Controlled Doping of Vacancy-Containing Few-Layer MoS₂ via Highly Stable Thiol-Based Molecular Chemisorption

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ABSTRACT MoS₂ is considered a promising two-dimensional active channel material for future nanoelectronics. However, the development of a facile, reliable, and controllable doping methodology is still critical for extending the applicability of MoS₂. Here, we report surface charge transfer doping via thiol-based binding chemistry for modulating the electrical properties of vacancy-containing MoS₂ (v-MoS₂). Although vacancies present in 2D materials are generally regarded as undesirable components, we show that the electrical properties of MoS₂ can be systematically engineered by exploiting the tight binding between the thiol group and sulfur vacancies and by choosing different functional groups. For example, we demonstrate that NH₂-containing thiol molecules with lone electron pairs can serve as an n-dopant and achieve a substantial increase of electron density (Δn = 3.7 × 10¹² cm⁻²). On the other hand, fluorine-rich molecules can provide a p-doping effect (Δn = −7.0 × 10¹¹ cm⁻²) due to its high electronegativity. Moreover, the n- and p-doping effects were systematically evaluated by photoluminescence (PL), X-ray photoelectron spectroscopy (XPS), and electrical measurement results. The excellent binding stability of thiol molecules and recovery properties by thermal annealing will enable broader applicability of ultrathin MoS₂ to various devices.

KEYWORDS: molybdenum disulfide - surface charge transfer doping - chemisorption - sulfur vacancy - thiol chemistry

The discovery of graphene has promoted significant interest in other two-dimensional (2D) materials, especially transition metal dichalcogenides (TMDs), due to their unique electrical, chemical, and mechanical properties. Although graphene possesses a high mobility of up to 10⁶ cm²/V·s, the absence of a band gap seriously limits its application as an active channel material in electronic or optoelectronic devices such as photodetection or switching device applications. Alternatively, molybdenum disulfide (MoS₂), one of the most widely studied semiconducting TMDs, has a thickness-dependent energy band gap and band structure: an indirect band gap of 1.2 eV in a bulk state and a direct band gap of 1.8 eV in a monolayer form. Because of these reasons, MoS₂ has gained much attention as a promising channel material in next-generation nanoelectronics.

In general, a mechanical exfoliation approach using bulk MoS₂ can produce high-quality MoS₂ sheets with minimal defects. Field-effect transistors (FET) based on mechanically exfoliated MoS₂ show a high on/off current ratio of up to 10⁸, a steep subthreshold swing of 70 mV/dec, and a large in-plane carrier mobility of 200–500 cm²/V·s. On the other hand, liquid and chemical exfoliation, physical vapor deposition (PVD) such as vapor–solid growth, and chemical vapor deposition (CVD) of MoS₂ are more suitable for large-scale integration of nanoelectronic devices. However, chemically exfoliated and CVD or PVD-grown MoS₂ accompanies abundant disordered structural defects. Intrinsic and extrinsic defects such as vacancies, point defects, and grain boundaries on MoS₂ are inevitable during the synthesis process. Moreover, these defects are the major traps or scattering centers of charge carriers, leading to a relatively low mobility and current level in FETs. On the other hand, defects can provide new opportunities to tailor the physical and chemical properties of MoS₂.
chemical properties of MoS$_2$.\textsuperscript{22,23} In general, perfect MoS$_2$ sheets are free of dangling bonds, and therefore it is difficult to attach functional molecules on their surfaces. However, sulfur-containing groups can be bonded with unsaturated Mo edges or sulfur vacancies in MoS$_2$.\textsuperscript{24,25} On this background, surface functionalization of MoS$_2$ using sulfur vacancies and thiol molecules has been reported recently.\textsuperscript{14,26,27} In addition, defects can also serve as active sites to improve the hydrogen evolution reaction (HER) with a large cathodic current density and small Tafel slope and to realize sensors with excellent adsorption ability.\textsuperscript{28–30}

