Basal Plane Functionalization of Niobium Disulfide Nanosheets with Cyclopentadienyl Manganese(I) Dicarbonyl

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ABSTRACT: Bas situ photolysis to g	al plane-functionalized NbS $_2$ n generate the coordinatively uns	anoshe aturate	eets were obtained using <i>in</i> ed organometallic fragment		UV NMN	Å

cyclopentadienyl manganese(I) dicarbonyl ($CpMn(CO)_2$). Under UV irradiation, a labile carbonyl ligand dissociates from the tricarbonyl complex, creating an open coordination site for bonding between the Mn atom and the electron-rich sulfur atoms on the surface of the NbS₂ nanosheets. In contrast, no reaction is observed with 2*H*-MoS₂ nanosheets under the same reaction conditions. This difference in reactivity is consistent with the electronic structure calculations, which indicate × × × × × ×

stronger bonding of the organometallic fragment to electron-poor, metallic NbS₂ than to semiconducting, electron-rich MoS₂. X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy, and powder X-ray diffraction (PXRD) were used to characterize the bonding between Mn and S atoms on the surface-functionalized nanosheets.

INTRODUCTION

Transition-metal dichalcogenides (TMDs), which can be grown as ultrathin layers or exfoliated into nanostructures, have the potential to serve as the building blocks of novel devices, including photovoltaics, transistors, flexible electronics, sensors, and catalysis supports. While TMDs have a wide range of electronic properties ranging from semiconducting $(WS_2, WSe_2, MoS_2, MoSe_2)^1$ or semimetallic $(WTe_2, NbS_2)^1$ to superconducting $(NbS_2), MbS_2$ introducing new functionality into them without disrupting their structure and electronic properties has proven to be challenging. Apart from isoelectronic substitutions, 5-9 it is difficult to incorporate other atoms, such as electronic dopants or magnetic elements, into the sheets without introducing unintentional defects or producing undesirable side products. While there has been measured success in tuning transition-metal dichalcogenide (TMD) properties via local gating¹⁰⁻¹² and novel CVD heterostructures,^{7,13,14} these techniques struggle with limited scalability. Synthetic techniques that enable the large-scale production of surface-functionalized TMDs nanosheets would be useful for a variety of future applications.

One possible strategy for introducing new atoms that can modify and enhance the intrinsic properties of TMDs is through selective surface- or edge-functionalization of the sheets. While numerous methods of edge-functionalized TMDs have been demonstrated, covalent functionalization of the basal plane surface is more difficult due to the lack of dangling bonds available there.^{15–19} Although various surface functionalization methods, including noncovalent interactions^{20,21} and covalent bonding at defect sites,^{22–24} have been investigated, some have been met with limited success. For example, rather than actually forming covalent bonds at defect sites, thiols were found to instead physiosorb as disulfide dimers on the surface of MoS_2 .^{25,26} Promisingly, however, more recent work has shown that Lewis acids or strong electrophiles such as diazonium compounds and alkylating agents can be used to exploit the electron-rich nature of the TMD surface, providing a potentially viable option for covalent basal plane functionalization.^{27,28} In recent publications, one-electron metallocene reductants were used to enhance the degree of surface functionalization of MoS_2 and WS_2 by alkyl halides,²⁹ and Michael addition of maleimides was also shown to anchor molecules to the basal plane surface through covalent C–S bonding.^{30,31} Chalcophilic, late transition-metal ions (Co, Fe, Ni, Au, Pt) have also been shown to coordinate to the basal plane and edge surfaces of MoS_2 and WS_2 , providing a route to supported single-atom catalysts.^{32–37}

Motivated by the desire to broaden the current toolbox for functionalization of TMDs, we have explored a new method that exploits the electron-accepting ability of the metallic TMD niobium disulfide (NbS₂) to functionalize its basal plane. The rationale for this approach is to use a coordinatively unsaturated, electropositive organometallic fragment to donate electron density to the half-filled $4d_{z2}$ band of the TMD while

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forming a coordinate covalent bond to a sulfur atom on the basal plane surface.

To demonstrate this concept, we reacted the 18-electron piano stool complex, cyclopentadienyl manganese(I) tricarbonyl (CpMn(CO)₃), with NbS₂ by photochemically removing one of the labile CO ligands *in situ* to open a coordination site on the Mn atom. The coordinatively unsaturated $[CpMn(CO)_2]$ fragment was expected to coordinate to a sulfur atom on the basal plane.

We characterized the products of the reaction using Fouriertransform infrared (FTIR) spectroscopy to confirm the bonding mode of the fragment to the surface. We also used X-ray photoelectron spectroscopy (XPS) to compare the oxidation states of atoms in the product and in pristine NbS₂ and performed electronic structure calculations to understand the bonding between Mn and the basal plane sulfur atoms.

The covalent attachment of an organometallic fragment to the basal plane of an NbS_2 nanosheet potentially provides an anchor point from which more specialized attachments can be derived. The aromatic cyclopentadienyl ligand, for example, can be functionalized by various organic groups, opening the door to tailoring of the material properties of TMD nanosheets.

EXPERIMENTAL SECTION

Bulk TMD Synthesis. Stoichiometric amounts of niobium powder (Strem Chemicals) and sublimed sulfur powder (Sigma-Aldrich) were ground together and placed in an evacuated quartz ampoule. The ampoule was heated at 950 °C for 72 h in a tube furnace before cooling (\sim 3 °C/min) to room temperature. Bulk MoS₂ powder was purchased commercially from Sigma-Aldrich.

