Supporting information for

Liquid-Phase Photo-induced Covalent Modification (PICM) of Single-Layer Graphene by Short-Chain Fatty Acids

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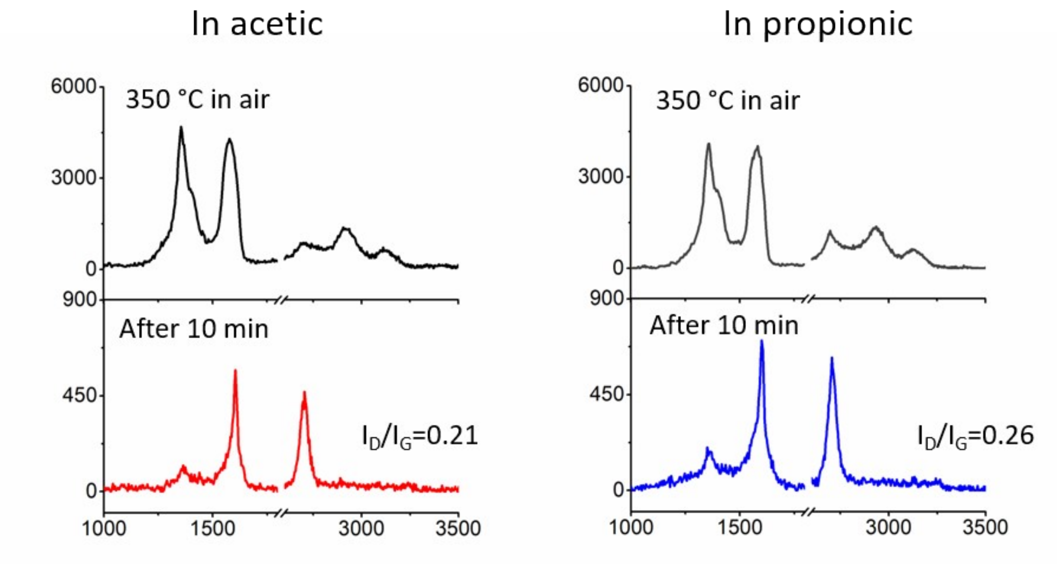

Fig. S1 Thermal treatment of graphene after PICM in acetic and propionic acids solutions, respectively.

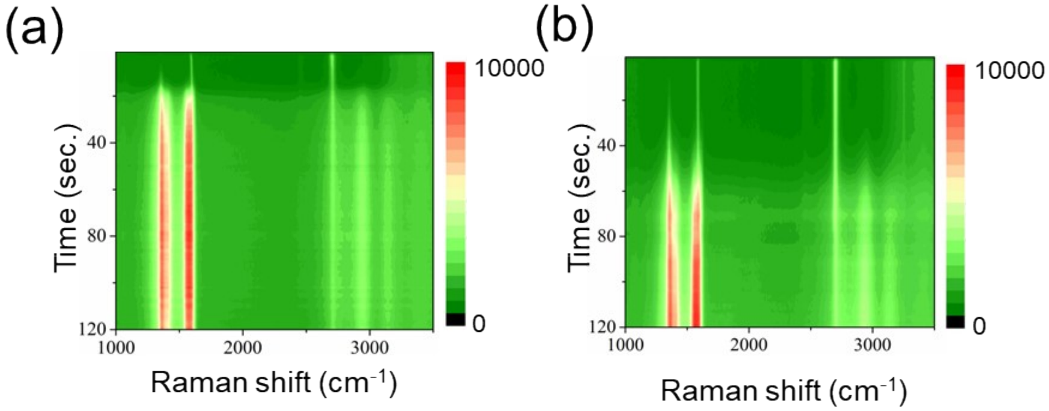

Fig. S2. A typical in-situ Raman spectroscopy during the PICMs of graphene monolayers in aqueous solution (0.1 M) of propionic acid (a) and butyric acid (b), respectively.

