

Covalent Patterning of 2D MoS₂

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Abstract: The development of an efficient method to patterning 2D MoS₂ into a desired topographic structure is of particular importance to bridge the way towards the ultimate device. Herein, we demonstrate a patterning strategy by combining the electron beam lithography with the surface covalent functionalization. This strategy allows us to generate delicate MoS₂ ribbon patterns with a minimum feature size of 2 μm in a high throughput rate. The patterned monolayer MoS₂ domain consists of a spatially well-defined heterophase homojunction and alternately distributed surface characteristics, which holds great interest for further exploration of MoS₂ based devices.

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) are deemed promising for the next generation semiconductor platforms owing to their extraordinary properties.^[1–2] As a representative, monolayer MoS₂ - a direct bandgap semiconductor - is one of the most appealing 2D TMDCs due to its exceptional physical properties and potential applications in electronic and optoelectronic devices.^[3–6] Patterning of the 2D MoS₂ surface is a crucial step towards further integration of MoS₂ into miniaturized devices.^[7] Patterned MoS₂ nanostructures have been obtained through either bottom-up or top-down strategies. The bottom-up strategies usually involve the growth or self-assembly of molecular building blocks onto the pre-defined substrates;^[8–10] the top-down strategies use litho-

graphic techniques to engineer the morphology, phase, shape and chemical composition of the material surface towards the desired geometry and device properties.^[11–19] Combining the bottom-up surface chemistry with the top-down lithographic technologies allows controlling the patterned structures in a more versatile and precise manner, facilitating efficient manufacture. So far, such a concept has applied in graphene systems,^[20–21] yet rarely to a 2D MoS₂ surface.^[22]

The functionalization chemistry of the inert MoS₂ basal plane has been a burgeoning field in recent years. A variety of inorganic and organic compounds is employed to modify the MoS₂ surface.^[23–24] Yet, only a few types of reagents such as diazonium salts,^[25] organohalides,^[26] and maleimides^[27] can form robust covalent bonds with the MoS₂ surface. Among them, diazonium salts are the most extensively used ones. The high reactivity of diazonium salts enables the coupling of functional groups on both pristine^[28] and activated MoS₂ surface.^[25,29–30] The reactions between activated MoS₂ and diazonium salts can lead to a high degree of functionalization in a short reaction time. For example, the maximum degree of functionalization can reach 40% per sulfur atom.^[30] Moreover, the properties of the functionalized surface can be systematically tuned by varying the functional groups.^[30] These advantages of the diazonium chemistry based surface modification, and its compatibility with other lithographic techniques, have made it ideal for covalent patterning of the MoS₂ surface.

Herein, we demonstrate an efficient approach to patterning 2D MoS₂ through covalent functionalization of electron beam lithography (EBL) defined guiding patterns. This approach leads to the formation of high-quality, patterned MoS₂ ribbons with a minimum feature size of 2 μm in a high throughput rate. The covalent functionalization reaction introduced here allows modifying the phase and chemical composition of MoS₂ in one development process. The resulting patterned MoS₂ displays switchable surface characteristics and a lateral heterophase in a spatially defined manner, confirmed by scanning Raman spectroscopy and photoluminescence (PL) mapping.

The principle of covalent functionalization of 2D MoS₂ on Si/SiO₂

Figure 1a describes the main steps of covalent functionalization of MoS₂ on Si/SiO₂. The MoS₂ deposited on Si/SiO₂ was initially activated, resulting in the negatively charged MoS₂. Then the activated MoS₂ was reacted with the electrophile, 4-bromobenzenediazonium tetrafluoroborate, yielding the functionalized

