial micro-XPS system (PHI Quantes, ULVAC) with an Al anode as X-ray source (Al-Kα 1486.6 eV). The sample was prepared by spin-coating a GO solution onto a cleaned Si substrate. Each spectrum is an average of 1-10 scans with a pass energy of 280 eV and a step size of 1 eV for survey spectra and a pass energy of 55 eV and a step size of 0.1 eV for high resolution spectra. An ion gun was used during each scan to neutralize charging phenomena.

Software: ImageJ 1.54d and IgorPro 9.05 were used additionally to the software equipped to the instruments. The image drift of AFM/ IR images was corrected by a homemade program based on Levenberg-Marquardt algorithm. [S1]

DFT calculation: Density functional theory (DFT) calculations were carried out to estimate the IR peaks. We assumed that -CH_3, -OCH_3, -CH_2COOH, and -CH_2COOCH_3 were covalently attached to graphene along with the hydroxy group (-OH) or hydrogen atom (-H). Each structure was fully optimized at B3LYP/6-31G(d) level of theory using Gaussian 16 software (Gaussian, Inc., Pittsburgh, PA). The theoretical IR spectrum was calculated at the B3LYP/6-31G(d) level of theory for each energy-minimized structure by freezing the coordinate of the graphene moiety.[S2] The vibrational frequencies were scaled by 0.96.

Supporting figures

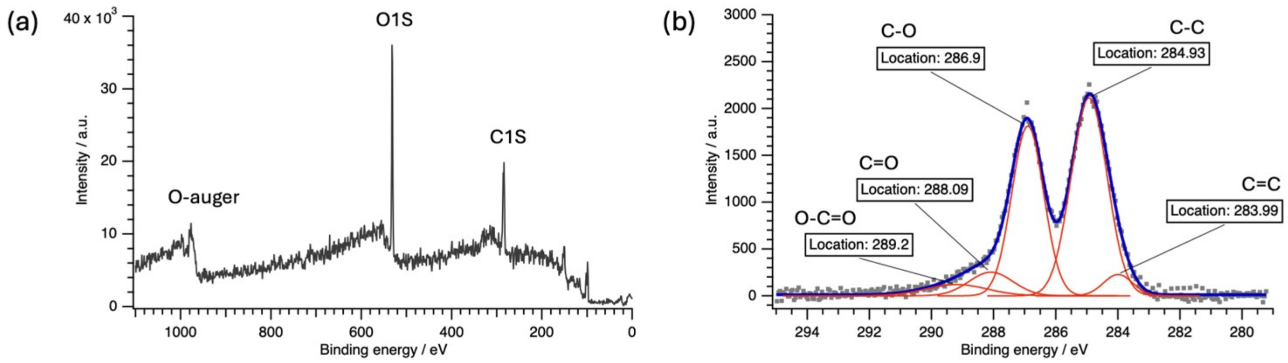

Figure S1. XPS spectrum of GO on Si obtained with survay scan (a) and high resolution scan at C1s peak (b).

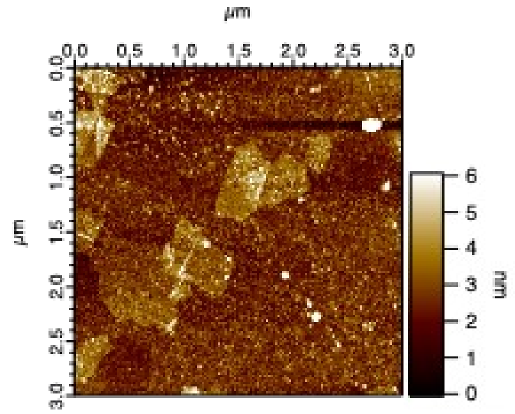

Figure S2. AFM height image of GO on Si corresponding to the area in Figure 2c.