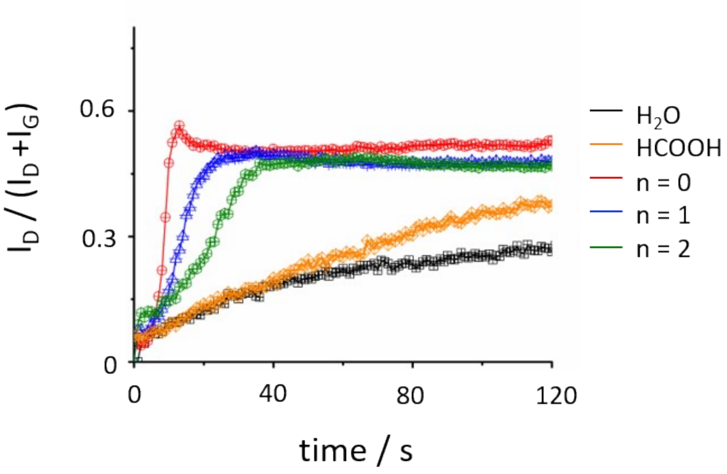

Fig. S3 The intensity ratio between D and (D+G) bands ($I_D/(I_D+I_G)$) as a function of time

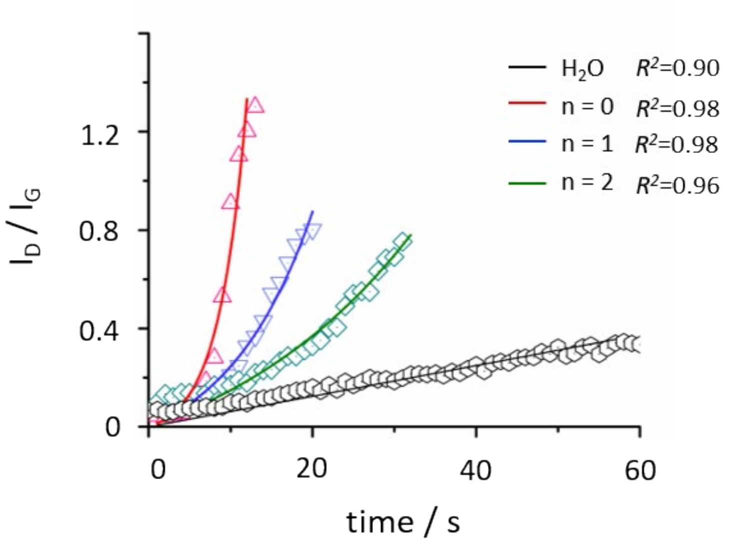

Fig.S4 Fitting of ID/IG at the initial stage with formula 1 (formic is similar with water), R^2: residual square

Modification at wide area

PICM at a wide area was conducted using graphene monolayers supported on SiO_2/Si substrate in 1 M of acetic acid aqueous solution with ~ 6 MW/cm^2 by repeating photolithographic mode at 20 × 20 µm as shown in Fig. S4. In detail, 20×20 points of 1µm square area of graphene were modified by automatic movements of the sample stage. Each point of graphene was irradiated with 488 nm laser for 10 s for obtaining over 1 of I_D/I_G value as shown in the I_D/I_G map in Fig. S4a. Some darker spots in the optical image are visible, which probably correspond to multilayer graphene as reported by the company (marked with yellow circles in Fig. S4b). Raman information (I_{2D}/I_G=0.6) confirms the black spots are multilayer of graphene. As shown in Figure below, the D/G ratio at the darker spot (spot 2) is slightly lower than that at the bright spot (spot 1), indicating that the PICM efficiently at the multilayer is lower resulting in low covalent modifications. This is one of reason of the weaker luminescence in the missing point. In addition to this, luminescence is expected to be significantly quenched on the multi-layers part of the graphene.

