Lithium-Free Covalent Chemical Functionalization of Two-Dimensional Molybdenum Disulfide

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Supplemental Figures for AVS Abstract

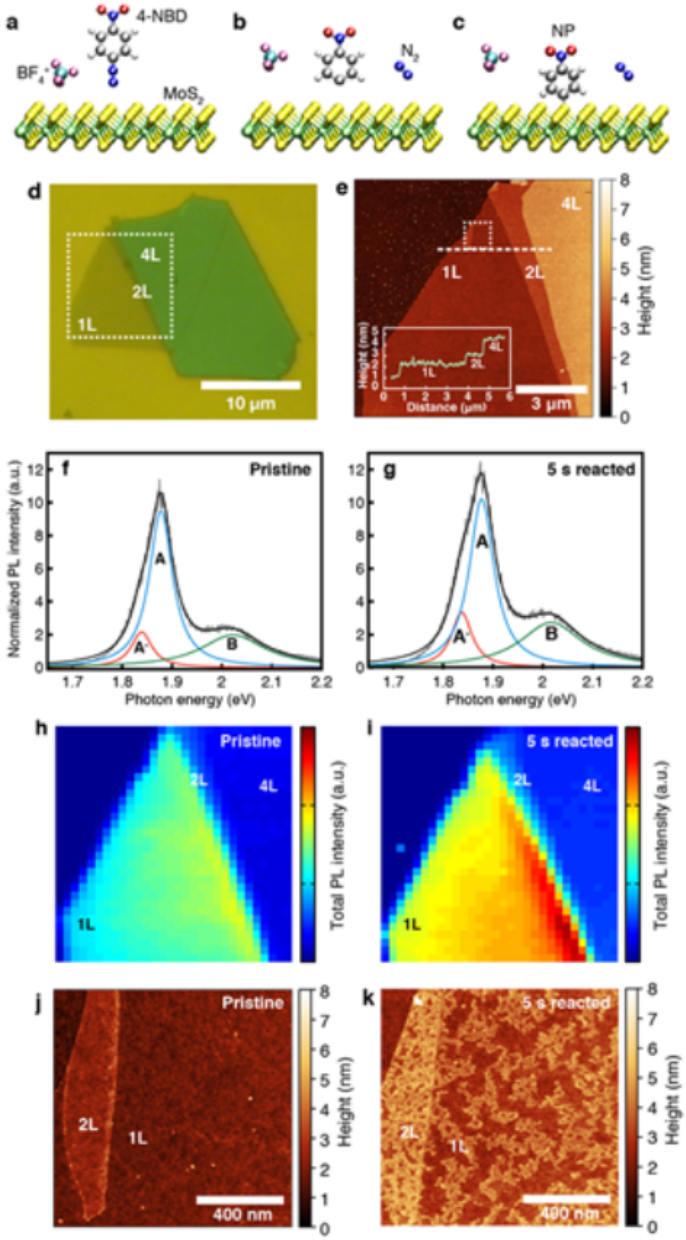

Figure 1: Covalent functionalization of MoS_2. (a)-(c) Schematic illustrations of the functionalization reaction. The aryl diazonium salt 4-nitrobenzenediazonium (4-NBD) tetrafluoroborate (BF_4) is dissolved in aqueous solution. Charges at the MoS_2 surface cause the diazonium group to break from the molecule as a nitrogen (N_2) molecule. The resulting nitrobenzene radical forms a covalent bond to a sulfur atom on the surface, resulting in a nitrophenyl (NP) functional group. **(d)** Optical microscope image of mechanically exfoliated MoS_2 flake with monolayer (1L), bilayer (2L), and four-layer (4L) regions marked. **(e)** Atomic force microscope (AFM) image of the region marked by the dotted square in panel (d) of the pristine MoS_2 flake. Inset: Height profile along the dashed line. **(f)** Representative photoluminescence (PL) spectrum of 1L MoS_2 before reaction with 4-NBD, and **(g)** after 5 s reaction. Lorentzian lineshapes were used to fit the A and B exciton and A^- trion peaks. The spectra are normalized to the height of the Raman peaks. **(h)** Spatial map of total integrated intensity of PL for MoS_2 in the region marked by the dotted square in panel (d) before reaction and **(i)** after 5 s reaction. The PL intensity is highest for monolayer MoS_2 due to its direct bandgap. **(j)** AFM image of the region in the dashed square in panel (e), with mainly 1L MoS_2 and a small region of 2L MoS_2, before reaction and **(f)** after 5 s reaction. Many small protrusions in chain-like shapes are observed.

