

Supporting information for

Light-mediated Covalently Patterned Graphene Substrate for Graphene-Enhanced Raman Scattering (GERS)

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EXPERIMENTAL METHODS

Sample preparation

The monolayer graphene protected by poly (methyl methacrylate) (PMMA) was purchased from Graphenea and subsequently transferred onto a coverslip. The protective PMMA layer was removed by acetone and 2-propanol. The quality of the single-layer graphene was monitored after transferring by estimating the I_{2D}/I_G ratio from the Raman spectra. Before transferring graphene, the coverslip was ultrasonically washed with acetone, NaOH solution (1 M), and Milli-Q water, respectively. The light-triggered covalent patterning on the graphene layer was selectively achieved by the nanolithography technique. The PCIM was carried out in pure water and acetic acid solution separately in order to attach different functional groups on the graphene surface. A diamond cutter was employed to mark the functionalized region for differentiating the patterned and pristine region.

Chemicals

Milli-Q water obtained from a Milli-Q-plus system with a resistivity greater than $18 \text{ M}\Omega\cdot\text{cm}^{-1}$. Acetic acid and stearic acid were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Rhodamine 6G (Rh6G) was purchased from FUJIFILM Wako Pure Chemical Corporation (Japan). DiO dye was purchased from Sigma-Aldrich. All the reagents were used without any further purification.

Langmuir-Blodgett (LB) method

Langmuir-Blodgett (LB) method was carried out to make a homogenous monolayer or multilayer of DiO dye molecules on the graphene substrate. Surface tension was recorded to check the state of the stearic acid and dye molecules on the interface between air and liquid. To systematically investigate the GERS on the modified graphene, we form a combination of stearic

acid and DiO dye layers on the graphene surface. DiO dye molecules were dissolved in 0.1 mg/mL (3.51×10^{-4} M) stearic acid (chloroform as solvent). The molar ratio between stearic acid and dye was kept $\sim 10:1$. Then, a 100 μ l mixture of stearic acid and dye molecules was distributed on the water surface with a micro-syringe. Standing for 30 min to let the dye molecules homogeneously distributed. The target surface tension is set up at 30 mN/mm. The PICM-G was followed to pick up the dye molecules. Since SA layers were carefully picked up at the solid phase, we expect that rearrangement of LB film after deposition was minimized and thus the dye molecules could be homogeneously distributed both on the PG and the PICM-G region.

Raman spectroscopy

Raman spectroscopic measurements were carried out using an inverted optical microscope (Ti-U, Nikon) equipped with a piezoelectric sample stage. A continuous-wave 488 nm (Sapphire SF 488-100 CW CDRH) laser was used for the photoinduced covalent functionalization (PICM) on the graphene layer. The PICM was achieved with an input power of ~ 6 MW/cm², while the Raman measurements were carried out by reducing the power to ~ 0.78 MW/cm² with the same laser. Alongside two other lasers (532, and 633 nm) were also employed for the Raman measurements. The input power density during the Raman measurements was controlled by the combination of neutral density filters. The laser beam was focused using a 60 X objective lens (Nikon), and the Raman scattering signals was collected using the same objectives in a backscattering geometry. The collected Raman signals were guided to a liquid nitrogen-cooled CCD spectrograph (iHR320, Horiba) having a grating of 600 grooves/mm. A corresponding long-pass filter (Chroma) was placed just before the spectrograph for blocking the Rayleigh scattering during the Raman measurements. The PICM and Raman mapping were conducted by OMEGA software

(Comscope, AIST-NT/ Horiba). Origin Lab 9.1 and MATLAB (MathWorks) were used for the Raman data analysis.

Atomic force microscopy (AFM) measurement

AFM was carried out with an OmegaScope™ (AIST-NT, HORIBA) system in tapping mode at ambient conditions. Al reflecting coating (160 AC-NA) AFM cantilever was used to obtain images resolved by 512×512 or 1024×1024 pixels. Omega software (AIST-NT/HORIBA) and Gwyddion software were utilized for AFM data analysis.