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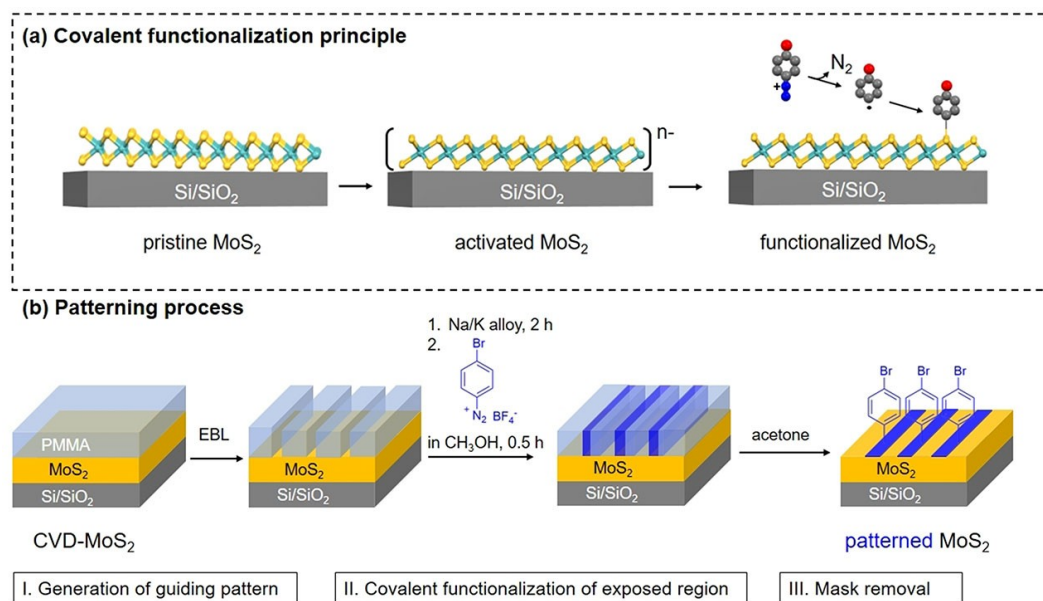


Figure 1. Covalent patterning of MoS₂ surface. (a) The concept for covalent functionalization of 2D MoS₂ on Si/SiO₂ via a reductive pathway. (b) Schematic illustration of the patterning process on CVD-MoS₂ surface: I. Generation of guiding pattern by selective removal of the PMMA mask at designed locations using electron beam lithography (EBL); II. The unmasked region was then activated using Na/K alloy followed by the functionalization reaction with 4-bromobenzenediazonium salts whereas the masked region was preserved; III. Removal of PMMA mask in acetone bath, resulting in the pristine and functionalized MoS₂ ribbons alternately distributed on the patterned domain.

MoS₂. To evaluate the feasibility of this concept, we first performed a proof-of-concept study using mechanically exfoliated MoS₂ (me-MoS₂) samples (Figure S1a). Activating MoS₂ on Si/SiO₂ (100 nm) was achieved by covering the surface of MoS₂ with Na/K alloy under argon atmosphere for 2 h. The wettability and the solvent-free nature of Na/K alloy reductant ensure the efficient reduction of MoS₂^[24] and easy purification. The follow-up reaction of activated MoS₂ with 4-bromobenzenediazonium tetrafluoroborate was completed by immersion of the activated film into a 4-bromobenzenediazonium tetrafluoroborate/ anhydrous methanol solution under argon atmosphere (see Supporting Information for details). The optical images (Figure S1b) show a color change of MoS₂ flakes from green to blue, indicating a change of optical properties upon functionalization. Elemental mapping of functionalized MoS₂ (B-MoS₂, where B denotes the 4-bromophenyl group) nanosheets (Figure S2) using scanning electron microscopy coupled energy dispersive X-ray spectroscopy (SEM-EDS) shows evenly distributed carbon and bromine signals over the flakes, verifying the successful incorporation of bromophenyl functional groups to the MoS₂ surface.