Intercalation and Exfoliation of NbS₂ and MoS₂. We previously showed that the intercalation of sub-stoichiometric amounts (ca. 0.1 equiv) of *n*-butyllithium facilitates the solvent exfoliation of MoS₂ without damaging the resulting few-layer nanosheets or inducing the 2*H* to 1T structural transition.³⁸ This method was used to prepare colloidal suspensions of both NbS₂ and MoS₂ nanosheets (Scheme 1a-c) under an argon atmosphere: 0.434

Scheme 1. Synthetic Scheme for Functionalization of NbS₂ Nanosheets: (a) Bulk TMD, (b) Li Edge Intercalation, (c) TMD Exfoliation, and (d) TMD Functionalization



mL (1.0 mmol) of *n*-BuLi (2.3 M in hexane, Sigma-Aldrich) and 1.57 g (10 mmol) of bulk NbS₂ were added to 40 mL of ultradry hexane and continually stirred at room temperature for 72 h. The resulting black solid intercalated compound, Li_xNbS_2 ($x \sim 0.1$), was washed with 30 mL of hexane three times and then dried under vacuum at room temperature. The dried preintercalated NbS₂ was exfoliated by horn sonication in 45% EtOH/H₂O for 2 h (40%, 700 W). The

resulting brown-red solution was centrifuged at 6000 rpm for 30 min to separate exfoliated sheets from unreacted bulk solids. The top twothird of the supernatant containing the exfoliated sheets (1 mg/mL) was decanted and then lyophilized to obtain a dry brown powder.

As a control experiment, the procedure was repeated with MoS_2 under an argon atmosphere: 0.434 mL (1.0 mmol) of *n*-BuLi (2.3 M in hexane, Sigma-Aldrich) and 1.60 g (10 mmol) of MoS_2 (Sigma-Aldrich) were added to 40 mL of ultradry hexane. The mixture was stirred under an argon atmosphere at room temperature for 72 h. The resulting solid intercalated compound, $Li_{0.1}MoS_2$, was washed with 30 mL of hexane three times and then dried under vacuum at room temperature. The dried powder was exfoliated by horn sonication in 45% EtOH/H₂O for 2 h (40%, 700 W). The resulting brown-green solution was centrifuged at 6000 rpm for 30 min. The top two-third of the supernatant containing the exfoliated sheets (1 mg/mL) was decanted and then lyophilized to obtain a dry brown powder.

Functionalization. Exfoliated NbS₂ (10 mg, 63.7 μ mol) and CpMn(CO)₃ (2 mg, 9.8 μ mol) (Alfa Aesar) were suspended in 10 mL of ultradry hexanes in an airtight quartz vessel. Separately, exfoliated MoS₂ (10 mg, 62.5 μ mol) and CpMn(CO)₃ (2 mg, 9.8 μ mol) (Alfa Aesar) were also suspended in 10 mL of dry hexanes in an airtight quartz vessel.

Under argon, the mixtures were irradiated with a 300W Xe arc lamp with a UV 290–370 nm band-pass filter for 8 h under gentle stirring. The resulting products were each washed three times with 10 mL of dry hexane in an argon glovebox to remove unreacted solutes. The samples were dried under vacuum at room temperature to obtain solid powders, which were stored in an argon atmosphere prior to further characterization. The final product yield was approximately 50% due to losses during recovery of the solid powders.

X-ray Powder Diffraction. Ambient temperature powder X-ray diffraction (PXRD) patterns were acquired using a Rigaku SmartLab SE X-ray diffractometer with a Cu K α radiation source ($\lambda = 0.15406$ nm), a 10 mm beam mask, a $1/2^{\circ}$ divergence slit, a tube voltage of 45 mV, and a tube current of 40 mA. All diffraction patterns were obtained using a step size of 0.01° (2θ) between 5 and 60° at a scanning rate of 5° min⁻¹ unless otherwise noted. Diffraction patterns were indexed using Appleman software.³⁹

Fourier Transform Infrared Spectroscopy. FTIR spectra of dried powders were collected on a Nicolet iS5 FTIR spectrometer under ambient conditions over a range of 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹.

UV-visible Spectroscopy. UV-vis spectra were obtained using an Agilent Cary 60 spectrophotometer within a 200–800 nm wavelength range. Samples were suspended in a 45% ethanol/water solution within an airtight quartz cuvette.

X-ray Photoelectron Spectroscopy (XPS). Samples of exfoliated NbS₂, exfoliated MoS₂, NbS₂-MnCp(CO)₂, and CpMn-(CO)₃-treated MoS₂ were drop-cast from hexane suspensions onto clean sapphire wafers in a nitrogen atmosphere glovebox. Wafers were sealed in an inert atmosphere holder prior to transfer to the XPS sample chamber. XPS experiments were performed using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low-energy electrons (<5 eV) and argon ions. Binding energies were calibrated using sputter-cleaned Cu (Cu $2p_{3/2}$ = 932.62 eV, Cu $3p_{3/2} = 75.1$ eV) and Au foils (Au $4f_{7/2} = 83.96$ eV). Peaks were charge-referenced to the CH_x band in carbon 1s spectra at 284.8 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the X-ray cross sections and inelastic mean free path of the electrons. The analysis spot size was $\sim 200 \ \mu m$ in diameter.

Thermogravimetric Analysis (TGA). A Q600-series SDT (TA instruments) was used to obtain thermogravimetric data. Samples were loaded into Pt pans in an argon glovebox and then transferred to the TGA instrument to limit exposure to air prior to measurement.

Samples were heated from 30–400 $^\circ C$ (5 $^\circ C$ min $^{-1}) under a flow of air (40 mL min<math display="inline">^{-1}).$

Atomic Force Microscopy (AFM). Samples for AFM were prepared by drop-casting a dilute suspension of $NbS_2-MnCp(CO)_2$ in dry hexanes onto clean Si wafers. AFM measurements were conducted in ambient atmosphere using a Bruker Icon I AFM in PeakForce Tapping mode. Image analysis was done using the NanoScope Analysis suite and ImageJ software.