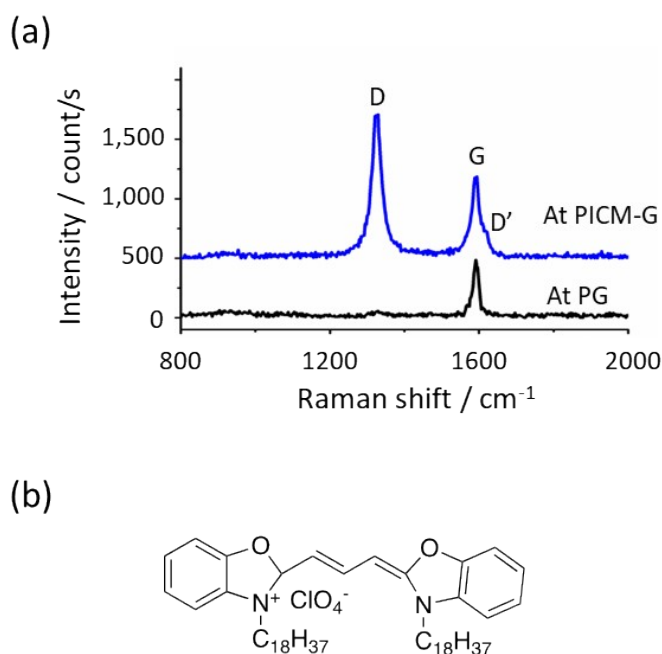


Fig. S1. (a) Raman spectra of graphene heterojunction consisting of pristine (black) and chemically patterned region (blue), measured by 633 nm (to reduce the effect of laser on patterned functionalization, low excitation energy (633nm) was used for Raman scattering). The patterned region manifests a pronounced defect-induced D band at 1326 cm⁻¹ together with the characteristic

G band of graphene at 1594 cm^{-1} , while the areas with no laser exposure resemble the pristine features, exhibiting an I_D/I_G ratio of <0.2 ; (b) Chemical structure of DiO molecule.

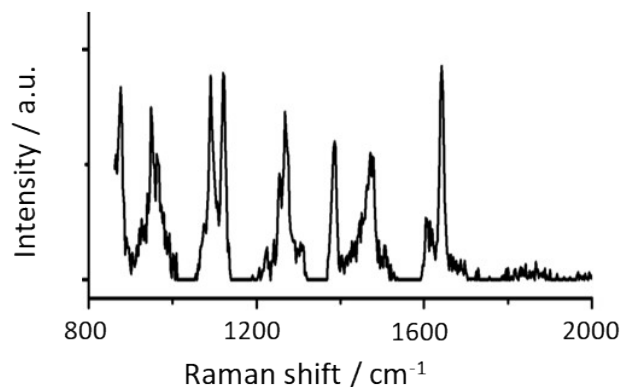


Fig. S2. Raman spectra of pure DiO powder excited by 633 nm.

Langmuir-Blodget film for GERS measurements

As depicted in Fig. S4, a mixture of stearic acid (SA) and DiO was distributed on the water surface. SA, an amphoteric molecule, was used to trap and distribute the dye molecules. After compressing the layer to the saturated pressure, the layers were picked up on a graphene surface. Fig. S5 shows the Raman spectra of one to three LB layers on the PICM-G. While no obvious Raman signal of DiO was detected from a single LB layer, clear peaks of DiO have been observed from double and triple layers of LB films. It is worth mentioning here that only D and G bands of graphene were detected (see Fig. S7) in the case of LB layers composed of pure SA without any dyes. The lack of Raman signals from the first layer is presumably due to the ultralow concentration of the adsorbed DiO molecule. To confirm our prediction, we further prepared a single LB layer on the PICM-G region with a high concentration of DiO ($[DiO] / [SA] > 0.1$). In this case, Raman signals

were observed from the single layer (Fig. S8), indicating that the GERS intensity is influenced by the density of dye molecules present on surface. However, a high concentration of DiO in the LB layers causes spatial heterogeneity of GERS intensity. This heterogeneity is most likely due to the rearrangement of LB layers after the deposition according to our AFM study (Fig. S6). Thus, in the following experiments, triple LB layers with the molar ratio of $[SA] / [DiO] > 10$ were used to obtain homogeneously distributed DiO molecules on surface.