Comparison of the Raman spectra ($\lambda_{\text{exc}} = 633 \text{ nm}$) of B-MoS₂ to pristine me-MoS₂ (Figure S4a) reveals two additional peaks at 150 and 226 cm⁻¹ in B-MoS₂, corresponding to the J₁ and J₂ modes of 1T-phase MoS₂. This demonstrates that 1T-phase was present in B-MoS₂, which was consistent with other reductive functionalization studies.^[25–26,29] Noticeably, the peak at 226 cm⁻¹ can also be assigned to LA mode associated with the defects of the MoS₂ lattice.^[31–32] Previous studies have pointed out that the intensity of this peak relative to either the E¹_{2g} or

A_{1g} mode of MoS₂ linearly correlates to the density of defects, similar to the D/G intensity ratio in the graphene system.^[31] Our recent experimental study also verified that the activation of this phonon mode was indeed related to the surface functionalization.^[33]

Bearing this in mind, we used the relative intensity of the LA mode as a probe to identify the ideal reaction conditions for covalent functionalization. We performed a control experiment by reacting me-MoS₂ directly with diazonium salts without activation (Figure S3). The Raman spectrum of a functionalized sample prepared without activation (Figure S3d, black trace) displays a much lower intensity of the LA mode compared to that prepared with activation (Figure S3d, red trace). In particular, for the functionalized MoS₂ prepared with activation (B-MoS₂), the intensity of the LA mode relative to E¹_{2g} mode was more than three times higher than that for the sample prepared without activation (me-MoS₂, see detailed data in Table S1). As a higher relative intensity of the LA mode reflects a higher density of defects (surface addends), the control experiment demonstrates that activation of MoS₂ film before functionalization is the key to obtain efficient functionalization. Achieving a high degree of functionalization on the defined surface area is necessary because it will enable a better contrast to the pristine surface area, which favors a well-resolved pattern in the following study.

In addition, we monitored the Raman spectrum of B-MoS₂ at extended reaction time (Figure S4a) and plotted the peak intensity ratios of LA/E¹_{2g} and LA/A_{1g} as a function of the reaction time (Figure S4b). Interestingly, the relative intensity of the LA mode increased by eight fold compared to the pristine

me-MoS₂ when the reaction underwent 30 min. However, extending the reaction time did not increase the relative peak intensity of the LA mode further, implying that the degree of functionalization was saturated after 30 min.

Covalent patterning of a CVD-grown MoS₂ surface

A schematic illustration of the patterning process on the chemical vapor deposition (CVD) grown MoS₂ surface is depicted in Figure 1b. The CVD-MoS₂ on Si/SiO₂ (300 nm) was firstly spin-coated with a layer of electron beam resist mask, poly (methyl methacrylate) (PMMA). Then the guiding pattern (Figure 2a) was created by selective removal of the PMMA mask at designed locations using electron beam lithography (EBL). The subsequent activation with Na/K alloy followed by the reaction with 4-bromobenzenediazonium salts allowed the unmasked areas to be functionalized, whereas the masked areas were preserved. The resulting film was thoroughly washed with methanol and water to remove all the physisorbed residues. After removal of PMMA mask by acetone, the patterned MoS₂ surface was characterized by optical microscopy, atomic force microscopy (AFM), SEM-EDS, Raman spectroscopy, and photoluminescence (PL) spectroscopy (see Supporting Information for details).

The AFM image of the patterned MoS₂ surface after removal of PMMA (Figure 2b) shows a preserved structure in the functionalized region but a damaged structure in the pristine MoS₂ region, suggesting the surface modification improved the robustness of the MoS₂ surface against the possible delamination or fracture during the purification steps. Taking the surface roughness into consideration, a clear variation of height (inset height profile, Figure 2b) between the functionalized MoS₂ stripes (pointed out by the blue arrows) and pristine MoS₂ gap can still be identified along the measured region. In particular, two functionalized stripes maintain roughly the same height, about 1.2 nm thicker than the pristine MoS₂ gap. A height increase of functionalized MoS₂ stripes relative to the pristine

MoS₂ gap was possibly due to the joint effect of intercalation and surface covalent functionalization.^[28,34] We further characterized the patterned MoS₂ surface under ambient conditions by Kelvin probe force microscopy (KPFM). The surface potential map (Figure S5a) displays an alternately distributed ribbon pattern, suggesting a clear surface potential variation between the functionalized and pristine MoS₂ regions. The dramatic variation of surface potential (Figure S5b) can be attributed to significant change of electronic properties caused by the intercalation and chemical functionalization.^[35–37]

The SEM image of the patterned MoS₂ surface (Figure 3a and b) displays clear boundaries between functionalized and pristine MoS₂ regions. Elemental mapping of the patterned MoS₂ surface using EDS shows discernible C and Br signals (Figure 3c), originated from the introduced bromophenyl functional groups. In particular, the C and Br signals accumulated in the unmasked region of the guiding pattern (Figure 3d and Figure S6), suggesting that the functional groups were only bounded to the unmasked MoS₂ surface. The moderate signal to noise ratio in Figure S6b was likely related to the lower content of Br (1/6 of C).