To further enhance the applicability of ultrathin TMDs including few-layer MoS$_2$ as a 2D active channel material, the development of a more facile and universal method for modulating their electrical properties is essential. However, few-layer MoS$_2$ cannot be doped via traditional techniques such as ion implantation due to its ultrathin nature. Chemical and molecular doping via surface charge transfer thus were previously demonstrated using various types of molecules such as potassium,\textsuperscript{31} benzyl viologen (BV),\textsuperscript{32} polyethyleneimine (PEI),\textsuperscript{33} chloride molecules,\textsuperscript{34} cesium carbonate,\textsuperscript{6} and self-assembled monolayers.\textsuperscript{35,36} However, these approaches still suffer from stability issues or mainly focus on reducing the contact resistance to improve the performance of FETs. Therefore, it is highly desired to develop a more reliably and systematic way to adjust the doping level of few-layer MoS$_2$ to facilitate wider application to future nanoelectronic devices.

In this work, we report a facile and effective chemical doping method for modulating the carrier concentration of few-layer MoS$_2$ based on the attachment of thiol molecules on vacancy sites existing on MoS$_2$ surfaces. Because sulfur-containing functional groups can form covalent bonds with unsaturated Mo edges or sulfur vacancies in MoS$_2$, thiol molecules with various functional groups can easily be absorbed and tightly bound to sulfur vacancies of MoS$_2$ and can act as donors or acceptors via surface charge transfer. To demonstrate the doping effect, we chose two thiol-terminated molecules containing NH$_2$ or F-containing groups as n-doping and p-doping sources, respectively. NH$_2$ groups have lone electron pairs, and thus can donate electrons to MoS$_2$,\textsuperscript{36} while F-containing groups withdraw electrons from MoS$_2$ due to its high electronegativity.\textsuperscript{37} The proposed doping method was tested in FETs, and the observed electrical characteristics were shown to be consistent with the other experimental data. The excellent binding stability of thiol molecules and the reversibility of their doping effect can be exploited to realize more robust 2D devices such as sensors with better sensitivity and reversibility.

RESULTS AND DISCUSSION

To investigate the doping effect of thiol-terminated molecules, we prepared 4-layer MoS$_2$ samples after confirming the number of layers by a Raman scattering analysis and an atomic force microscopy (AFM) analysis, as shown in Figure S1 in the Supporting Information. The frequency difference of 24.5 cm$^{-1}$ between the E$_{1g}$ and A$_{1g}$ modes in the Raman spectra and the sample thickness of $\sim$2.7 nm (thickness of monolayer MoS$_2$ = $\sim$0.65 nm) from the AFM measurement support the successful acquisition of 4-layer MoS$_2$ via mechanical exfoliation.\textsuperscript{38} Figure 1a and 1b depict optical microscopy (OM) and AFM images of an as-exfoliated 4-layer MoS$_2$ sample with residual contaminants from adhesive tape. To remove the residue and also to create binding sites for molecular attachment (this will be discussed in detail later), the MoS$_2$ samples were annealed at 250 °C in air for 1 h, and thus a clean surface was obtained (Figure 1c and d). Moreover, because thermal annealing was performed at a relatively low temperature of below 300 °C, triangular etch pits were not formed.\textsuperscript{39,40} Meanwhile, the AFM image obtained for the sample annealed at 310 °C in air for 1 h reveals the formation of surface etch pits with an average size of 113 nm, as shown in Figure S2 in the Supporting Information.

