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Electronic Supporting Information

Covalent chemical functionalization of semiconducting layered chalcogenide nanosheets

Duo O. Li[1], Matthew S. Gilliam[2,3], Ximo S. Chu[1], Ahmed Yousaf[2,3], Yuqi Guo[1], Alexander A. Green[2,3], and Qing Hua Wang[1]*

1. Materials Science and Engineering, School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ, 85287
2. School of Molecular Sciences, Arizona State University, Tempe, AZ, 85287
3. Biodesign Center for Molecular Design and Biomimetics, The Biodesign Institute, Arizona State University, Tempe, AZ, 85287

* Corresponding author: qhwang@asu.edu

Raman spectra of MoS_2, $MoSe_2$, WS_2, and WSe_2

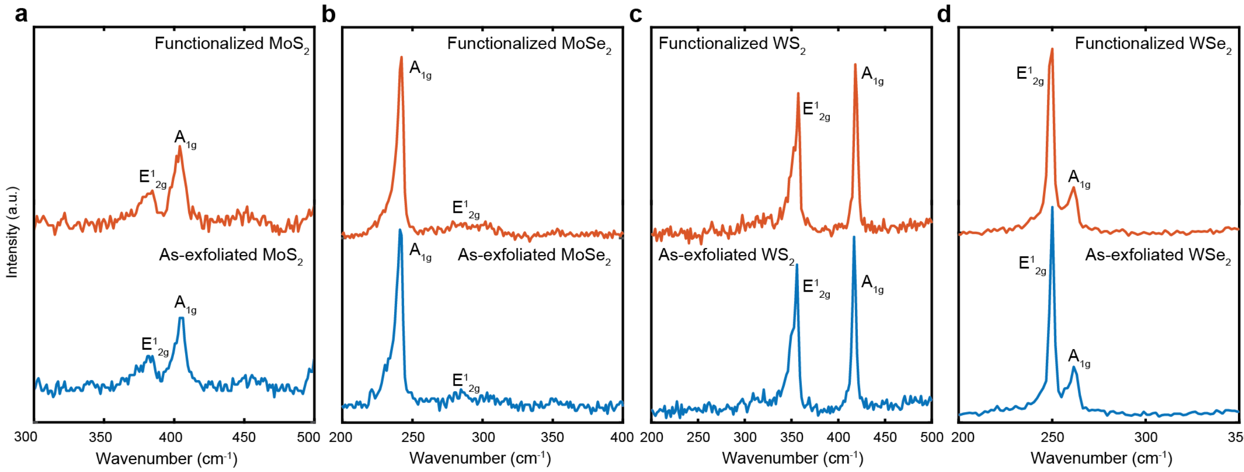

Figure S1: Representative Raman spectra of TMDCs as-exfoliated (lower blue traces) and after diazonium functionalization (upper red traces) for (a) MoS_2, (b) $MoSe_2$, (c) WS_2, and (d) WSe_2.