Raman spectra of both pristine CVD-MoS₂ (Figure 4a, black trace) and functionalized MoS₂ ribbons (Figure 4a, red trace) show the characteristic E_{2g}¹, A_{1g}¹, and 2LA modes. Unlike pristine CVD-MoS₂, the functionalized MoS₂ ribbons show additional phonon modes at 153, 226 and 352 cm⁻¹, corresponding to the J₁, J₂, and J₃ modes of 1T-phase, demonstrating the presence of a 1T-phase in the functionalized MoS₂ ribbons. Interestingly, compared to the pristine CVD-MoS₂, the Raman spectrum of functionalized MoS₂ ribbons shows significantly increased intensity of the LA mode, suggesting a high degree of functionalization. The Raman line mapping of the intensity ratio of LA to E_{2g}¹ (or A_{1g}¹) (Figure S7a and S7b) vividly resembles the location and the width of the functionalized MoS₂ ribbons, which correlates well with the optical image of the patterned MoS₂ surface (Figure S7c). In specific, the functionalized ribbons corresponding to the regions with high intensity ratios can be easily identified.

Importantly, by applying our covalent patterning approach, a large area (100×100 μm²) and high quality of MoS₂ surface

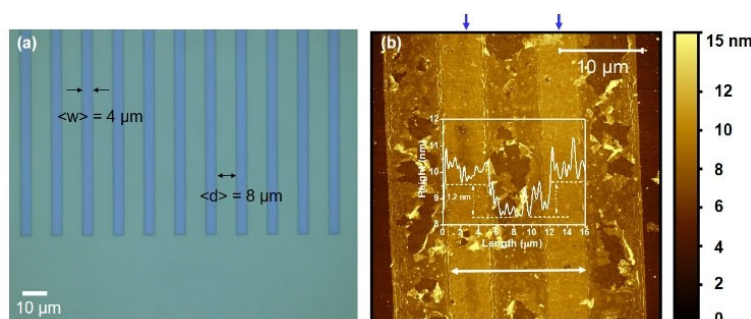


Figure 2. (a) Optical image of CVD-MoS₂ coated with PMMA after EBL patterning. The width of each unmasked MoS₂ ribbon is 4 μm. The width of the masked interspace is 8 μm. (b) AFM image of patterned MoS₂ surface after removal of PMMA. While the structure of functionalized MoS₂ ribbons (marked with blue arrows) remains mostly intact, the pristine MoS₂ surface shows fracture after the purification steps. The inset height profile of the measured region (marked with white arrow) indicates that the thickness of functionalized MoS₂ ribbons increased by 1.2 nm compared to pristine MoS₂.

