

Supporting Information

Reaction kinetics for the covalent functionalization of two-dimensional MoS₂ by aryl diazonium salts

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7 figures, 8 pages

Raman and photoluminescence spectroscopies

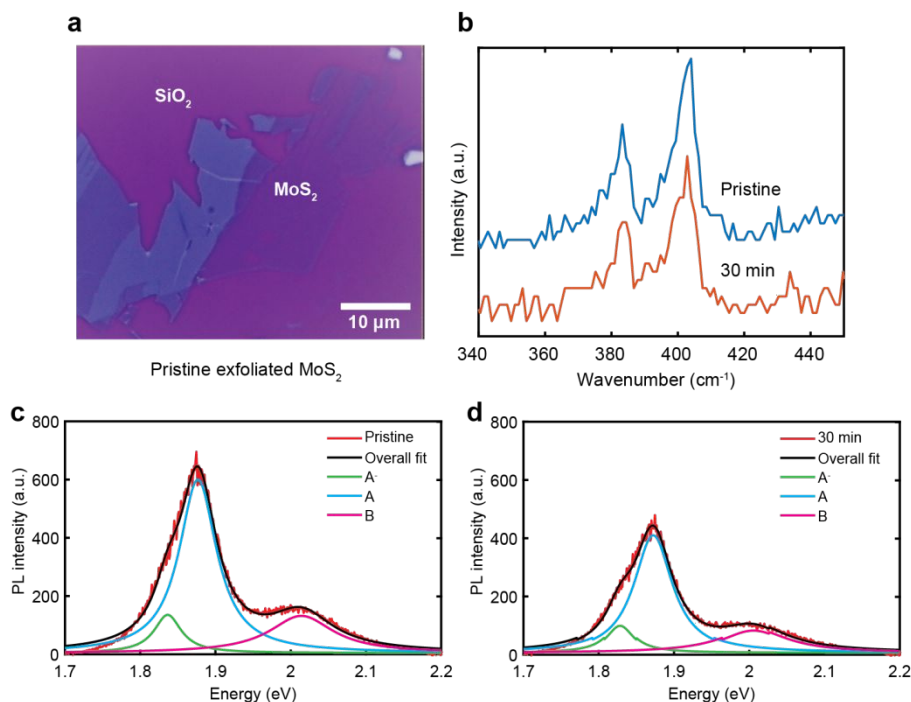


Figure S1: Raman and photoluminescence (PL) spectra. **(a)** Representative optical microscopy image of as-exfoliated MoS₂ flake from mechanical exfoliation supported on SiO₂/Si substrate. **(b)** Raman spectra of pristine monolayer MoS₂ and after 30 min functionalization with 4-NBD at 10 mM. **(c)-(d)** PL spectra of pristine monolayer MoS₂ and after 30 min functionalization, normalized to the intensities of the Raman peaks, and showing curve fitting of the A, A⁻ and B excitons.

In general, the minimal change in Raman and PL spectra indicate that the MoS₂ material generally retains its crystal structure and electronic and optical properties after functionalization.

The Raman spectra of MoS₂ before and after functionalization were also discussed in our previous work in Chu et al.,¹ which we will briefly summarize here. The positions and intensities of the characteristic peaks (the E_{2g} and A_{1g} peaks) indicate that the MoS₂ material remains semiconducting and in the same 2H phase. The LA(M) peak at around 225 cm⁻¹ (which is usually associated with structural defects for MoS₂)² is not observed in any of our spectra. We attribute the lack of this peak to the defect concentration below the threshold where it would be strong enough to be detected. In addition, the C-S bond may not be distorting the MoS₂ lattice enough to generate a significant LA(M) peak.

The PL spectrum shows a large peak at about 1.88 eV for the A exciton, and a smaller peak at about 2.02 eV for the B exciton, and there is also a smaller A⁻ trion peak. There is a decrease of the A exciton intensity by about 35% upon functionalization. This decrease is consistent with more detailed PL measurements from our earlier work in Chu et al.¹ which we interpret as due to primarily n-doping upon functionalization with 4-NBD because of the electron-donating NO₂ group.