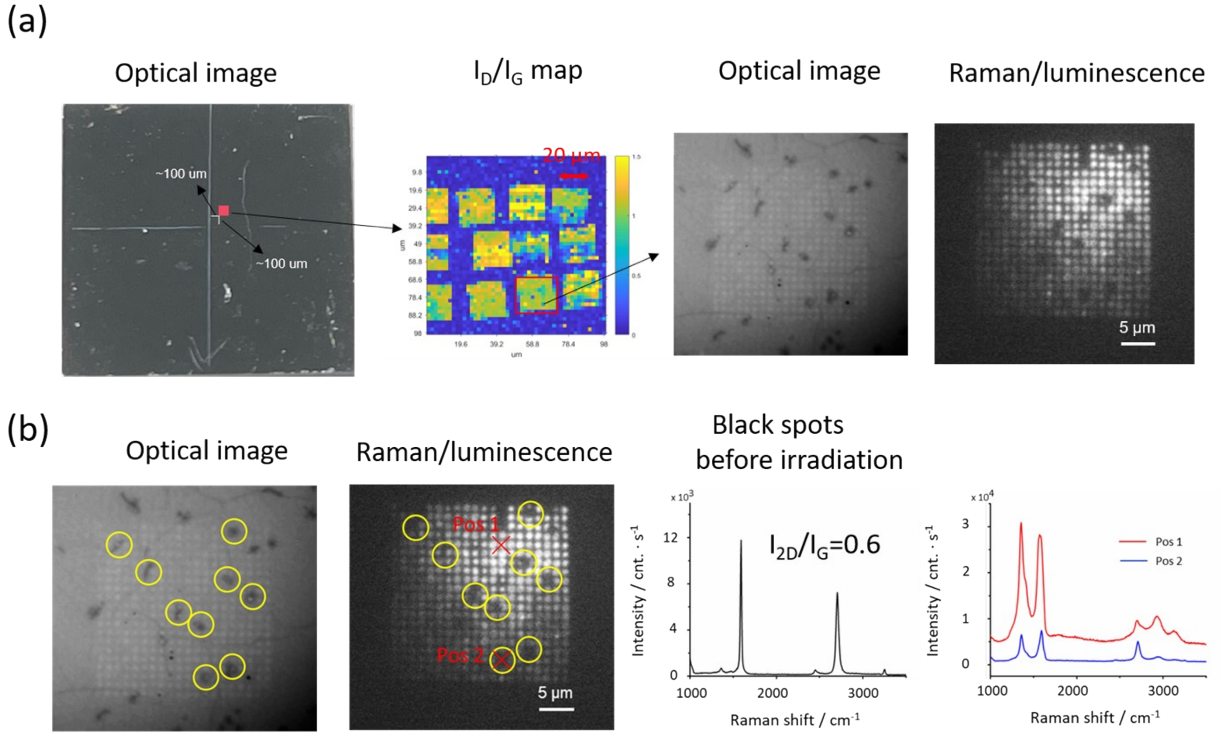

Fig. S5 (a) Optical and Raman maps of a graphene monolayers modified in an aqueous solution of acetic acid; (b) black spots in optical and Raman/luminescence images and corresponded Raman spectra.