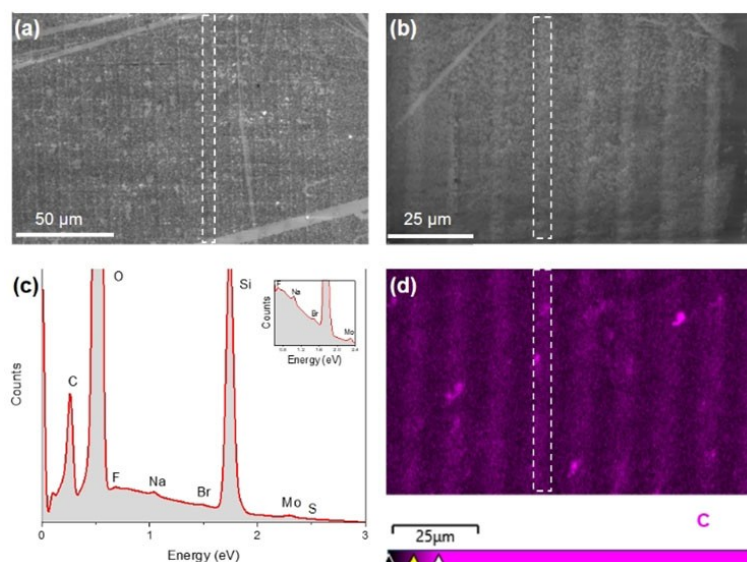


Figure 3. SEM-EDS characterization of patterned CVD-MoS₂ surface after removal of PMMA. (a–b) SEM images of patterned CVD-MoS₂ surface under the varied magnification. (c) Elemental composition of patterned CVD-MoS₂ surface. The inset shows the presence of Br in the detected region. (d) EDS mapping image of C distribution. The dashed block in (a, b, and d) indicates one of the functionalized MoS₂ ribbons.

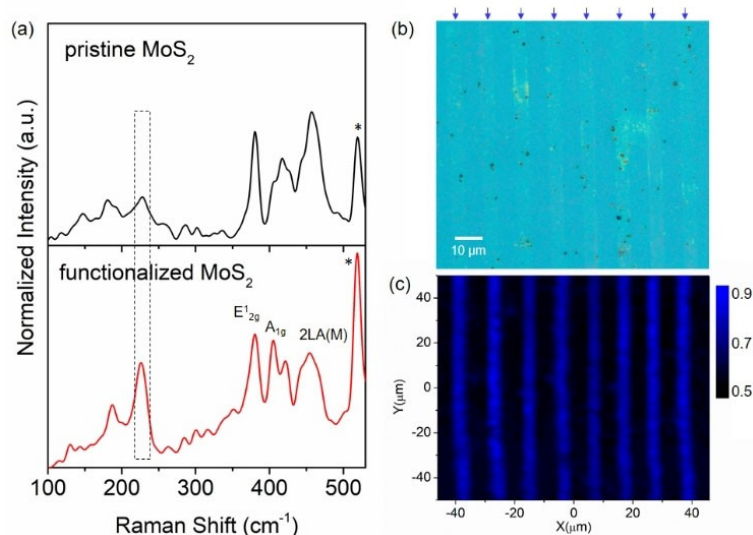


Figure 4. (a) Raman spectra ($\lambda = 633$ nm) of pristine (black) and functionalized (red) regions on the CVD-MoS₂ surface. The spectra were subjected to the baseline subtraction and normalized to the intensity of E_{12g} mode for comparison. The peaks marked with an asterisk are Raman modes of the underlying Si/SiO₂ substrate. The dashed block highlights the functionalization related LA mode at 226 cm⁻¹. (b) Optical image of the patterned CVD-MoS₂ surface after removal of PMMA: the functionalized MoS₂ ribbons (light green, marked with blue arrows) and pristine MoS₂ gaps (cyan) are alternately distributed. (c) Raman spatial map of the intensity ratio (LA/E_{12g}) on the patterned CVD-MoS₂ surface. The functionalized MoS₂ ribbons with high intensity ratios are shown as blue stripes.

with a delicate pattern can be generated (Figure 4b). The Raman spatial mapping of the intensity ratio of LA to E_{12g} displays a well-resolved pattern (Figure 4c), wherein the functionalized ribbons with high intensity ratios and the pristine MoS₂ gaps with low intensity ratios are alternately distributed. The Raman map with the gradient color scale (Figure S7d) displays higher relative intensity of LA mode in the center of the functionalized ribbons compared to the edges, suggesting that the center of the functionalized surface shows a higher

degree of functionalization. One possible reason for the variation of the degree of functionalization could be: the center of the exposed MoS₂ surface, rich in defects (Figure 2b), triggers the initial binding of functional groups onto MoS₂. The tethered addends then act as nucleation centers, facilitating the proliferation of the addends over the surface. The mechanism about the propagation of functionalization along the defects has been monitored and investigated in details by another group.^[28]