AFM images from isotherm study

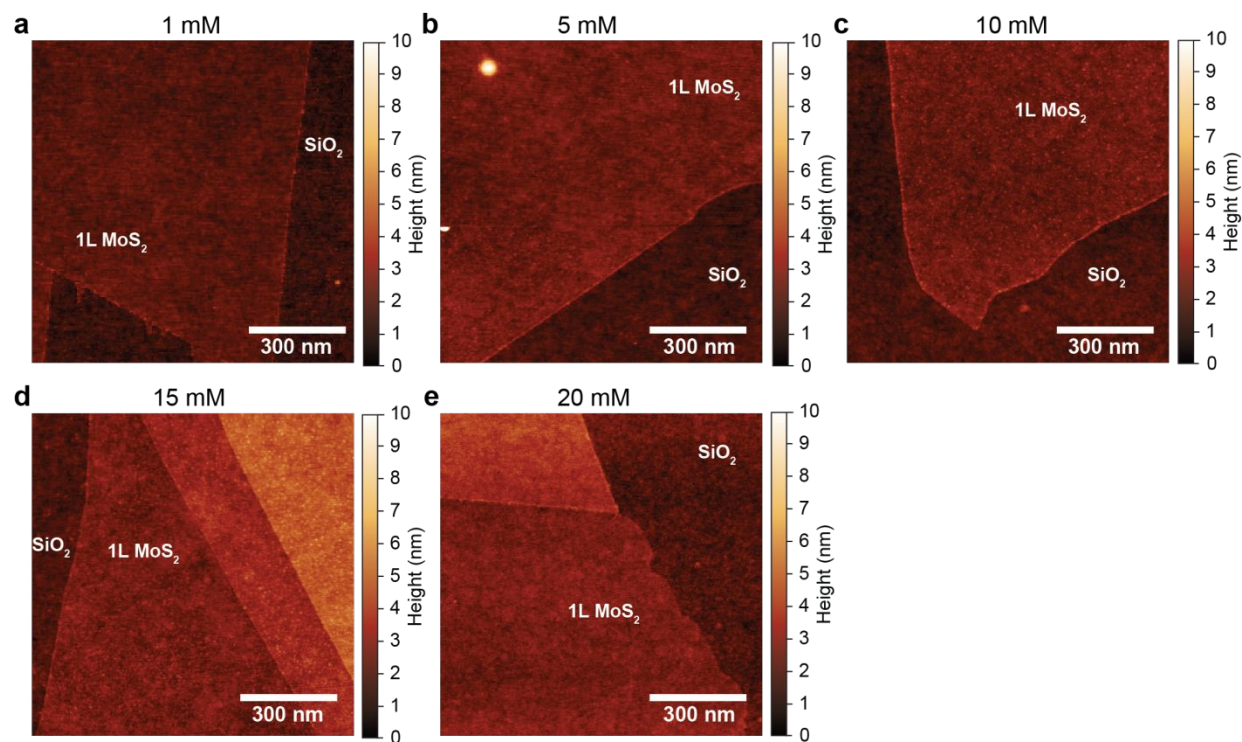


Figure S2: Atomic force microscopy (AFM) images of pristine MoS₂. **(a)-(e)** AFM images of MoS₂ samples used for isotherm study. Samples are shown here before any functionalization occurs and monolayers are labeled as “1L MoS₂”. The samples are then functionalized for 5 s using 4-NBD solutions with initial concentrations of 1 mM, 5 mM, 10 mM, 15 mM and 20 mM, respectively.