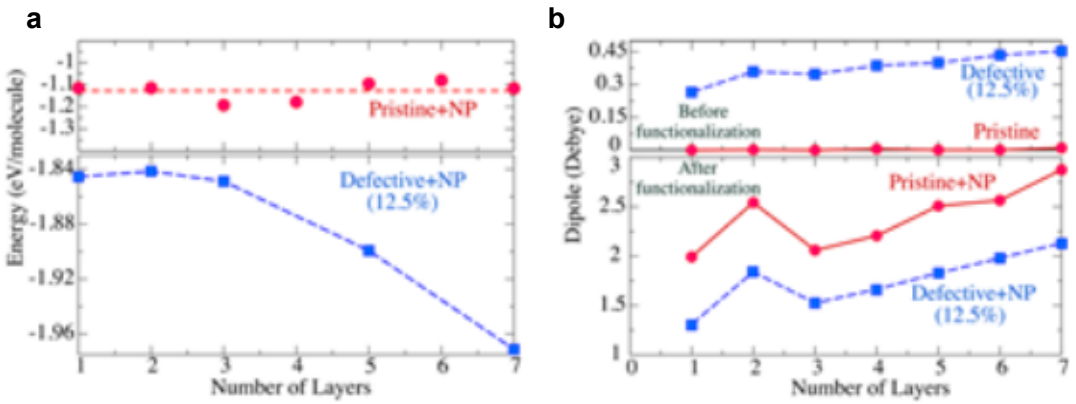

Figure 2: Theoretical calculations of the effects of defects, coverage and number of layers on the functionalization of MoS_2. (a) Binding energy (eV per molecule) as a function of the number of layers for pristine (upper panel) and defective (lower panel) MoS_2 surface with 12.5% S-vacancy concentration. The dashed line in the pristine case is the average along the entire set of thicknesses, and in the defective case is the interpolation between the points. **(b)** Dipole moment at the MoS_2 surface as a function of the number of layers for pristine and defective (12.5% S-vacancies) MoS_2 before (upper panel) and after (lower panel) the functionalization.

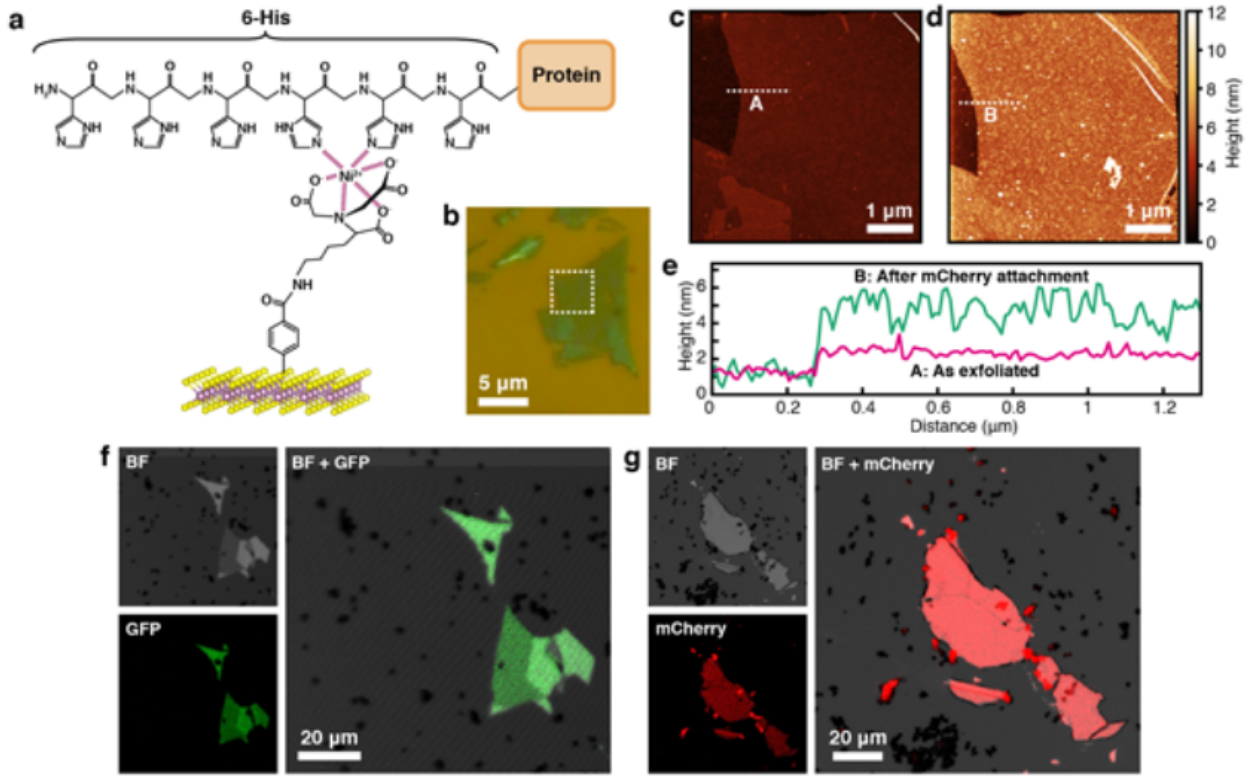

Figure 3: Attachment of active proteins to MoS_2. (a) Schematic of NTA-Ni-chelation attachment of poly-histidine (His) tagged protein, linked to MoS_2 surface via diazonium functionalization chemistry. The diazonium salt used here was 4-carboxybenzene diazonium (4-CBD) tetrafluoroborate. **(b)** Optical microscope image of mechanically exfoliated MoS_2 flakes featured in panels (c) and (d). **(c)** AFM image of pristine MoS_2 in the region indicated by the dashed square in panel (b). **(d)** AFM image in the same region as panel (c) after attachment of mCherry (red fluorescent protein) following initial 10 min functionalization with 4-CBD. **(e)** Height profiles along lines A and B in panels (c) and (d). **(f-h)** Bright field (BF), confocal fluorescence microscopy images in GFP (green) and mCherry (red) channels, and fluorescence images overlaid onto BF images, after protein attachment process. **(f)** GFP attachment. **(g)** mCherry attachment.