RESULTS AND DISCUSSION

The PXRD powder pattern in Figure 1a shows that the bulk 3R-NbS₂ sample (as synthesized) crystallized as the trigonal



Figure 1. XRD powder patterns of (a) NbS₂, (b) Li_xNbS_2 , and (c) exfoliated NbS₂. The (*) represents the partial hydration of the gallery as $Li_xNbS_2(H_2O)_y$.

layered polytype, consistent with the literature XRD pattern (PDF 01-089-3041),⁴⁰ indexed in the rhombohedral space group *R*3*m* with lattice constants of a = b = 3.333 and c = 17.931 Å. Diffraction data for the bulk 2*H*-MoS₂ sample (Figure S1) was identified as the hexagonal layered polytype, consistent with the literature XRD pattern (PDF 00-037-1492),⁴¹ indexed in space group *P*63/*mmc* with lattice constants of a = b = 3.159 and c = 12.299 Å.

To avoid significantly changing the d-band filling during intercalation, the pristine bulk TMDs were reacted with substoichiometric amounts of *n*-butyllithium (10:1 mol ratio) to produce partially exfoliated, lithium-intercalated samples, Li_xNbS_2 and Li_xMoS_2 , where $x \approx 0.1$. The Li_xNbS_2 powder pattern shows a slight broadening of the (003) and (006) reflections to lower angles due to the presence of Li⁺ cations and solvent molecules in the galleries. This increased the average interplanar spacing by approximately 0.25 Å relative to pristine NbS₂. Additionally, the appearance of a weak reflection at 13.71° is consistent with reported values of the (002) reflection of stochiometric LiNbS2. Hydration of the intercalated Li ions by atmospheric water during XRD characterization resulted in the formation of a small amount of a $Li_xNbS_2(H_2O)_y$ phase, as evidenced by the appearance of a significantly shifted (003) reflection to a lower angle (*).

The XRD powder pattern of the exfoliated NbS₂ nanosheets shown in Figure 1 lacked discernible intensity for the (003), (006), and (009) reflections, which arise from the periodic layered structure of pristine NbS₂. The absence of these reflections indicates a substantial separation of the NbS₂ layers relative to the bulk. Additionally, the pattern showed two low-intensity peaks at 31.04 and 55.33°, which could be indexed to the (100) and (110) reflections, respectively. The reduced intensity of these reflections (as compared to the bulk) is consistent with other recent studies of exfoliated NbS₂.^{42–44} Attempts to obtain a diffraction pattern for the functionalized NbS₂ nanosheets were unsuccessful due to the low signal-tonoise ratio.

The PXRD results for $\text{Li}_x \text{MoS}_2$ ($x \approx 0.1$) and exfoliated MoS_2 (Figure S1) were comparable to that of exfoliated NbS_2 . The results indicated that MoS_2 was successfully intercalated and subsequently exfoliated into nanosheets.

As detailed in the Methods section, both exfoliated NbS₂ and MoS₂ were functionalized via *in situ* photolysis of CpMn(CO)₃. In the case of exfoliated NbS₂, the resulting product, NbS₂-MnCp(CO)₂, was characterized by FTIR spectroscopy to understand the bonding mode of the CpMn(CO)₂ fragment to the NbS₂ surface. The piano stool arrangement of the carbonyl ligands in CpMn(CO)₃ and the rapid rotation of the Cp ring provide a local C_{3v} symmetry to the Mn complex and result in A₁ + E stretching modes for the carbonyl groups. The A₁ and E stretching frequencies (2019.1 and 1927.3 cm⁻¹, respectively) in the FTIR spectra were assigned based on literature reports, as shown in Figure 2.^{42,45}



Figure 2. FTIR spectra comparing (a) $NbS_2-MnCp(CO)_2$, (b) $CpMn(CO)_2$ -RSH (re-plotted with data from ref 49), and (c) $CpMn(CO)_3$.

Previous literature reports indicate that typically only one carbonyl group photodissociates. This process leaves a single open coordination site on the Mn atom for coordination with the electron-rich sulfur atoms in NbS₂.^{46–49} Following the irradiation of CpMn(CO)₃ in the presence of exfoliated NbS₂, the surface-bound NbS₂–MnCp(CO)₂ complex is expected to have a local symmetry of C_s, and the C–O stretching modes should transform as A' + A". Experimentally, these stretching vibrations were observed at 1924.4 and 1849.2 cm⁻¹ (A' and A", respectively), as shown in Figure 2a. The noticeable red shift in both observed ν (CO) vibrations can likely be ascribed to an increase in the electron density on Mn caused by

coordination with an electron-rich sulfur atom on the NbS₂ basal plane. The increased electron density at Mn results in an additional π -back donation to the C–O ligands, which weakens the C–O bonds.

This result is consistent with earlier reports of IR spectra for similar complexes. For example, in the model complex $CpMn(CO)_2$ -SR, where SR is the 3,5-dimethyl-tetrahydro-2*H*-1,3,5-thiadiazine-2-thione (DTTT) ligand, Mn is bonded to S in a monodentate fashion, and the local symmetry at Mn is also approximately C_s . The two CO stretching vibrations are shifted to lower frequencies relative to $CpMn(CO)_3$.⁴⁶ Similar shifts have also been observed for several $CpMn(CO)_2$ -RSH complexes (Figure 2b) in which the RSH ligand is bonded to the Mn via the sulfur atom.⁴⁹

UV-visible spectra corroborated the results of the IR spectral analysis. The metallic nature of the NbS₂ nanosheets resulted in a relatively featureless absorption curve (Figure S2a). However, a broad band centered around 450 nm indicated some degree of excitonic absorption in the nanosheets. The strong UV absorbance near 330 nm for the CpMn(CO)₃ complex was attributed to the charge transfer between the metal and carbonyl ligands. The absorption spectrum of the functionalized NbS₂ nanosheets showed an increased scattering effect due to limited redispersion of the functionalized nanosheets. However, an absorption band near 360 nm was identified. The band was attributed to the shifting of the 330 nm band of the CpMn(CO)₃ complex to a longer wavelength upon coordination of the CpMn(CO)₂ fragment to the NbS₂ surface during UV irradiation.^{51,52}

Exfoliated MoS_2 under the same *in situ* photolysis conditions did not exhibit any observable carbonyl stretches in the FTIR spectrum of the isolated solid product (Figure S3). Although MoS_2 has both abundant basal plane and edge reactive sites, as well as defect sites, this result suggests that there is negligible reactivity between the photochemically generated CpMn-(CO)₂ fragments and sulfur atoms in MoS_2 under these reaction conditions. The limited reactivity between CpMn-(CO)₂ and MoS_2 demonstrates that the presence of basal plane and edge sulfur sites is not always sufficient for promoting functionalization.