AFM images from time dependence study

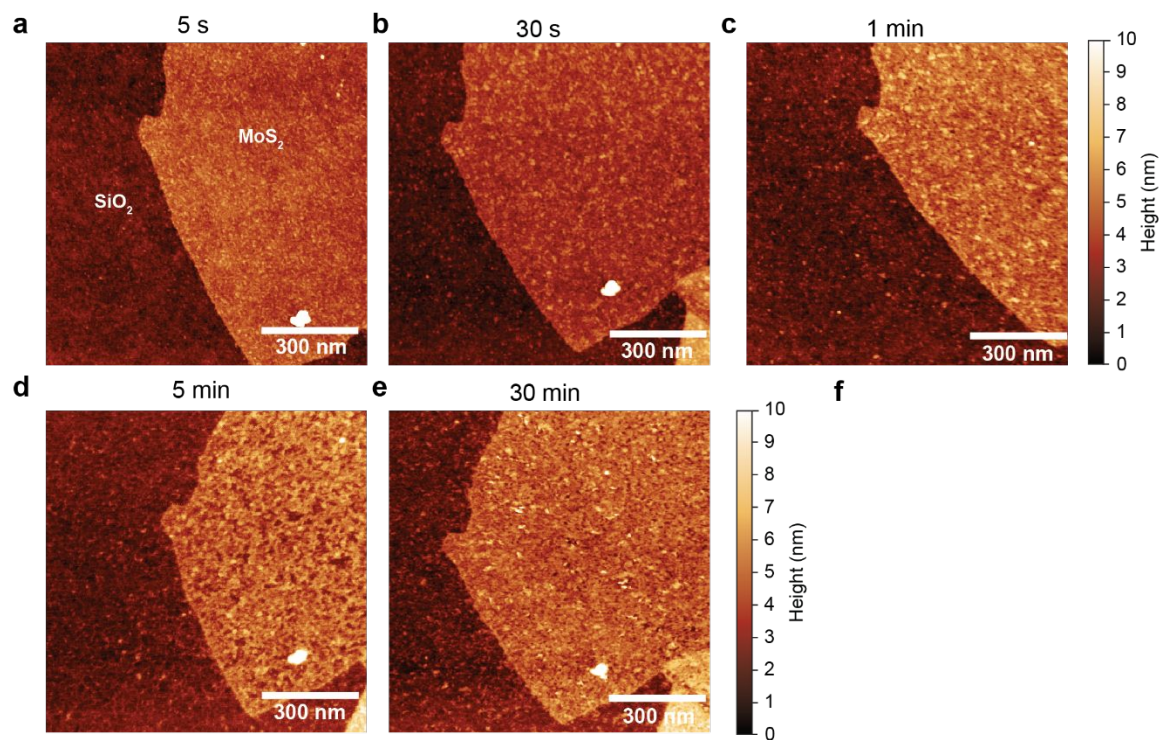


Figure S3: Time dependence of functionalization. **(a)-(e)** AFM images of monolayer MoS₂ taken after different reaction times in a 4-NBD solution of 5 mM concentration at reaction times of 5 s, 30 s, 1 min, 5 min, and 30 min.

