Supporting Information

Laser-Triggered Bottom-Up Transcription of Chemical Information:
Toward Patterned Graphene/MoS₂ Heterostructures

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I. Materials and fabrication procedures

Materials

Monolayer graphene (10 mm×10 mm) covered by poly (methyl methacrylate) (PMMA) was purchased from ACS material. Monolayer CVD-MoS2 (10 mm×10 mm) on silicon wafer (Si/SiO2, 300 nm SiO2) was purchased from 6Carbon Technology. 4-bromobenzenediazonium tetrafluoroborate (96 %), 4-methoxybenzenediazonium tetrafluoroborate (98 %), 4-nitrobenzenediazonium tetrafluoroborate (97 %), bromobenzene (≧99.5 %, GC), 4-bromobenzylphosphonic acid (97 %), anhydrous methanol, ethanol, isopropanol (IPA), and tetrahydrofuran (THF) were purchased from Sigma Aldrich and used as received.

Preparation of patterned MoS2 surface

The patterned MoS2 was prepared according to the protocol we have developed previously.1 Briefly, CVD-MoS2 was firstly covered by a single PMMA layer. Then it was accelerated to 3500 rpm for 45 s by a Convac ST 145 spin-coater, and heated at 180 °C for 90 s. The hardened resist (thickness 200 nm) was patterned in a subsequent e-beam lithography (EBL) step, using a SUPRA Zeiss SEM (10 keV). Irradiated areas of the resist were removed by immersion in isopropanol/ isobutyl methyl ketone solution. As a result, the open-lying areas of CVD-MoS2 can be locally functionalized. In an argon filled glovebox (<0.1 ppm O2 and H2O), the CVD-MoS2 with above prepared guiding pattern was firstly treated with Na/K (molar ratio 1:3) alloy for 2 h. After the alloy layer was removed, the film was immediately soaked in 4-bromobenzenediazonium tetrafluoroborate/ anhydrous methanol (0.1 mmol/mL, 3 mL) solution in darkness for 0.5 h. The resulting film was thoroughly washed with methanol and de-ionized water to remove all the physisorbed residues. Finally, the PMMA mask was removed by soaking the sample in an acetone bath for three times (30 min for each). The sample was then dried under ambient conditions.

Assembly of patterned G/MoS2 heterostructures

The patterned G/MoS2 heterostructures were fabricated by placing the single layer graphene directly on the top of the patterned MoS2 surface followed by the laser irradiation. Specifically, the single layer graphene with PMMA mask was placed on the top of the patterned MoS2 surface followed by drying in the fumehood at room temperature overnight. Subsequently the sample was heated at 130 °C for 0.5 h. The vertical stack was then subjected to the laser irradiation, resulting in the formation of
patterned G/MoS$_2$ heterostructures. In the end, the PMMA mask was removed by soaking the sample in an acetone bath for three times (30 min for each). The sample was then dried under ambient conditions.

II. Characterization and instrumentation

Raman spectroscopy
Raman spectroscopic measurements were performed on a confocal Raman microscope (WITec, alpha 300RA) with a 532 nm excitation laser, which was focused with a 100× objective (NA = 0.90, 0.26 mm working distance). The Raman emission was dispersed by 600 grooves/mm. The spectrometer was calibrated in frequency using a standard silicon wafer. For the single irradiation process, the laser energy of 7 mW with the integration time 10 s was applied. The Raman maps with the better contrast were obtained by employing a writing-reading cycle. For the laser writing process, the covalent domains were irradiated with a green laser at 17 mW for 1s. For the reading process, the laser energy of 5 mW with the exposure time of 1 s was applied to the entire patterned surface.

Photoluminescence (PL)
PL measurements were carried out on a confocal Raman microscope (WITec, alpha 300RA) with a 532 nm excitation laser, which was focused with a 100× objective (NA = 0.90, 0.26 mm working distance). The PL spectra were recorded with a lens-based spectrometer with a CCD camera (1024×128 pixels, cooled to -65 °C) using a grating of 600 lines/mm. The diffraction-limited focus resulted in a lateral resolution of about 200 nm, and a focal depth of about 1 μm. For the PL spatial mapping, the laser energy of 3 mW with the integration time 0.1-0.5 s was applied.