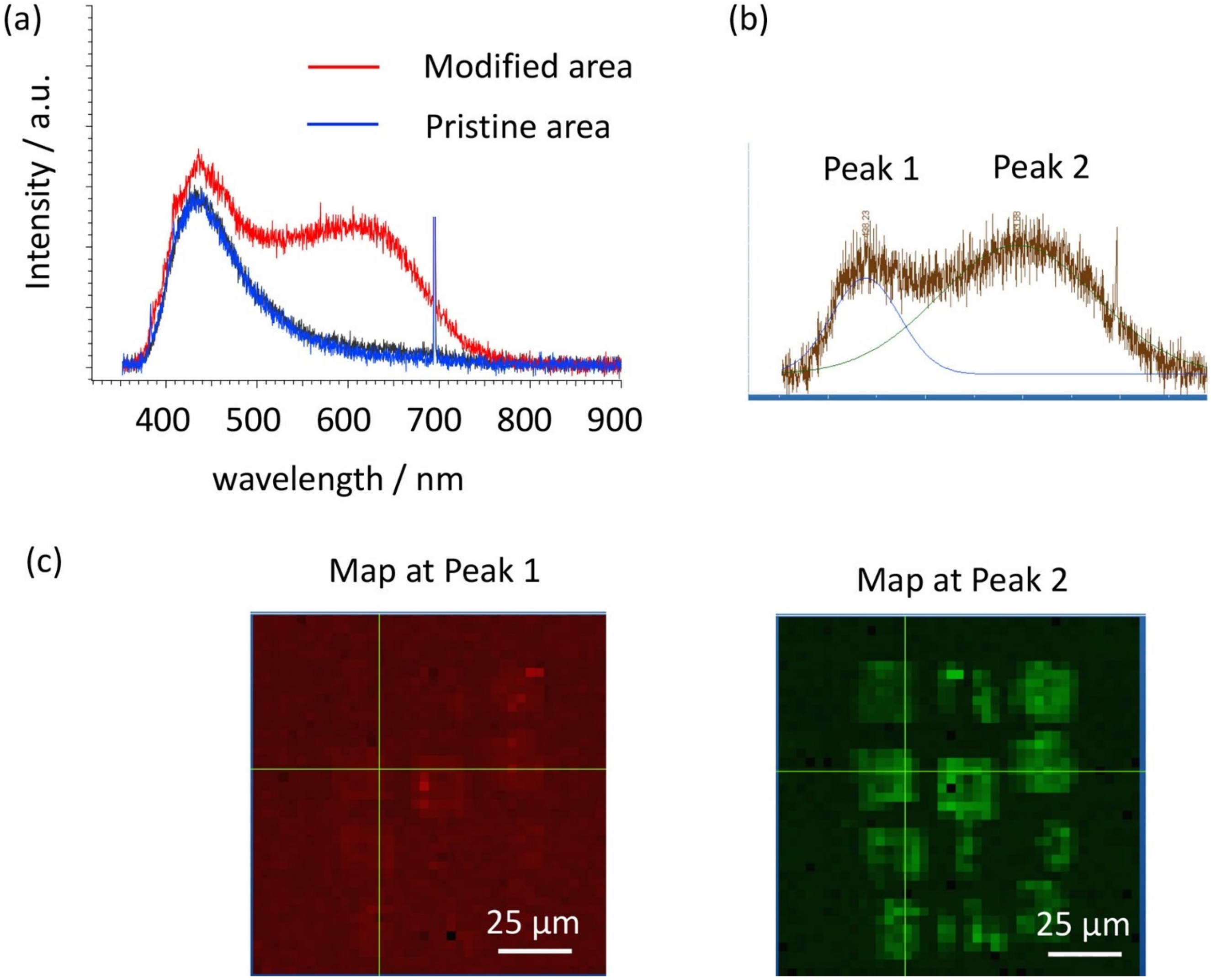

Fig. S6 Luminescence analysis on the PICM graphene in acetic acid aqueous solution. (a) Averaged luminescence spectra at the modified area (red) and unmodified (pristine) area (blue) of the graphene monolayers. (b) Peak fitting analysis on a luminescence spectrum. The 'peak 1' centered at ~ 435 nm is originated from substrate, while the 'peak 2' at 620 nm is assigned to the luminescence from the functioned graphene. (c) Luminescence intensity map at the 'peak 1' (left) and at the 'peak 2' (right).

Table S1 Summary of wavelength dependence at functioned area of graphene

Wavelength (nm)	Energy (eV)	D	G^-	G
488	2.54	1353.9	1564.9	1596.1
532	2.33	1343.9	1566.1	1594.9
633	1.95	1326.5	1566.8	1593.4