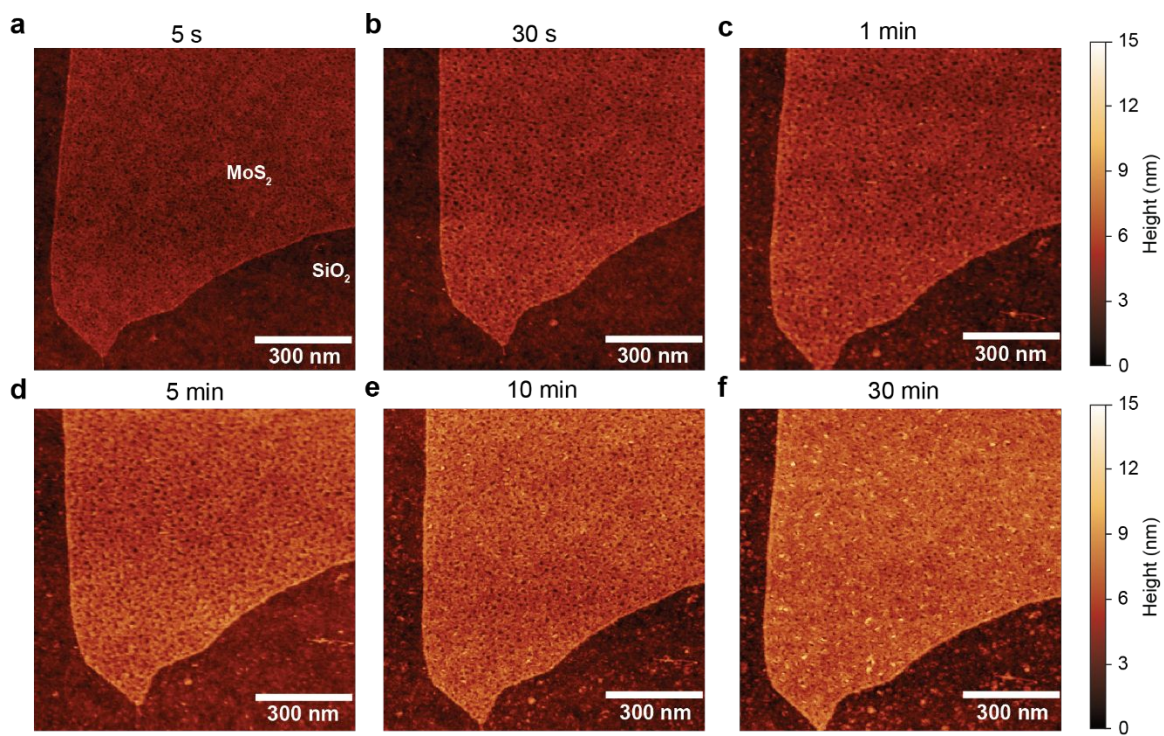


Figure S4: Time dependence of functionalization. **(a)-(f)** AFM images of monolayer MoS_2 taken after different reaction times in a 4-NBD solution of 10 mM concentration at reaction times of 5 s, 30 s, 1 min, 5 min, 10 min and 30 min.

AFM amplitude / peak force error images

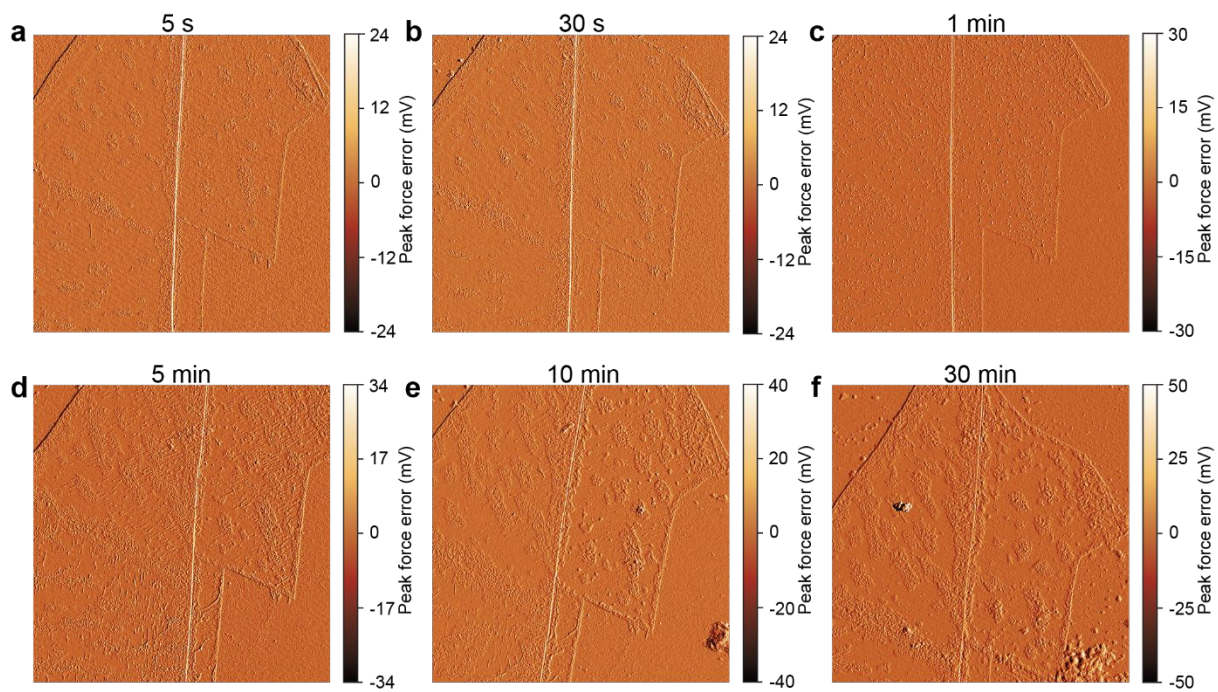


Figure S5. Time dependence of functionalization shown by amplitude / peak force error images, corresponding to the AFM topography images shown in Figure 6 of the main text. The 4-NBD reaction times are 5 s, 30 s, 1 min, 5 min, 10 min and 30 min.