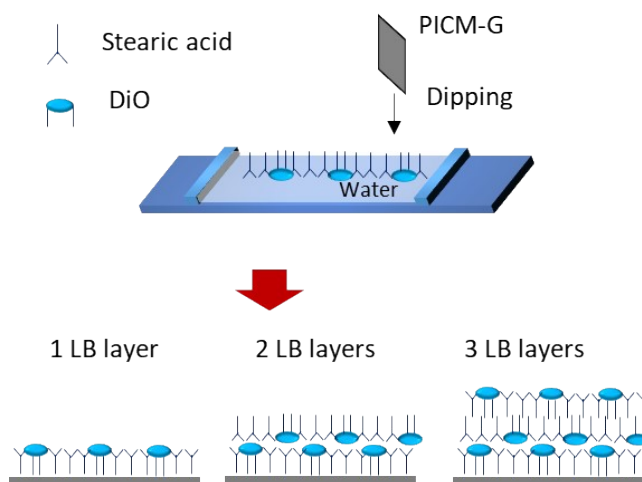


Fig. S3. Schematic drawing of LB of DiO dye molecules on the PICM-G substrate.

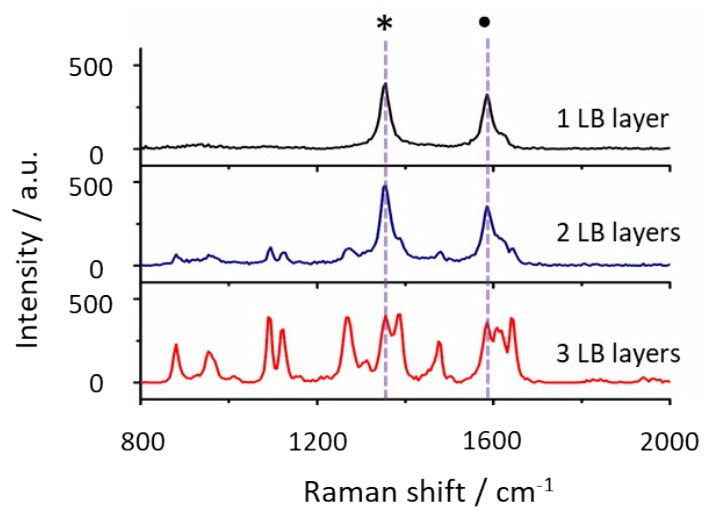


Fig. S4. Raman spectra of DiO molecule with different layer numbers of the LB film on the PICM graphene substrate. Raman signals of DiO molecules are detected over double LB layers. The peaks marked with ‘*’ and ‘•’ correspond to the D and G bands of the graphene, respectively.