To better understand these results, density functional theory (DFT) was used to calculate the formation energy and electronic structure of the CpMn(CO)₂ fragments (Figure S4) bonded to the MoS₂ and NbS₂ basal planes (Figure S5). While these calculations suggested that both CpMn(CO)₂-functionalized products have negative formation energies (-1.17 and -0.74 eV per CpMn(CO)₂ for NbS₂ and MoS₂, respectively; see the Supporting Information for calculation details), the bonding of CpMn(CO)₂ to MoS₂ is far weaker than to NbS₂. Ball and stick drawings of the optimized structures of both CpMn(CO)₂-functionalized TMDs are shown in Figure 3.

Probing the electronic structures of the functionalized compounds helps us to understand the difference in reactivity of CpMn(CO)₂ with the two TMDs. As shown in Figure 4a, the calculated density of states (DOS) reveals that the d states of the Mn atom overlap more in energy with the p and d states of NbS₂ than with those of MoS₂. This indicates a stronger bonding interaction of CpMn(CO)₂ with NbS₂ than with MoS₂. For NbS₂, electron donation from Mn (a 3d metal) is energetically favorable as it should fill the A'1 partially occupied band (i.e., the half-filled dz^2 band). However, for MoS₂, that band is already fully occupied, and electron



Figure 3. Top and side views of the optimized structures of (a) $NbS_2-MnCp(CO)_2$ and (b) $MoS_2-MnCp(CO)_2$.

donation would involve filling the empty E' band, which is much higher in energy.

We can also visualize and quantify how electrons transfer between TMDs and $CpMn(CO)_2$ by mapping the electron density difference during bond formation (Figure 4). While the Mn-S bonds with the two TMDs both show charge accumulation, Bader charge analysis⁵⁰ indicates that the number of electrons transferred from one $CpMn(CO)_2$ to NbS₂ and MoS₂ are 0.74 and 0.35, respectively. These differences are consistent with the above band structure analysis and help us rationalize the experimentally observed trend in reactivity of NbS₂ and MoS₂.

It should be noted that these DFT calculations did not account for potential side reactions, such as dimerization of $CpMn(CO)_3$ or the formation of solvent-coordinated intermediates.⁵³ It is possible that certain solvents may form fragment-stabilizing intermediates that could have an impact on the formation of the final products.

In an effort to better understand the interaction between $CpMn(CO)_2$ and NbS₂, the NbS₂-MnCp(CO)₂ sample was investigated by XPS. The Nb_{3d} spectrum of unmodified bulk NbS_2 (Figure 5a) could be fitted to the spin-orbit doublet of Nb⁴⁺, with peaks at 205.9 eV $(3d_{3/2} \text{ of Nb}^{4+})$ and 203.1 eV $(3d_{5/2} \text{ of } Nb^{4+})$. The Nb $3d_{3/2}$ and $3d_{5/2}$ binding energies are separated by approximately 2.7 eV with a peak height ratio of approximately 2:3. The observed Nb 3d spectrum of NbS₂- $CpMn(CO)_2$ (Figure 5c) is similar to that of the bulk NbS₂ and was fitted with three pairs of peaks: 209.9 and 207.2 eV $(3d_{3/2} \text{ and } 3d_{5/2} \text{ of } Nb^{5+})$, 206.6 and 203.9 eV $(3d_{3/2} \text{ and } 3d_{5/2})$ of Nb⁴⁺), and 206.0 and 203.3 eV ($3d_{3/2}$ and $3d_{5/2}$ of Nb⁴⁺). In each case, the Nb $3d_{3/2}$ and $3d_{5/2}$ peaks are separated by approximately 2.7 eV with a peak ratio of approximately 2:3. The presence of the Nb⁵⁺ peak set at 209.9 and 207.2 eV is indicative of superficial oxidation of the NbS₂ nanostructures. This oxidation is commonly observed in XPS samples of NbS₂.



Figure 4. Partial density of states plotted relative to the Fermi level (2 dotted lines) for (a) $NbS_2-MnCp(CO)_2$ and (b) $MoS_2-MnCp(CO)_2$. Charge density difference isosurfaces of the corresponding structures are shown on the right. The electron density of the displayed isosurfaces is set at values of $\pm 0.025 \text{ e/Å}^3$, where the green and orange regions reflect charge depletion and charge accumulation, respectively.



Figure 5. XPS spectra of pristine NbS₂ are shown for (a) Nb 3d and (b) S 2p regions. XPS spectra of exfoliated NbS₂ after functionalization with $CpMn(CO)_2$ are shown for (c) Nb 3d, (d) S 2p, and (e) Mn 2p regions, and an (f) XPS survey scan.

Due to the sensitivity of NbS₂ to oxygen, surface oxidation likely occurred during sample preparation for the XPS experiments.⁵⁴ Apart from the surface oxidation, the binding energies of Nb⁴⁺ species were similar in the Nb 3d spectra of bulk NbS₂ and NbS₂-MnCp(CO)₂. These results suggest that

coordination of $CpMn(CO)_2$ to the surface sulfur atoms of NbS_2 does not significantly alter the oxidation state of the Nb atoms.

The S 2p spectrum of bulk NbS₂ (Figure 5b) was fitted with two pairs of peaks: 160.5 and 161.6 eV $(2p_{3/2} \text{ and } 2p_{1/2} \text{ of}$



Figure 6. Atomic force microscopy (AFM) images of exfoliated NbS_2 -MnCp(CO)₂ nanosheets (a) and their detailed lateral morphology (b).