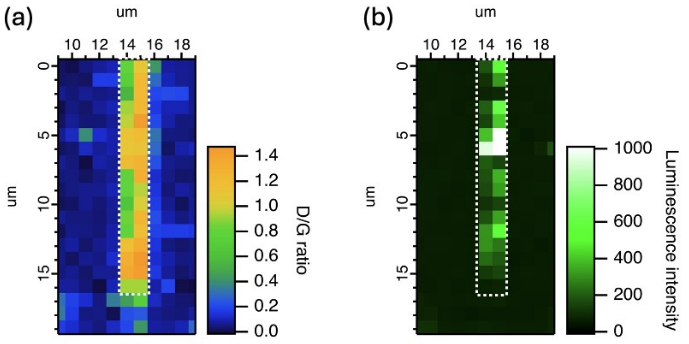

Figure S3. Confocal Raman imaging of D/G ratio (a) and luminescence intensity (b) of the PICM region. The PICM was performed by focusing a 532 nm laser and scanning the beam at a constant speed along a vertical direction in the presence of acetic acid in water. The PICM region is marked as a white dashed line in each image.

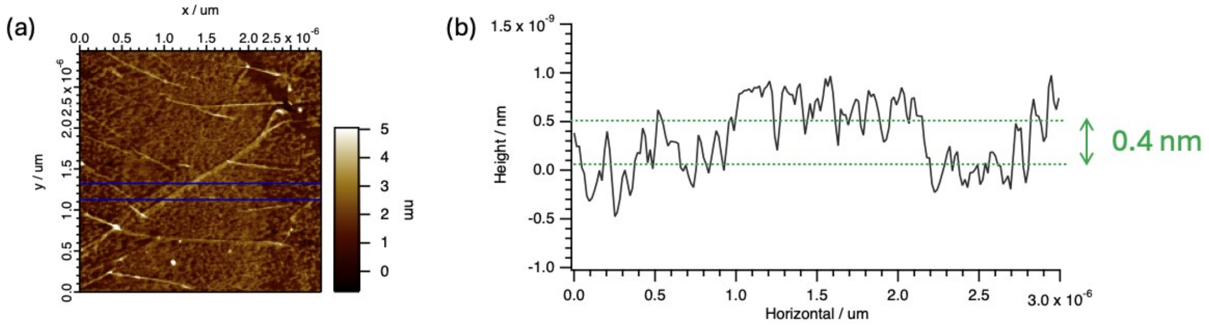

Figure S4. AFM height image of PICM graphene (a) and the corresponding averaged height profile (b) along the region indicated by the blue lines in (a). The height of GO flakes is approximately 1 nm (Figure 1a), which is 0.7 nm higher than that of pristine graphene (0.3 nm). Since the PICM reaction introduces functional groups only on one side of the graphene sheet, the expected height increase is about 0.35 nm. This value is in good agreement with the experimentally observed height increase of approximately 0.4 nm in Figure S4, suggesting that the functionalization at the PICM area is monolayer.

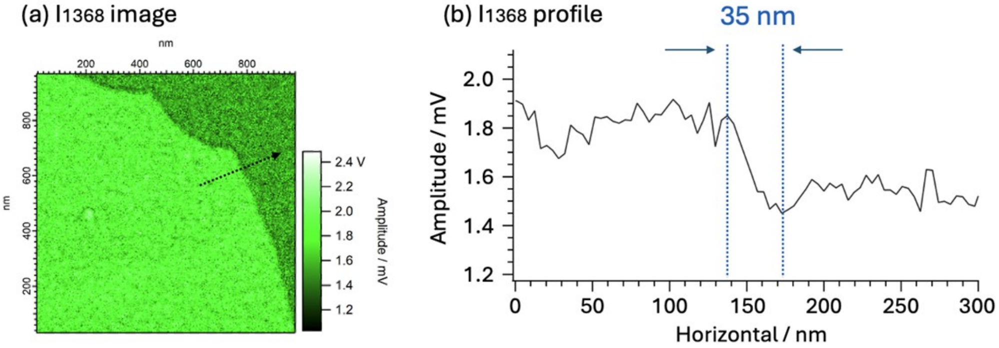

Figure S5. Estimation of the spatial resolution of the used AFM-IR probe. (a) IR image at 1368 cm^{-1} obtained on GO on Si. (b) 1368 cm^{-1} intensity profile at an arrow indicated in (a).