Having the covalently patterned MoS₂ surface in hand, we then examined the PL behavior of this structured construct. The PL spectrum of pristine CVD-MoS₂ (Figure 5a) displays one predominant peak at 1.88 eV and a small shoulder at 2.02 eV, attributed to the A exciton and B exciton, respectively. In comparison, the functionalized MoS₂ ribbons show a significantly decreased intensity with a slightly down-shifted peak position of the A exciton, which was likely due to the collective effect of phase transformation (2H-phase to 1T-phase)^[26,38] and *n*-doping. The *n*-doping induced PL evolution has been reported in other functionalized MoS₂ systems as well.^[28,39–40] Similar phenomena can also be observed when comparing the PL spectra of the same CVD-MoS₂ sample before and after electron beam bombardment (Figure S8).

Besides, the contribution of the B exciton became more pronounced in the functionalized MoS₂ region than in the pristine MoS₂ region, which was likely attributed to the presence of higher density of non-radiative defects (functionalized surface)^[41] in the functionalized MoS₂ region. The functionalized MoS₂ ribbons can be distinguished as the high intensity bright stripes in the PL intensity map of B exciton (Figure 5c) and the low intensity dark stripes in the PL intensity map of A exciton (Figure 5b). The switchable PL response of patterned MoS₂ surface signifies the potential to specially modulate the optical properties of MoS₂ via covalent functionalization. By applying this covalent patterning approach, we can pattern more complicated structures. For example, the FAU logo was created through EBL followed by covalent patterning process (Figure S9). This pattern featured with the minimum width of a character of 2 μm can be visualized through PL intensity mapping of the A and B exciton.

In summary, we demonstrated an effective method for covalent patterning of MoS₂ surface. By combining EBL with diazonium chemistry directed surface functionalization, we generated high-quality and well-defined patterns with a minimum feature size of 2 μm on the CVD grown MoS₂ surface. The resulting patterned MoS₂ surface displays switchable surface characteristics in a spatially defined manner, confirmed by scanning Raman spectroscopy and PL mapping, which may hold great promise for the development of state-of-the-art

electronic and optoelectronic devices. The covalent patterning method opens a convenient avenue for spatially designing, engineering, and derivatizing MoS₂ nanostructures, which would benefit further exploration of surface chemistry of MoS₂-like 2D platforms and facilitate efficient manufacture.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: functionalization · MoS₂ · patterning · PL · Raman spectroscopy

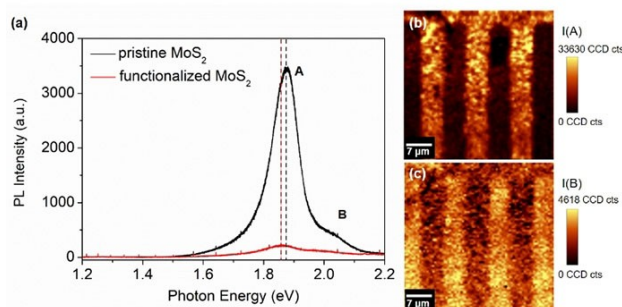


Figure 5. (a) PL spectra ($\lambda = 532$ nm) of pristine and functionalized MoS₂ regions on the patterned CVD-MoS₂ surface. The dashed lines indicate the peak position of the A exciton in pristine (black) and functionalized (red) MoS₂. (b) PL intensity map of the A exciton. (c) PL intensity map of the B exciton.

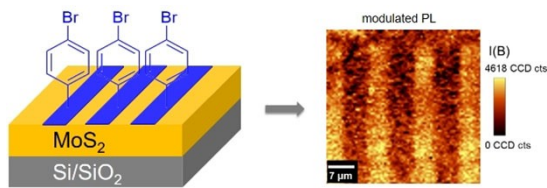
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The patterned 2D MoS₂ surface was achieved through covalent functionalization of electron beam lithography (EBL) defined guiding areas. The patterned MoS₂ surface displays switchable surface characteristics in a

spatially defined manner, confirmed by scanning Raman spectroscopy and PL mapping, which may hold great promise for the development of state-of-the-art electronic and optoelectronic devices.

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1 – 7

Covalent Patterning of 2D MoS₂