S²⁻), 161.3 and 162.4 eV ($2p_{3/2}$ and $2p_{1/2}$ of ²S²⁻). The S 2p spectrum of NbS₂-MnCp(CO)₂ (Figure 5d) was fitted with three pairs of peaks: 160.7 and 161.9 eV ($2p_{3/2}$ and $2p_{1/2}$ of S²⁻), 161.5 and 162.7 eV ($2p_{3/2}$ and $2p_{1/2}$ of ²S²⁻), and 163.4 and 164.6 eV ($2p_{3/2}$ and $2p_{1/2}$ of S⁰). These peaks were assigned based on values reported in the literature.⁵⁵ The latter pair of peaks were at significantly higher binding energy than any peaks observed in the S 2p spectrum of bulk NbS₂. This suggests that a fraction of the sulfur atoms in the sample (~15%) are more oxidized than those in NbS₂. This fraction likely represents the surface sulfur atoms that form Mn–S bonds with the CpMn(CO)₂ fragment.

Additionally, a small amount of oxidized sulfur (<3% atom) can be observed in the peak deconvoluted into 168.2 eV $(2p_{3/2})$ and 169.4 eV $(2p_{1/2})$. These peaks are consistent with the equivalent surface oxidation identified in the Nb 3d spectrum.

The Mn $2p_{3/2}$ spectrum of NbS₂-MnCp(CO)₂ (Figure 5e) reveals a distinct Mn 2p peak with a binding energy of 641.7 eV. The specific oxidation state of Mn is uncertain due to the similar binding energies of the different oxidation states of Mn.

XPS characterization of the parent $CpMn(CO)_3$ molecule was complicated by the fact that the complex rapidly sublimed in the high vacuum of the XPS chamber. Given the tendency of the complex to sublime, our observation of a Mn signal from functionalized NbS₂ (Figure 5e) supports the idea that the $CpMn(CO)_2$ moiety is chemisorbed or chemically bonded to NbS₂. This conclusion is also consistent with the results of the FTIR analysis.

To estimate the amount of Mn present on the surface of the functionalized NbS₂ sample, the elemental surface composition was calculated from the XPS data. For bulk NbS₂, the sample consisted of 25 ± 2 atom % Nb and 52 ± 3 atom % S, giving an apparent S:Nb ratio of 2. The composition of NbS₂– MnCp(CO)₂ was 3 ± 0.3 atom % Mn, 15.1 ± 2 atom % Nb, and 31 ± 2 atom % S, resulting in an apparent Mn/S/Nb ratio of 0.2:2:1. This elemental ratio is in good qualitative agreement with TGA data (Figure S6), which showed a mass loss at 400 °C of approximately 10%. The calculated mass loss (as Cp(CO)₂) at a Mn/Nb ratio of 0.2:1 is 15%.

In contrast to the NbS₂–MnCp(CO)₂ sample, the XPS spectrum of CpMn(CO)₃-treated MoS₂ (Figure S7) showed no detectable Mn signal. The Mn detection limit is approximately 0.10 atom% under the conditions of the XPS experiment. The lack of a discernible Mn signal indicates that the level of MoS₂ functionalization is at least an order of

magnitude lower than that of NbS₂. This result is consistent with both the FTIR data and electronic structure calculations for CpMn(CO)₂-treated MoS₂ vs NbS₂.

The elemental surface composition analysis results revealed that a significant amount of Mn was present on the surface of the NbS₂-MnCp(CO)₂ sample. Typically, the edge-site sulfur atoms in nanostructured MoS₂ and NbS₂ are reported as the most active sites, while the basal plane sulfur atoms are considerably less reactive. Atomic force microscopy (AFM) was used to understand the particle size and morphology of the NbS_2 -MnCp(CO)₂ samples and to develop a stronger understanding of the site selectivity of $CpMn(CO)_2$ bonding to NbS₂. As shown in Figure 6, the NbS₂-MnCp(CO)₂ samples contained an abundance of nanosheets with an average thickness of 4-10 nm. Histograms of the edge lengths and surface areas of these particles are provided in the Supporting Information (Figure S8). Because the lateral dimensions of the nanosheets are predominantly in the 100-200 nm range (mean diameter 170 nm, i.e., 1-2 orders of magnitude greater than their thickness), it is clear that they are primarily oriented with the layer stacking axis perpendicular to the substrate plane. This implies that photoelectrons detected in XPS experiments are sampling the basal plane surface. As a line-of-sight technique, XPS should be relatively insensitive to molecules bound to edge sites, since the exposed edge area is small and shadowed to some extent.

Because the XPS experiment is primarily sampling the basal plane surface of the nanosheets, we can compare the observed 0.2:2:1 Mn/S/Nb atomic ratio to a calculated saturation coverage of CpMn(CO)₂. The unit cell area (per NbS₂ formula unit) is $a^2 \sin(\pi/3) = 9.62$ Å² (Figure S9). The van der Waals diameter of the Cp ring has been estimated as 6.5 Å,⁵⁶ implying a footprint of ~40 Å² for the CpMn(CO)₂ fragment. This implies that saturation coverage of the basal plane would correspond to a Mn:Nb ratio of about 0.25, in good agreement with the experimental number. While it is likely that CpMn(CO)₂ is also bound to sulfur atoms at edge sites, we cannot draw any conclusions about the edge coverage from the XPS data.

CONCLUSIONS

We have shown that *in situ* photolysis of $CpMn(CO)_3$ under UV light results in the coordination of the electropositive fragment $CpMn(CO)_2$ to electron-rich sulfur atoms on the basal plane of NbS₂. Electronic structure calculations indicate that basal plane functionalization is energetically favorable due

to the filling of the A'1 partially occupied band of NbS₂. This contrasts with MoS_2 , which would result in filling the empty E' band, which is energetically unfavorable.

As a potentially scalable method, functionalization of the basal plane surface of NbS_2 (and possibly other metallic TMDs) by bonding to a coordinately unsaturated transition-metal complex is interesting for potential applications. This straightforward, direct attachment process does not rely on defect chemistry or on intentional oxidation or reduction of the nanosheets. Surface-bound transition-metal complexes may act as electronic dopants by modulating the d-band filling of the nanosheets and possibly as magnetic contacts for experiments that involve injection and collection of spin-polarized carriers. Additionally, the electrophilic substitution of cyclopentadienyl ligands potentially provides an anchoring point for chemically or electronically modifying the connection to the TMD basal planes.