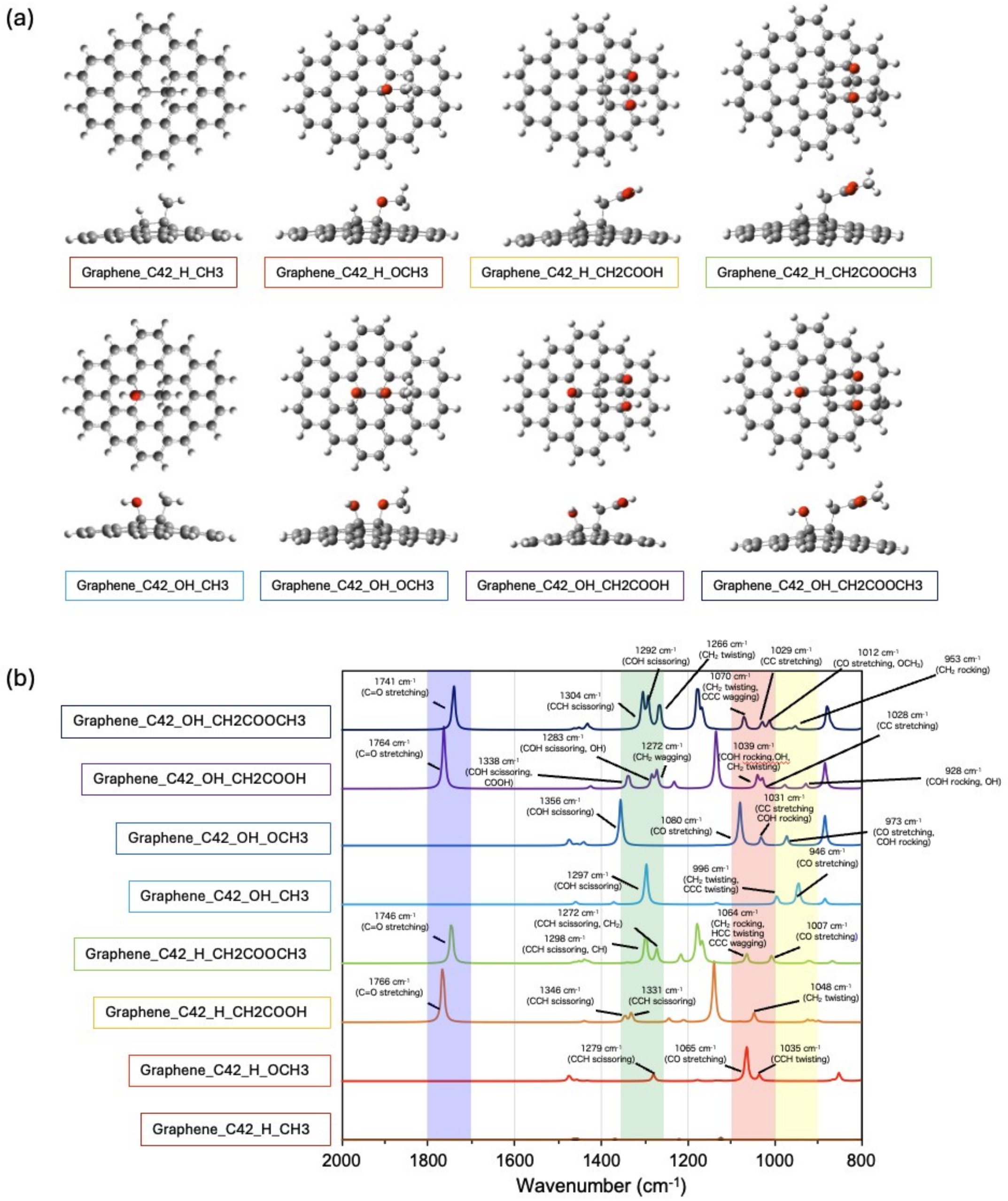

Figure S6. DFT calculation of possible structure under PICM in acetic aqueous solution. (a) Top and side views for the covalent connection of the models; White, gray, and red atoms indicate hydrogen, carbon, and oxygen, respectively. (b) Calculated IR spectra for the eight cases each model (wavenumber scale factor is 0.96).

References

[S1] P. Thevenaz, U. Ruttimann, M. Unser, IEEE TRANSACTIONS ON IMAGE PROCESSING 1998, **7**, 27-41.

[S2] T. You, N. Yang, Y. Shu, P. Yin, JOURNAL OF RAMAN SPECTROSCOPY 2019, **50**, 1510-1518.