Kelvin probe force microscopy (KPFM)
The KPFM measurement was performed under ambient conditions using a Bruker Dimension Icon microscope with non-contact mode (AFM tip: SCM-PIT-v2, platinum-iridium coated). Amplitude-modulated KPFM in a dual pass configuration was used. A modulation bias of 1.5 V was applied to the cantilever. In the first scan the topography is received and in the second pass the potential profile is measured while keeping the tip at a constant distance (50 nm) from the sample surface.
III. Supplementary data for the patterned G/MoS$_2$ heterostructures

Table S1. Summary of Raman characteristics of graphene related peaks. The band position (Pos), full width at half maximum (FWHM), and peak intensity ratios are extracted from the Lorentzian function fitted Raman spectra.

|                | Pos (G) | FWHM (G) | Pos (2D) | FWHM (2D) | Pos (D) | FWHM (D) | I(D)/I(G) | I(G)/I(2D) |
|----------------|---------|-----------|----------|------------|---------|----------|-----------|------------|
| graphene       | 1584.8  | 19.9      | 2690.9   | 38.2       | -       | -        | -         | 0.6        |
| vdw G/MoS$_2$  | 1585.5  | 38.3      | 2686.6   | 35.5       | -       | -        | -         | 0.3        |
| covalent G/MoS$_2$ | 1598.2  | 59.7      | 2684.6   | 55.0       | 1355.4  | 121.1    | 0.42      | 1.9        |
| G/OMe-MoS$_2$  | 1582.6  | 18.8      | 2688.1   | 33.6       | -       | -        | -         | 0.5        |
| G/NO$_2$-MoS$_2$ | 1583.2  | 17.9      | 2688.7   | 33.8       | -       | -        | -         | 0.5        |

Figure S1. (A) Raman spectra ($\lambda = 532$ nm) of pristine MoS$_2$, functionalized MoS$_2$ (fun-MoS$_2$), vdw G/MoS$_2$ heterostructures and covalent G/MoS$_2$ heterostructures. The dashed line indicates the peak
position of $A_{1g}$ mode for pristine MoS$_2$. (B) Plot of peak positions of $A_{1g}$ mode. (C) Plot of the full width of half maximum (FWHM) of $A_{1g}$ mode.

**Figure S2.** (A) Raman spectra ($\lambda = 532$ nm, irradiation time = 20 s) of vdW G/MoS$_2$ domains at different laser powers. (B) Raman spectra ($\lambda = 532$ nm) of covalent G/MoS$_2$ domains at different laser powers. The color codes for the respective laser powers: black (0.1 mW), red (1.4 mW), blue (3.4 mW), pink (7.0 mW), and green (13.6 mW).

**Figure S3.** Plot of $I(D)/I(G)$ ratios of vdW (black) and covalent (red) G/MoS$_2$ domains as a function of laser power.
Figure S4. (A) Raman spectra ($\lambda = 532$ nm, laser power = 7 mW) of vdW G/MoS$_2$ domains at extended irradiation times. (B) Raman spectra ($\lambda = 532$ nm) of covalent G/MoS$_2$ domains at extended irradiation times. The color codes for the respective irradiation times from bottom to top: black (10 s), red (15 s), blue (20 s), pink (25 s), green (30 s), navy (35 s), purple (40 s), and brown (50 s).

Figure S5. Plot of $I(D)/I(G)$ ratios of vdW (black) and covalent (red) G/MoS$_2$ domains against irradiation time.
Figure S6. (A) Optical image of patterned CVD-MoS\(_2\) surface. The black arrows indicate the location of functionalized MoS\(_2\) stripes (width = 4 μm). (B) Optical image of patterned G/MoS\(_2\) heterostructures. The black arrows indicate the covalent domains.

Figure S7. Raman spatial maps (λ = 532 nm) of the patterned G/MoS\(_2\) heterostructures obtained from the single irradiation process. (A) Raman map of the intensity of G band. (B) Raman map of the
intensity of D band. (C) Raman map of the intensity ratio of 2D to G bands. (D) Raman map of the intensity of \( \text{E}_{2g}^{1} \) mode. (E) Raman map of the intensity of \( \text{A}_{1g} \) mode. (F) Raman map of the intensity of LA mode. The covalent domains feature the higher \( I(\text{D}) \), lower \( I(2\text{D})/I(\text{G}) \), and higher \( I(\text{LA}) \) in Raman maps.

**Figure S8.** Raman spatial maps (\( \lambda = 532 \) nm) of other patterned G/MoS\(_2\) heterostructures. (A-C) Raman maps of the intensity of LA mode, the intensity ratio of D to G bands, and the intensity ratio of 2D to G bands for the FAU pattern. (D-F) Raman maps of the intensity of LA mode, the intensity ratio of D to G bands, and the intensity ratio of 2D to G bands for the dot arrays. The covalent domains are highlighted with the white circles in D and E. The covalent domains feature the higher \( I(\text{LA}) \), higher \( I(\text{D})/I(\text{G}) \), and lower \( I(2\text{D})/I(\text{G}) \) in Raman maps.