Raman spectra of Bi_2S_3 and Sb_2S_3

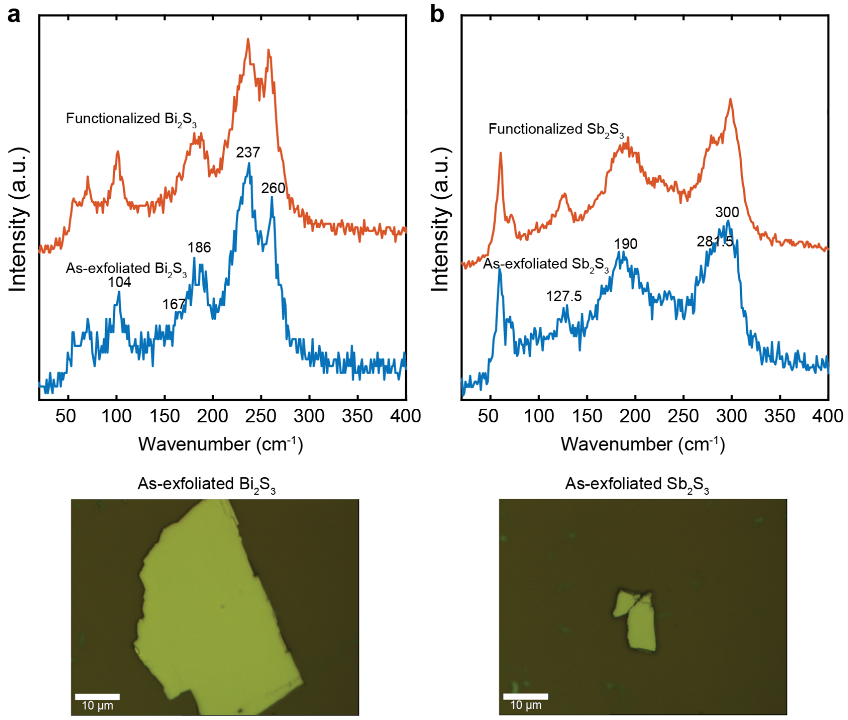

Figure S2: Representative Raman spectra for as-exfoliated (lower blue traces) and after diazonium functionalization (upper red traces) for (a) Bi_2S_3 and (b) Sb_2S_3. Optical microscope images for the as-exfoliated flakes on SiO_2/Si wafers are shown below the spectra.