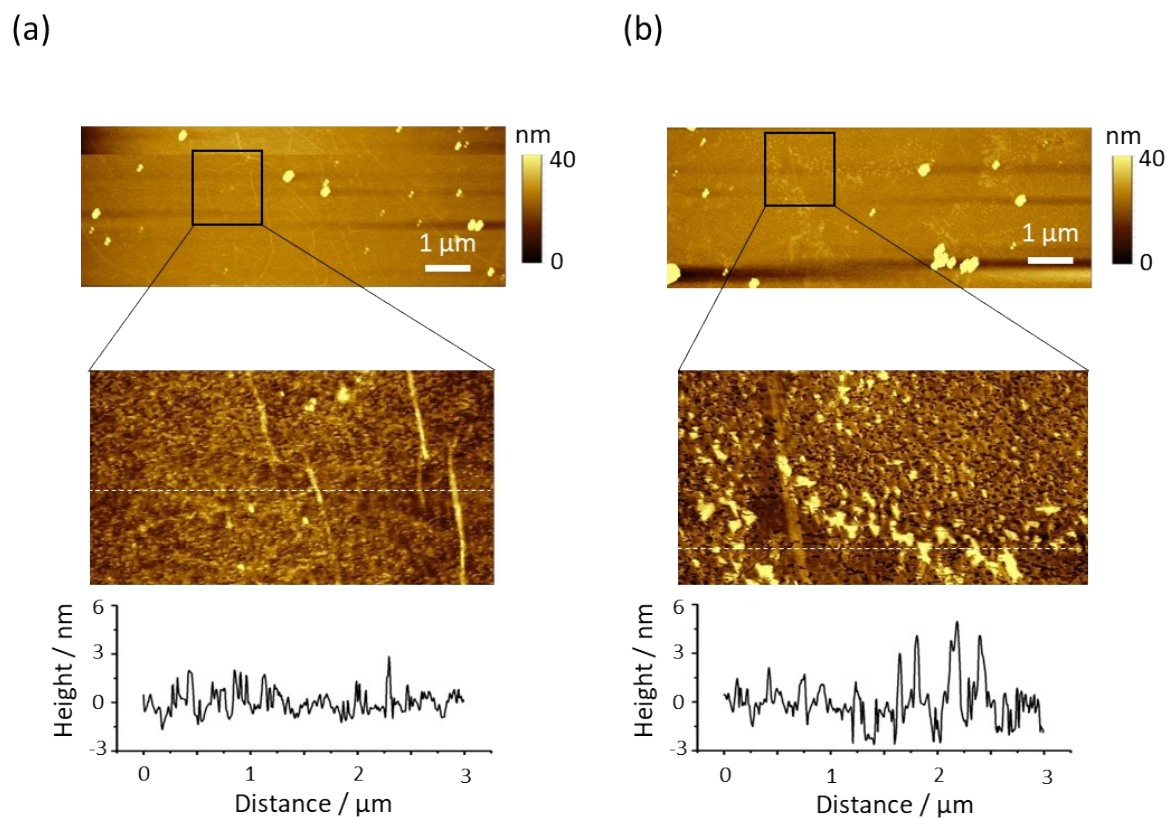


Fig. S5. AFM measurement on single LB layer at the molar ratio of [SA] / [DiO] $\sim 10:1$ (a) and $\sim 10:3$ (b), respectively. The corresponding height profiles are presented at the bottom.

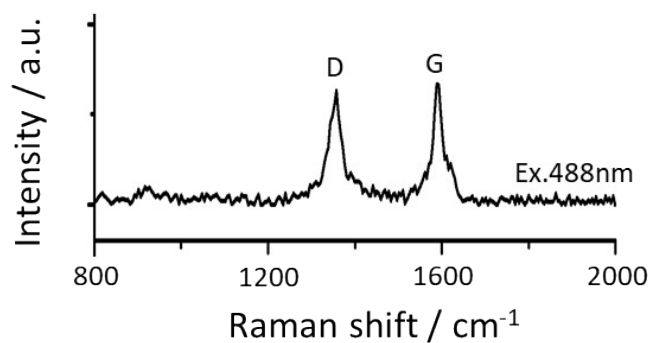


Fig. S6. Raman response of pure SA on the PICM region.

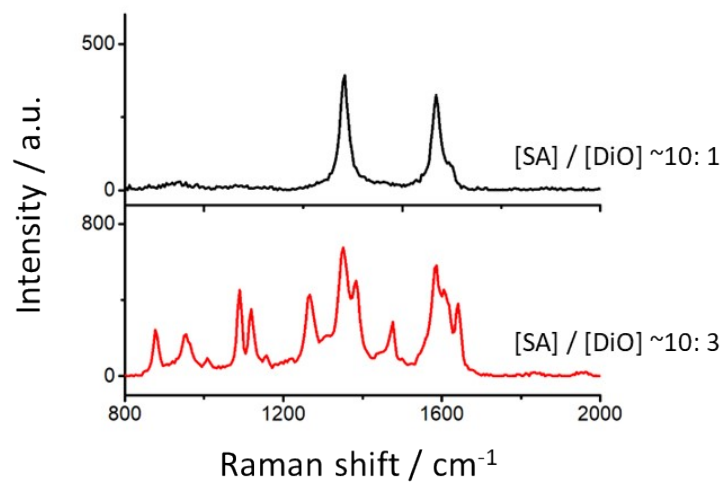


Fig. S7. Raman spectra of monolayer LB layer of DiO with low (black, [SA] / [dye]~10: 1) and high concentration (red, [SA] / [dye]~10: 3).