IV. Reference experiments

A. Attempts to generate covalent G/MoS\(_2\) heterostructures using MoS\(_2\) modified by other light inert groups as the bottom layer.

In an argon filled glovebox (<0.1 ppm O\(_2\) and H\(_2\)O), the CVD-MoS\(_2\) was firstly treated with Na/K (molar ratio 1:3) alloy for 2 h. After the alloy layer was removed, the film was immediately soaked in diazonium salts (4-nitrobenzenediazonium tetrafluoroborate or 4-methoxybenzenediazonium tetrafluoroborate)/ anhydrous methanol (0.1 mmol/mL, 3 mL) solution in darkness for 0.5 h. The resulting film was thoroughly washed with methanol and de-ionized water to remove all the physisorbed residues, yielding the 4-nitrophenyl group functionalized MoS\(_2\) (denoted as NO\(_2\)-MoS\(_2\))
or 4-methoxylphenyl group functionalized MoS$_2$ (denoted as OMe-MoS$_2$). The monolayer graphene with PMMA mask was placed on the top of the functionalized MoS$_2$ surface followed by drying in the fume hood at room temperature overnight. Then the sample was heated at 130 °C for 0.5 h. The vertical stack of graphene and functionalized MoS$_2$ was subjected to the Raman laser irradiation. None of these stacked structures show an increased intensity of D band in Raman spectra (Figure S9), suggesting that graphene was not functionalized in these cases and the covalent heterostructures cannot form by using these light inert linkers nor without linkers.

**Figure S9.** Raman spectra ($\lambda = 532$ nm) of pristine MoS$_2$ (grey), vdW G/MoS$_2$ heterostructures (black), the vertical stack of graphene and OMe-MoS$_2$ (green), and the vertical stack of graphene and NO$_2$-MoS$_2$ (pink). All the spectra were normalized to the intensity of A$_{1g}$ mode of MoS$_2$ at 411 cm$^{-1}$ and plotted with the Y-axis off-set.

**B. Verification of the role of Br-containing linkers in the photon-triggered interface coupling reaction.**

**B1. Functionalization of graphene with bromobenzene.**

One drop of bromobenzene (BB)/ ethanol (80 mM) solution was drop-cast on a clean surface of a
silicon wafer followed by evaporating off the solvent in the fumehood at room temperature overnight, yielding the BB@Si/SiO$_2$. Then the monolayer graphene with PMMA mask was placed on the top of the BB@Si/SiO$_2$. After drying in the fumehood at room temperature overnight, the sample was heated at 130 °C for 0.5 h. The vertical stack of G/BB was then subjected to the laser irradiation (Figure S10A). With increasing laser intensity, the Raman spectra (Figure S10B) of G/BB display significantly increased D band and reduced 2D band, suggesting the graphene layer in G/BB was successfully functionalized by laser irradiation.

Figure S10. (A). Schematic illustration of the fabrication process for G/BB on a silicon substrate. The laser-triggered region (grey area) results in the functionalization of graphene (orange area). (B) Raman spectra (λ = 532 nm) of G/BB@Si/SiO$_2$ at varied laser powers.

B2. Fabrication of covalently linked graphene and SiO$_2$ heterostructures.

The generation of a self-assembled (SAM) layer on a silicon substrate was firstly performed according to the literature reported procedure.$^2$ Specifically, the freshly cleaned silicon wafer was immersed into a freshly prepared 4-bromobenzylphosphonic acid/THF solution (80 mM) for 24 h followed by drying with N$_2$ flow. The sample was then annealed at 100 °C under Ar for 1 h. After cooling to room temperature, the sample was washed with THF and ethanol, giving the SAM modified silicon surface (SAM@Si/SiO$_2$). Subsequently, the single layer graphene with PMMA mask was placed on the top of
SAM@Si/SiO₂. After drying out in the fumehood at room temperature overnight, the sample was heated at 130 °C for 0.5 h. The vertical stack was then subjected to the laser irradiation (Figure S11A). The covalently linked graphene and SiO₂ heterostructures (G/SAM@Si/SiO₂) formed along the laser-scanned path, as evidenced by the increased D band and decreased 2D band in the Raman spectra of irradiated regions (Figure S11B).

**Figure S11.** (A). Schematic illustration of the fabrication process for G/SAM on a silicon substrate. The laser-triggered region (grey area) results in the functionalization of graphene (orange area). (B) Raman spectra (λ = 532 nm) of G/SAM at varied laser powers. The applied laser powers from bottom to top are 0.1, 1.4, 3.4, 7.0, and 13.6 mW, respectively.

**References**

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