We are optimistic that the insights gained from this study can be leveraged to identify and investigate other organometallic complexes that might be effective for functionalizing the basal planes of a number of TMDs, including MoS_2 .

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02366.

Details of electronic calculation methods, AFM analysis details, supplementary FTIR, PXRD, and XPS data (7 pp.) (PDF)

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Author Contributions

The experimental plan was conceived by T.E.M., J.D.D., and M.A.T.N. Synthesis and characterization experiments were carried out by J.D.D. and M.A.T.N. P.X. performed and interpreted electronic structure calculations, and J.R.S. carried

out and interpreted XPS experiments. The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Grigorieva, I. V.; Geim, A. K. Van Der Waals Heterostructures. *Nature* **2013**, *499*, 419–425.

(2) Fisher, W. G.; Sienko, M. J. Stoichiometry, Structure, and Physical Properties of Niobium Disulfide. *Inorg. Chem.* **1980**, *19*, 39–43.

(3) Lee, C.-H.; Cruz Silva, E.; Calderin, L.; Nguyen, M. A. T.; Hollander, M. J.; Bersch, B.; Mallouk, T. E.; Robinson, J. A. Tungsten Ditelluride: A Layered Semimetal. *Sci. Rep.* **2015**, *5*, No. 10013.

(4) Liu, Z.-L.; Cai, L.-C.; Zhang, X.-L. Novel High Pressure Structures and Superconductivity of Niobium Disulfide. *J. Alloys Compd.* **2014**, *610*, 472–477.

(5) Dholakia, D. A.; Solanki, G. K.; Patel, S. G.; Agarwal, M. K. Optical Band Gap Studies of Tungsten Sulphoselenide Single Crystals Grown by a DVT Technique. *Sci. Iran.* **2003**, *10*, 373–382.

(6) Santiago-Ortiz, Y.; Torres, G. I.; Diaz, A.; Cabrera, C. R. Surface Analysis and Photoelectrochemical Studies of Mixed Polycrystals of p-WSe₂/WS₂. *J. Electrochem. Soc.* **1995**, *142*, 2770–2776.

(7) Gong, Y.; Lin, J.; Wang, X.; Shi, G.; Lei, S.; Lin, Z.; Zou, X.; Ye, G.; Vajtai, R.; Yakobson, B. I.; Terrones, H.; Terrones, M.; Tay, B. K.; Lou, J.; Pantelides, S. T.; Liu, Z.; Zhou, W.; Ajayan, P. M. Vertical and In-Plane Heterostructures from WS₂/MoS₂ Monolayers. *Nat. Mater.* **2014**, *13*, 1135–1142.

(8) Ho, C. H.; Wu, C. S.; Huang, Y. S.; Liao, P. C.; Tiong, K. K. Temperature Dependence of Energies and Broadening Parameters of the Band-Edge Excitons of $Mo_{1-X}W_xS_2$ Single Crystals. *J. Phys.: Condens. Matter* **1998**, *10*, No. 9317.

(9) Komsa, H.-P.; Krasheninnikov, A. V. Two-Dimensional Transition Metal Dichalcogenide Alloys: Stability and Electronic Properties. J. Phys. Chem. Lett. **2012**, *3*, 3652–3656.

(10) Baugher, B. W. H.; Churchill, H. O.; Yang, Y.; Jarillo-Herrero,
P. Optoelectronic Devices Based on Electrically Tunable P-N Diodes
In A Monolayer Dichalcogenide. *Nat. Nanotechnol.* 2014, *9*, 262–267.
(11) Pospischil, A.; Furchi, M. M.; Mueller, T. Solar-Energy
Conversion and Light Emission in an Atomic Monolayer P-N

Diode. Nat. Nanotechnol. 2014, 9, 257–261.
(12) Ross, J. S.; Klement, P.; Jones, A. M.; Ghimire, N. J.; Yan, J.;
Mandrus, D. G.; Taniguchi, T.; Watanabe, K.; Kitamura, K.; Yao, W.;
Cobden, D. H.; Xu, X. Electrically Tunable Excitonic Light-Emitting
Diodes Based On Monolayer WSe₂ p-n Junctions. Nat. Nanotechnol.
2014, 9, 268–272.

(13) Lee, C. H.; Le, G.-H.; Van der Zande, A. M.; Chen, W.; Li, Y.; Han, M.; Cui, X.; Arefe, G.; Nuckolls, C.; Heinz, T. F.; Guo, J.; Hone, J.; Kim, P. Atomically Thin p-n Junctions with Van Der Waals Heterointerfaces. *Nat. Nanotechnol.* **2014**, *9*, 676–681.

(14) Shi, S. F.; Wang, F. Two-Dimensional Materials: Atomically Thin p-n Junctions. *Nat. Nanotechnol.* **2014**, *9*, 664–665.

(15) Chhowalla, M.; Shin, S. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.

(16) Zhu, W.; Yogeesh, M. N.; Yang, S.; Aldave, S. H.; Kim, J.-S.; Sonde, S.; Tao, L.; Lu, N.; Akinwande, D. Flexible Black Phosphorus Ambipolar Transistors, Circuits and AM Demodulator. *Nano Lett.* **2015**, *15*, 1883–1890.

(17) Voiry, D.; Goswami, A.; Kappera, R.; e Silva, C. D.; Kaplan, D.; Fujita, T.; Chen, M.; Asefa, T.; Chlowalla, M. Covalent Functionalization of Monolayered Transition Metal Dichalcogenides by Phase Engineering. *Nat. Chem.* **2015**, *7*, 45–49.

(18) Chen, X.; McDonald, A. R. Functionalization of twodimensional transition-metal dichalcogenides. *Adv. Mater.* **2016**, *28*, 5738–5746.