Scanning tunneling microscopy images

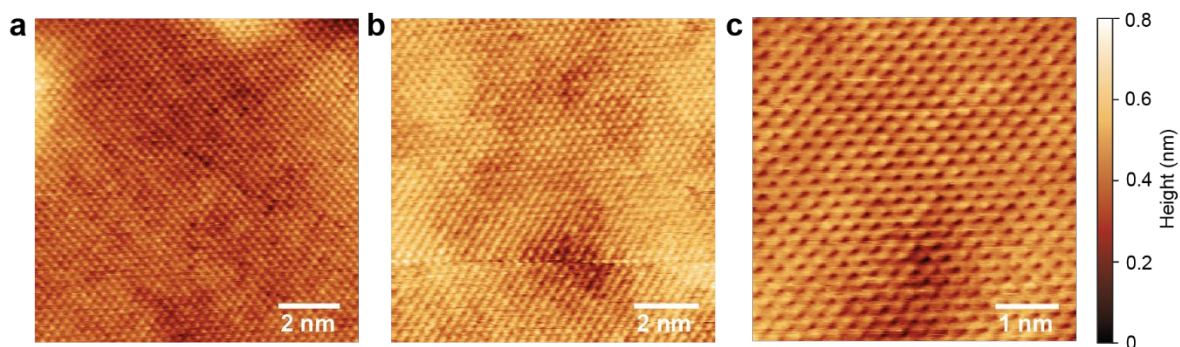


Figure S6. Representative scanning tunneling microscopy (STM) images of as-exfoliated pristine MoS₂ at different magnification levels. There are very few point defects in the MoS₂ surface prior to functionalization. STM imaging conditions: (a) 0.5 nA tunneling current, -1.5V applied bias; (b) 0.8 nA, -0.5 V; (c) 0.5 nA, -0.8V.

Height change due to polymerization

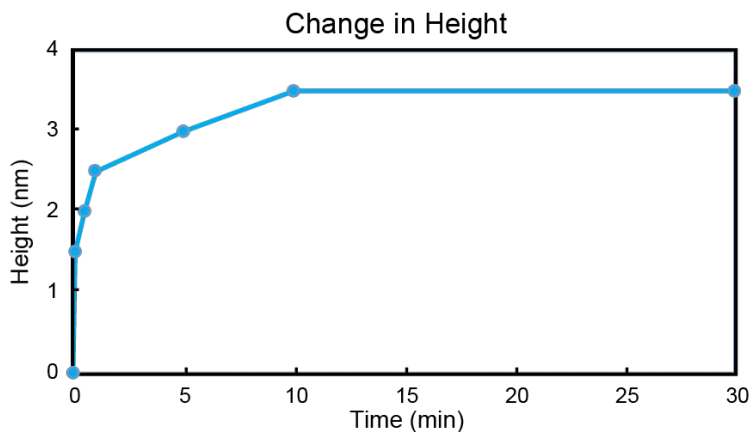


Figure S7. Change in height of features on MoS₂ surface as a function of reaction time from topographic data in Figure 6 of main text. The change in height is attributed to polymerization between molecules, and is much smaller and saturates at about 3.5 nm by 10 min, compared to the increase in lateral coverage due to covalent surface attachment, which continues for longer reaction times.

References

- [1] Chu, X. M. S.; Yousaf, A.; Li, D. O.; Tang, A. L. A.; Debnath, A.; Ma, D.; Green, A. A.; Santos, E. J. G.; Wang, Q. H. Direct Covalent Chemical Functionalization of Unmodified Two-Dimensional Molybdenum Disulfide. *Chem. Mater.* **30**, 2112-2128 (2018).
- [2] Mignuzzi, S. et al. Effect of disorder on Raman scattering of single-layer MoS₂. *Phys. Rev. B* **91**, 195411 (2015).