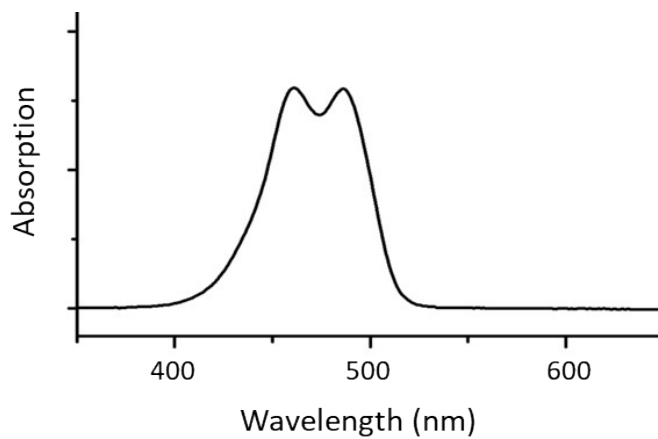


Fig. S8. UV-visible absorption of DiO dye

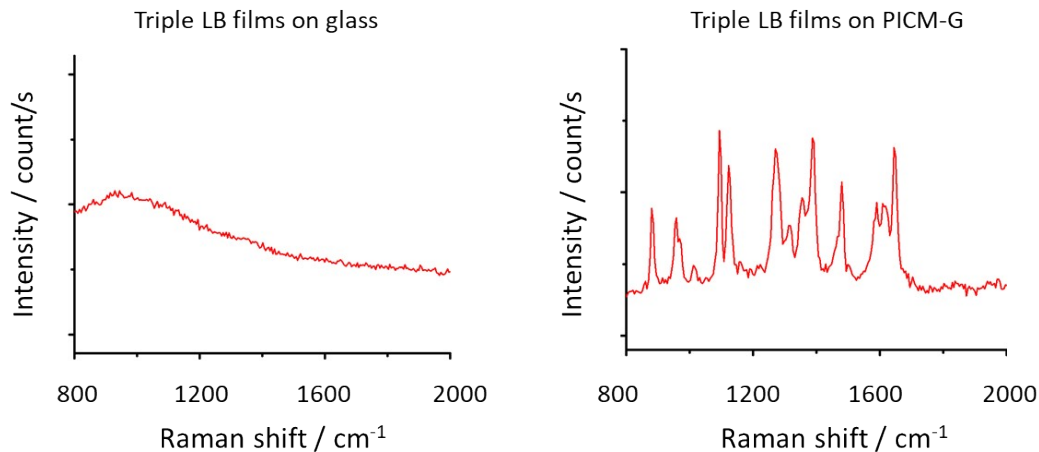


Fig. S9. Raman spectra of triple LB films of DiO on glass substrate and PICM-G substrate, respectively. Measured by 488 nm.

The background correction of Raman spectra

Top panel in Fig. S10 displays raw Raman spectra of Rhodamine 6G on the PG and the PICM-G area, respectively. Although the fluorescence was suppressed by graphene, the emission appears in the Raman spectra as a background. To identify Raman peaks better, the fluorescence background was subtracted from the spectra by a simple polynomial fitting (the bottom panel in Fig. S10).