(19) Park, J.; Yan, M. Covalent Functionalization of Graphene with Reactive Intermediates. *Acc. Chem. Res.* **2013**, *46*, 181–189.

(20) Kang, D. H.; Shim, J.; Jang, S. K.; Jeon, J.; Jeon, M. H.; Yeom, G. Y.; Jung, W.-S.; Jang, Y. He.; Lee, S.; Park, J.-H. Controllable Nondegenerate P-Type Doping of Tungsten Diselenide by Octadecyltrichlorosilane. *ACS Nano* **2015**, *9*, 1099–1107.

(21) Yu, S. H.; Lee, Y.; Jang, S. K.; Kang, J.; Jeon, J.; Lee, C.; Lee, J. Y.; Kim, H.; Hwang, E.; Lee, S.; Cho, J. H. Dye-Sensitized MoS₂ Photodetector With Enhanced Spectral Photoresponse. *ACS Nano* **2014**, *8*, 8285–8291.

(22) Yu, Z.; Pan, Y.; Shen, Y.; Wang, Z.; Ong, Z.-Y.; Xu, T.; Xin, R.; Pan, L.; Wang, B.; Sun, L.; Wang, J.; Zhang, G.; Zhang, Y. W.; Shi, Y.; Wang, X. Towards Intrinsic Charge Transport in Monolayer Molybdenum Disulfide by Defect and Interface Engineering. *Nat. Commun.* **2014**, *5*, No. 5290.

(23) Chou, S. S.; De, M.; Kim, J.; Byun, S.; Dykstra, C.; Yu, J.; Huang, J.; Dravid, V. P. Ligand Conjugation Of Chemically Exfoliated MoS₂. *J. Am. Chem. Soc.* **2013**, *135*, 4584–4587.

(24) Karunadasa, H. I.; Montalvo, E.; Sun, Y.; Majda, M.; Long, J. R.; Chang, C. J. A Molecular MoS₂ Edge Site Mimic for Catalytic Hydrogen Generation. *Science* **2012**, *335*, 698–702.

(25) Sarkar, D.; Xie, X.; Kang, J.; Zhang, H.; Liu, W.; Navarrete, J.; Moskovits, M.; Banerjee, K. Functionalization of Transition Metal Dichalcogenides with Metallic Nanoparticles: Implications for Doping and Gas-Sensing. *Nano Lett.* **2015**, *15*, 2852–2862.

(26) Chen, X.; Berner, N. C.; Backes, C.; Duesberg, G. S.; McDonald, A. R. Functionalization of Two-Dimensional MoS_2 : On the Reaction Between MoS_2 and Organic Thiols. *Angew. Chem., Int. Ed.* **2016**, *55*, 5803–5808.

(27) Lei, S. D.; Wang, X. F.; Li, B.; Kang, J. H.; He, Y. M.; George, A.; Ge, L. H.; Gong, Y. J.; Dong, P.; Jin, Z. H.; Brunetto, G.; Chen, W. B.; Lin, Z. T.; Baines, R.; Galvao, D. S.; Lou, J.; Barrera, E.; Banerjee, K.; Vajtai, R.; Ajayan, P. Surface Functionalization of Two-Dimensional Metal Chalcogenides by Lewis Acid-Base Chemistry. *Nat. Nanotechnol.* **2016**, *11*, 465–472.

(28) Knirsch, K. C.; Berner, N. C.; Nerl, H. C.; Cucinotta, C. S.; Gholamvand, Z.; Mcevoy, N.; Wang, Z.; Abramovic, I.; Vecera, P.; Halik, M.; Sanvito, S.; Duesberg, G. S.; Nicolosi, V.; Hauke, F.; Hirsch, A.; Coleman, J. N.; Backes, C. Basal-Plane Functionalization of Chemically Exfoliated Molybdenum Disulfide by Diazonium Salts. *ACS Nano.* **2015**, *9*, 6018–6030.

(29) Yan, E. X.; Cabán-Acevedo, M.; Papadantonakis, K. M.; Brunschwig, B. S.; Lewis, N. S. Reductant-Activated, High-Coverage, Covalent Functionalization of 1T'-MoS₂. ACS Mater. Lett. **2020**, 2, 133–139.

(30) Vera-Hidalgo, M.; Giovanelli, E.; Navío, C.; Pérez, E. Mild Covalent Functionalization of Transition Metal Dichalcogenides with Maleimides: A "Click" Reaction for 2H-MoS₂ and WS₂. *J. Am. Chem. Soc.* **2019**, *141*, 3767–3771.

(31) Quirós-Ovies, R.; Vazquez Sulleiro, M.; Vera-Hidalgo, M.; Prieto, J.; Gomez, I. J.; Sebastian, V.; Santamaria, J.; Perez, E. M. Controlled Covalent Functionalization of 2-H MoS2 with Molecular or Polymeric Adlayers. *Chem. - Eur. J.* **2020**, *26*, 6629–6634.

(32) Liu, H.; Grasseschi, D.; Dodda, A.; et al. Spontaneous Chemical Functionalization via Coordination of Au Single Atoms on Monolayer MoS₂. *Sci. Adv.* **2020**, *6*, No. eabc9308.

(33) Backes, C.; Berner, N.; Chen, X.; et al. Functionalization of Liquid-Exfoliated Two-Dimensional 2H-MoS₂. *Angew. Chem., Int. Ed.* **2015**, *54*, 2638–2642.

(34) Meza, E.; Diaz, R.; Li, C. Solution-Phase Activation and Functionalization of Colloidal WS₂ Nanosheets with Ni Single Atoms. *ACS Nano* **2020**, *14*, 2238–2247.

(35) Qi, K.; Cui, X.; Lin, G.; et al. Single-Atom Cobalt Array Bound to Distorted 1T MoS2 with Ensemble Effect for Hydrogen Evolution Catalysis. *Nat. Commun.* **2019**, *10*, No. 5231.

(36) Su, H.; Chen, L.; Chen, Y.; et al. Single Atoms of Iron on MoS_2 Nanosheets for N₂ Electroreduction into Ammonia. *Angew. Chem., Int. Ed.* **2020**, *59*, 20411–20416.