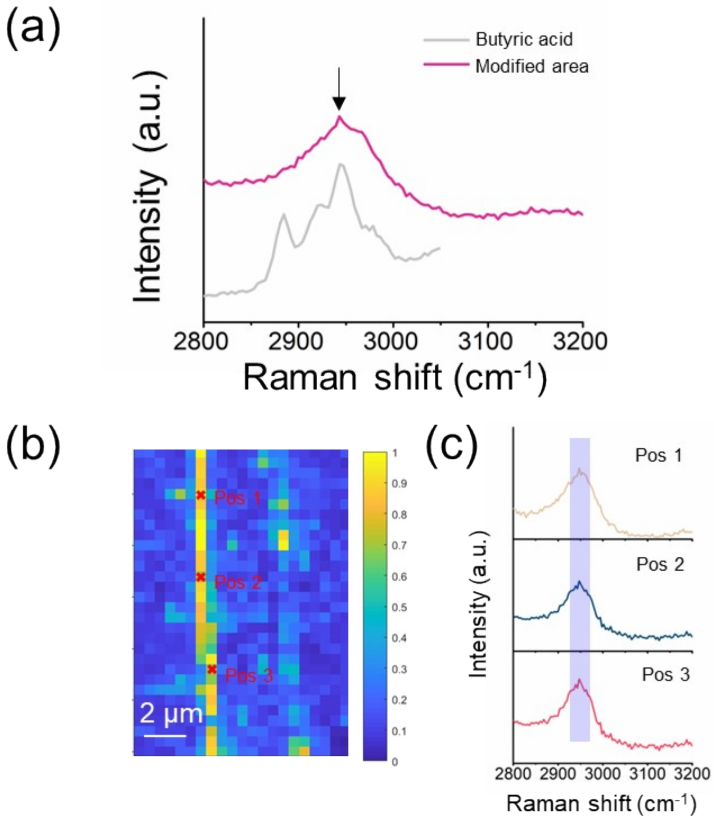

Fig. S7 (a) Signature of C-H stretching after PICM of graphene in butyric acid; gray line is Raman spectra from the butyric acid solution (highest peak: 2943 cm^{-1}); (b) Photo-pattern two lines in butyric acid; and (c) Corresponded Raman spectra on selected points.

DFT calculations

DFT calculations on alkyl groups covalently attached on graphene were conducted. We assumed that -CH_3, -OCH_3, -CH_2COOH and -CH_2COOCH_3 were covalently attached on graphene along with hydroxy group (-OH) or hydrogen atom (-H), respectively. For this simulation, the graphene part was frozen and the vibrational modes of -H/-CH_3, -H/-OCH_3, -H/-CH_2COOH, -H/-CH_2COOCH_3, -OH/-CH_3, -OH/-OCH_3, -OH/-CH_2COOH and -OH/-CH_2COOCH_3 were calculated (Figure S6a). The symmetrical CH stretching can be found at around 2950 cm^{-1} (Figure S6b and Table S2). All the vibrational modes are displayed in Figure S6. This simulation further supports the assignment of the observed Raman peak at 2943 cm^{-1} to the alkyl groups from the SCFA.