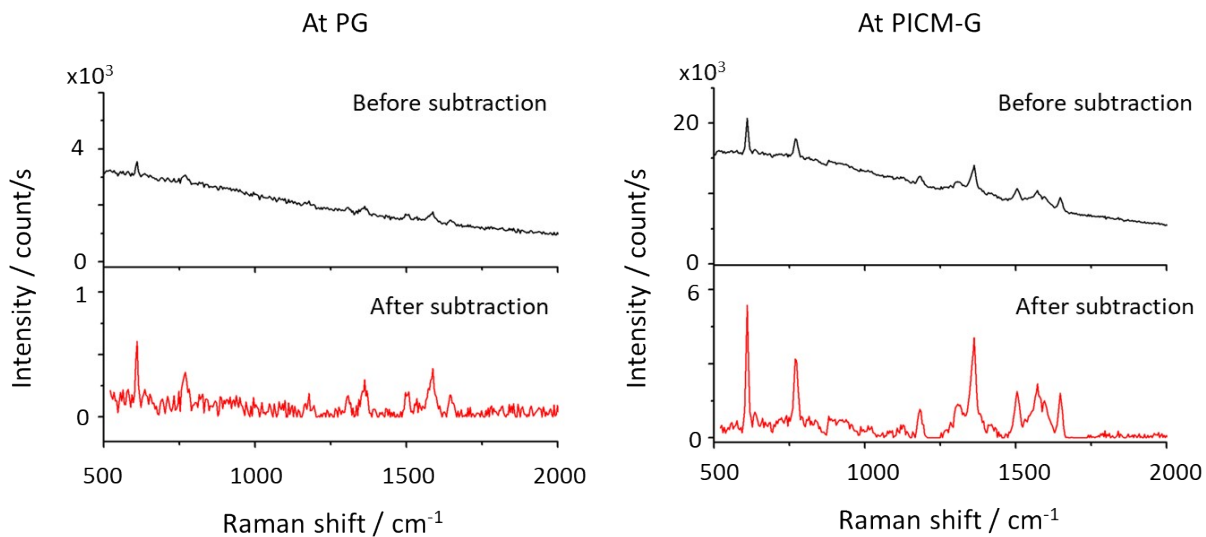


Fig. S10. GERS performance for Rh6G adsorbed on the PG and PICM-G region before (black) and after subtraction (red), respectively.

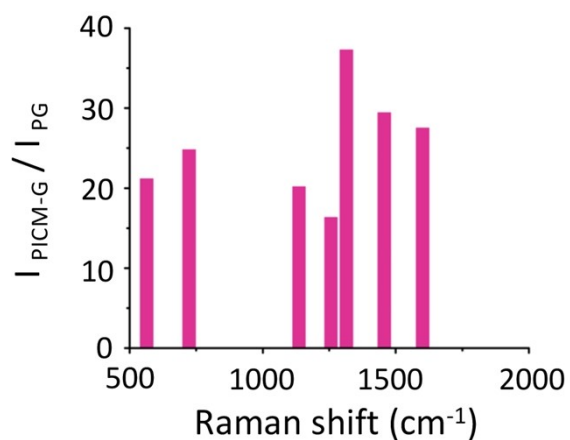


Fig. S11. Peak intensity ratio between the $I_{\text{PICM-G}}/I_{\text{PG}}$ of the Raman map shown in Figure 3b across the spectral region.

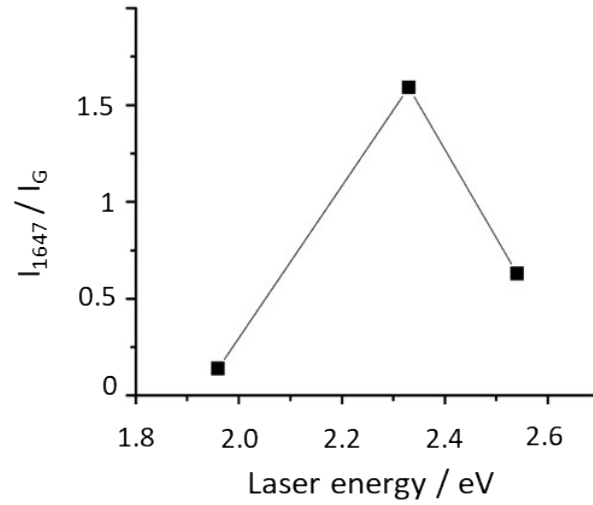


Fig. S12. The enhancement factor (normalized by G band) as function of laser excitation energy: 488 nm (2.54 eV), 532 nm (2.33 eV), 633 nm (1.96 eV).