(37) Lou, Y.; Zhao, Y.; Liu, H.; et al. Edge-Confined Pt₁/MoS₂ Single-Atom Catalyst Promoting the Selective Activation of Carbon-Oxygen Bond. *ChemCatChem* **2021**, *13*, 2783–2793.

(38) Fan, X.; Xu, P.; Li, Y. C.; Zhou, D.; Sun, Y.; Nguyen, M. A. T.; Terrones, M.; Mallouk, T. E. Controlled Exfoliation of MoS₂ Crystals into Trilayer Nanosheets. J. Am. Chem. Soc. **2016**, 138, 5143–5149.

(39) Benoit, P. H. Adaptation to Microcomputer of the Appleman-Evans Program for Indexing and Least-Squares Refinement of Powder-Diffraction Data for Unit-cell Dimensions. *Am. Mineral.* **1987**, 72, 1018–1019.

(40) Jellinek, F.; Brauer, G.; Muller, H. Molybdenum and Niobium Sulphides. *Nature*. **1960**, *185*, 376–377.

(41) Dickinson, R. G.; Pauling, L. The Crystal Structure of Molybdenite. J. Am. Chem. Soc. **1923**, 45, 1466.

(42) Li, W.; Wei, X.; Dong, H.; Ou, Y.; Xiao, S.; Yang, Y.; Xiao, P.; Zhang, Y. Colloidal Synthesis of NbS2 Nanosheets: From Large-Area Ultrathin Nanosheets to Hierarchical Structures. *Front. Chem.* **2020**, *8*, No. 189.

(43) Si, J.; Zheng, Q.; Chen, H.; Lei, C.; Suo, Y.; Yang, B.; Zhang, Z.; Li, Z.; Lei, L.; Hou, Y.; Ostrikov, K. Scalable Production of Few-Layer Niobium Disulfide Nanosheets via Electrochemical Exfoliation for Energy-Efficient Hydrogen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2019**, *11*, 13205–13213.

(44) Park, D. J. Vibrational Spectra of Tricarbonyl(π -cyclopentadienyl) manganese, bis-[tricarbonyl(π -cyclopentadienyl)-molybdenum], and Their Deuterated Derivatives. *Spectrochim. Acta, Part A* **1975**, *31*, 1789–1798.

(45) Adams, D. M.; Squire, A. Re-Assignment of the Vibrational Spectra of π -cyclopentadienyl- and Methyl- π -cyclopentadienyl-manganese Tricarbonyl. J. Org. Chem. 1973, 63, 381–388.

(46) Sert, S.; Ercag, A.; Senturk, O. S.; Sterenberg, B. T.; Udachin, K. A.; Ozdemir, U.; Sarikahya, F. U. Photochemical Reactions of Metal Carbonyls $[M(CO)_6 (M = Cr, Mo, W), Re(CO)_5 Br, Mn(CO)_3 Cp]$ with 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (DTTT) and the Crystal Structure of $[W(CO)_5 (DTTT)]$. Polyhedron 2003, 22, 1689–1693.

(47) Molvinger, K.; Childs, G. I.; Jobling, M.; Roper, M.; George, M. W.; Poliakoff, M. IR Evidence for the Generation of $(C_5H_5)Mn(CO)_2(N_2O)$ in Near-Critical N₂O at Room Temperature and in Polyethylene Matrices at Low Temperature. *Chem. Lett.* **2000**, *29*, 1260–1261.

(48) Kemnitz, C. R.; Ball, E. S.; McMahon, R. J. Photochemistry of $CpMn(CO)_3$ and Related Derivatives: Spectroscopic Observation of Singlet and Triplet $CpMn(CO)_2$. *Organometallics* **2012**, *31*, 70–84.

(49) Tan, K. Y. D.; Kee, J. W.; Fan, W. Y. CpMn(CO)₃-Catalyzed Photoconversion of Thiols into Disulfides and Dihydrogen. *Organometallics* **2010**, *29*, 4459–4463.

(50) Tang, W.; Sanville, E.; Henkelman, G. A. Grid-Based Bader Analysis Algorithm without Lattice Bias. *J. Phys.: Condens. Matter* **2009**, 21, No. 084204.

(51) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakoff, M. Structure and Reactivity of $(.eta.5-C_5H_5)Mn(CO)_2$ in Room-Temperature Solution. Evidence for Formation of a Dinuclear Intermediate Detected by Flash Photolysis and Time-Resolved Infrared Spectroscopy. *Organometallics* **1987**, *6*, 2600.

(52) Lundquist, R.; Cais, M. Ultraviolet Spectra of Organometallic Compounds. J. Org. Chem. 1962, 27, 1167–1172.

(53) Lugovskoy, S.; Lin, J.; Schultz, R. H. Ligand Substitution Reactions of the $CpMn(CO)_2(cyclohexane)$ Intermediate Studied by Time-Resolved Infrared Absorption Spectroscopy. *Dalton Trans.* **2003**, 3103–3110.

(54) Li, Z.; Yang, W.; Losovyj, Y.; Chen, J.; Xu, E.; Liu, H.; Werbianskyj, M.; Fertig, H. A.; Ye, X.; Zhang, S. Large-Size Niobium Disulfide Nanoflakes Down to Bilayers Grown by Sulfurization. *Nano Res.* **2018**, *11*, 5978–5988.

(55) Liang, K. S.; Cramer, S. P.; Johnston, D. C.; Chang, C. H.; Jacobson, A. J.; Neufville, J. P.; Chianelli, R. R. Amorphous Molybdenum Trisulfide and Tungsten Trisulfide. *J. Non-Cryst. Solids.* **1980**, *42*, 345–356.

(56) Li, L. J.; Khlobystov, A.; Wiltshire, J.; et al. Diameter-Selective Encapsulation of Metallocenes in Single-Walled Carbon Nanotubes. *Nat. Mater.* **2005**, *4*, 481–485.

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