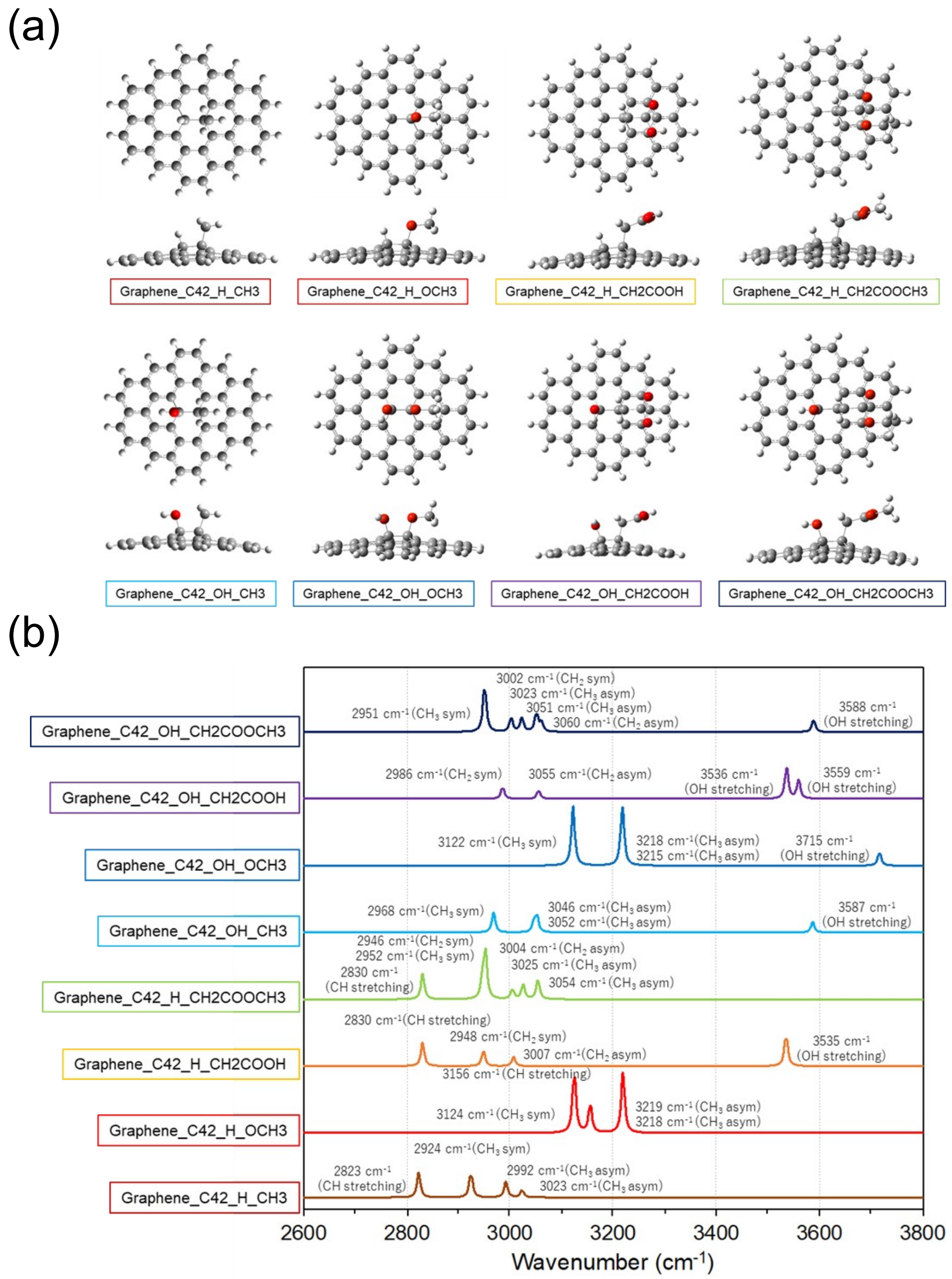

Fig. S8 DFT calculation in the case of PICM in acetic aqueous solution. (a) Top and side views for the covalent connection of the models; White, gray, and red atoms indicate hydrogen, carbon, and oxygen, respectively. (b) Raman spectra for the eight cases each model (wavenumber scale factor is 0.96).

Table S2 Raman peaks related to carboxylic acid estimated with DFT calculation

Possibilities	Peak position (cm^{-1})	Assignment
Graphene / -H /-CH_3	2823	CH stretching
	2924	CH_3 symmetrical stretching
	2992 / 3023	CH_3 asymmetrical stretching
Graphene / -H /-OCH_3	3124	CH_3 symmetrical stretching
	3156	CH stretching
	3219 / 3023	CH_3 asymmetrical stretching
Graphene /-H / -CH_2COOH	2830	CH stretching
	2948	CH_2 symmetrical stretching
	3007	CH_2 asymmetrical stretching
	3535	OH stretching
Graphene /-H / -CH_2COOCH_3	2830	CH stretching
	2946 / 2952	CH_2 / CH_3 symmetrical stretching
	3004 / 3025 / 3054	CH_2 / CH_3 asymmetrical stretching
Graphene / -OH / -CH_3	2968	CH_3 symmetrical stretching
	3046 / 3052	CH_3 asymmetrical stretching
	3587	OH stretching
Graphene / -OH / -OCH_3	3122	CH_3 symmetrical stretching
	3215 / 3218	CH_3 asymmetrical stretching
	3587	OH stretching
Graphene /-OH / -CH_2COOH	2986	CH_2 symmetrical stretching
	3055	CH_2 asymmetrical stretching
	3536 / 3559	OH stretching
Graphene /-OH / -CH_2COOCH3	2951 / 3002	CH_3 / CH_2 symmetrical stretching
	3023 / 3051 / 3060	CH_3 / CH_2 asymmetrical stretching
	3588	OH stretching