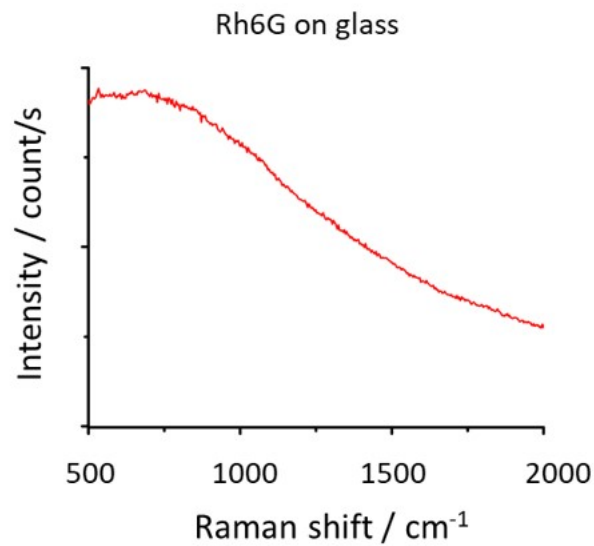


Fig. S13. Raman spectra of Rh6G distributed on glass substrate measured using 532nm.

Table S1. Average values of Pos(G), Pos(2D) and the corresponding shifts

Type of graphene	Pos (G) /cm ⁻¹	Shift of pos (G) /cm ⁻¹	Pos (2D)	Shift of pos (2D) /cm ⁻¹
Pristine	1588.0±2.3		2639.6±3.53	
		-3.8		0.3
PICM in acetic acid	1584.2±2.2		2639.9±3.18	

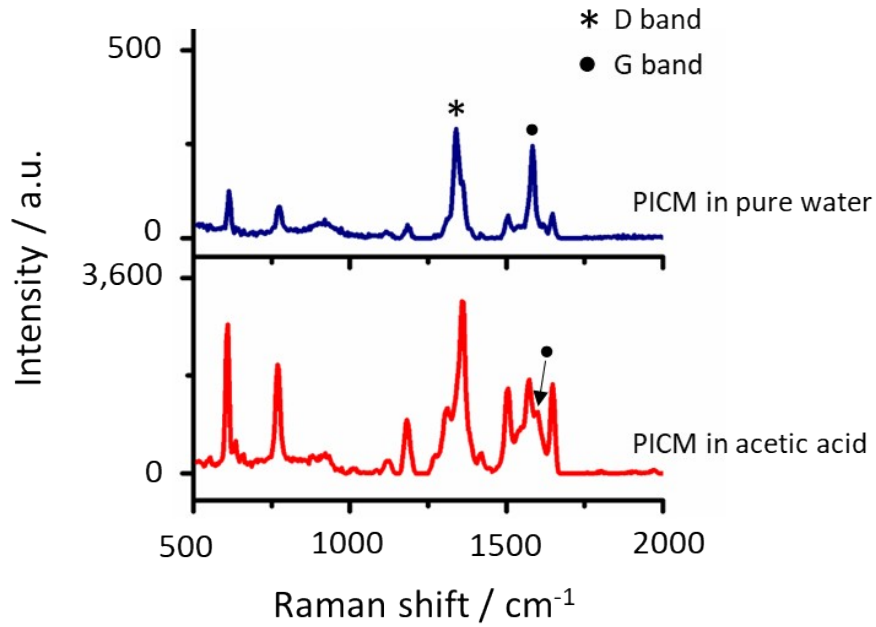


Fig. S14. Comparison of GERS performance of R6G on graphene layers modified with PICM in pure water (top) and acetic acid (bottom), respectively. (Excitation at 532 nm with 0.98 MW/cm²).