Electronic Supporting Information

Covalent chemical functionalization of semiconducting layered chalcogenide nanosheets

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Raman spectra of MoS₂, MoSe₂, WS₂, and WSe₂

Figure S1: Representative Raman spectra of TMDCs as-exfoliated (lower blue traces) and after diazonium functionalization (upper red traces) for (a) MoS₂, (b) MoSe₂, (c) WS₂, and (d) WSe₂.
Raman spectra of Bi$_2$S$_3$ and Sb$_2$S$_3$

**Figure S2:** Representative Raman spectra for as-exfoliated (lower blue traces) and after diazonium functionalization (upper red traces) for (a) Bi$_2$S$_3$ and (b) Sb$_2$S$_3$. 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= 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