X-ray photoelectron spectra of MoS_2 and $MoSe_2$

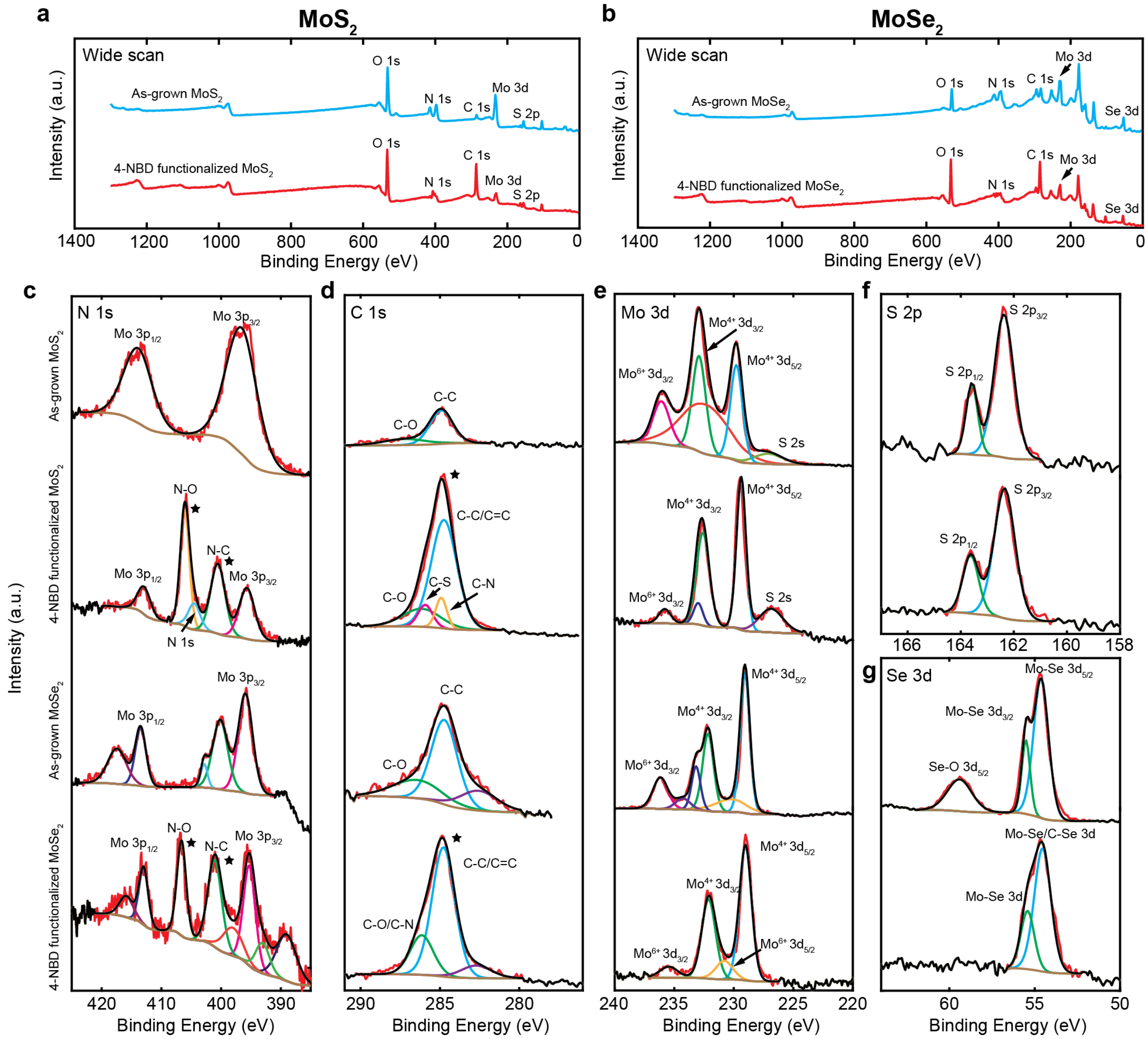

Figure S3: XPS spectra for CVD-grown MoS_2 and $MoSe_2$, before and after diazonium functionalization. (a) Wide scan spectra for MoS_2. (b) Wide scan spectra for $MoSe_2$. (c)-(g) Detailed scans for the (c) N 1s region, (d) C 1 s region, (e) Mo 3d region, (f) S 2p region, and (g) Se 3d region. Important peak changes after functionalization in the N and C regions are indicated by stars (★).

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical bonding on large area samples of MoS_2 and $MoSe_2$ grown on SiO_2/Si substrates using chemical vapor deposition (CVD), both before and after the diazonium functionalization. Large-area CVD samples are needed for XPS to accommodate the large x-ray spot size, so mechanically exfoliated flakes were not suitable. MoS_2 and $MoSe_2$ were chosen as representative sulfide and selenide materials for which we could reliably produce high quality large-area CVD samples.

The XPS spectra are shown in Figure S3. The wide scans are shown in Figure S3(a)-(b). In the N 1s region in panel (c), there was no clear N peak in the spectra of as-grown MoS_2 and $MoSe_2$. After the functionalization with 4-NBD for 30 min, sharp and clear peaks from N-O and N-C appear between the two Mo 3p peaks due to the attachment of nitrophenyl (NP) groups on both the MoS_2 and $MoSe_2$ surfaces. These peaks are indicated by stars (★). In the C 1s region in Figure S3(d), the intensities of the C peaks on both MoS_2 and $MoSe_2$ increase after functionalization, indicating that there is an increase in the amount of carbon-containing bonds on the surface, primarily from the covalently attached groups. The spectra also suggest that in addition to the C-O and C-C/C=C peaks, there are also contributions from C-S bonds[1,2] and C-N bonds[3] after functionalization. The C peaks with increased intensity are also marked by stars (★). In the Mo 3d region in Figure S3(e), the typical peaks for MoS_2 and $MoSe_2$ are present. There are also peaks from Mo^{6+} 3d and Mo^{4+} 3d likely due to residues of the MoO_3 CVD growth precursor, which is a common impurity in these types of samples.[4,5] Since the reaction time was only 30 min, the peak from the C-S bond in the S 2p region in panel (f) is too small to be seen (in our earlier work in Chu et al.[6] the C-S peak is most clear at 6 h of functionalization time). However, Se 3d peak in Figure S3(g) is broader after functionalization, which may be due to a contribution from the C-Se peak at about 54-55 eV,[7] and further demonstrates the covalent attachment of NP groups on $MoSe_2$ surface.

References

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