During the thermal treatment, sulfur vacancies can be artificially created because the sulfur vacancy formation energy is lower than the formation energies of other vacancies.\textsuperscript{32} Thus, we investigated the samples before and after thermal annealing using X-ray photoelectron spectroscopy (XPS) to identify whether sulfur vacancies were generated by the thermal treatment. All XPS spectra were calibrated using the C 1s peak at 284.5 eV as a reference. As shown in Figure 1e, the XPS spectra of Mo 3d consisted of three sets of peaks that can be respectively assigned to MoO$_3$ (yellow), intrinsic MoS$_2$ (i-MoS$_2$), and vacancy-containing MoS$_2$ (v-MoS$_2$). The deconvoluted Mo$^{4+}$ 3d$_{5/2}$ and Mo$^{5+}$ 3d$_{3/2}$ peaks depict the contributions of i-MoS$_2$ (doublets located at 232.3 and 229.1 eV) and v-MoS$_2$ (peaks at 231.8 and 228.8 eV).\textsuperscript{41} After thermal annealing, the intensity of the i-MoS$_2$ peak decreased, while the intensity of the v-MoS$_2$ peak significantly increased. As a result, the peaks of Mo$^{4+}$ 3d$_{5/2}$ and Mo 3d$_{3/2}$ were shifted to the lower binding energy side. This reveals that the density of sulfur vacancies was increased by the thermal annealing at 250 °C, because the v-MoS$_2$ peak is directly associated with sulfur vacancies.\textsuperscript{41} The generation of sulfur vacancies was further confirmed by the atomic ratio of S/Mo acquired from the XPS spectra. The S/Mo ratio decreased from 1.88 (as exfoliated, Figure 1f, top) to 1.39 (thermal-annealed, Figure 1f, bottom). The magnitude of the peaks corresponding to MoO$_3$, which can be deconvoluted into Mo$^{6+}$ doublets of 3d$_{5/2}$ and 3d$_{3/2}$, located at 232.8 and 235.4 eV, also slightly increased after thermal annealing, suggesting that MoS$_2$ was partially oxidized. This partial oxidation is related to the compensation of carrier density, which will be discussed in the next part.
To further evaluate the change of surface stoichiometry, we annealed the MoS2 sheets at 250 °C in air with increasing treatment time, as shown in Figure S3. With a longer treatment time, Mo4+ 3d3/2 and Mo4+ 3d5/2 peaks shifted to the lower binding energy side due to the increase of the v-MoS2 peak and the MoO3 peak, as shown in Figure S3a. We also observed that the ratio of i-MoS2 to v-MoS2 and S/Mo decreased with increasing annealing time, indicating an increase of sulfur vacancy concentration (Figure S3b). In particular, the change of the surface S/Mo ratio from 1.88 to 1.39 by annealing the sample for 1 h implies the formation of a substantial amount of sulfur vacancies. The evaluation of the surface stoichiometry provides a useful metric for quantitatively estimating the degree of vacancy creation by thermal annealing.

To compare the quality of MoS2 samples with and without thermal annealing, we systematically performed electrical characterizations using back-gated FETs made of as-exfoliated MoS2 and MoS2 annealed at 250 and 310 °C (Figure S4a). The transfer curve of the FET device with 250 °C-annealed MoS2 is close to that of pristine MoS2, and its on-current only slightly decreased compared to the pristine sample (Figure S4b), despite the formation of additional sulfur vacancies serving as an n-dopant. The small change of the on-current is attributed to the effect of partial oxidation, causing a p-doping effect. Additionally, the nonlinear output curve of the 250 °C-annealed MoS2 FET, as shown in the inset of Figure S4b, indicates the presence of a Schottky barrier between Ti and MoS2. On the other hand, the on-current level of the FET device with 310 °C-annealed MoS2 was greatly reduced (from 4.6 × 10−7 A to 4.6 × 10−12 A at gate-source voltage (VGS) = 20 V), and the on/off ratio thus became lower than 10. This can be explained by a high defect density and the existence of many etch pits. Thus, we used the v-MoS2 samples treated at 250 °C to investigate the thiol-binding-based chemical doping of vacancy-containing MoS2.

Figure 2a presents a schematic illustration of the thiolated ligand conjugation mechanism on v-MoS2. After the cleavage of S–H bonds, remaining sulfur atoms can be chemically absorbed on the sulfur vacancies. We presumed that the different ligand molecules attached on MoS2 can enable charge transfer between MoS2 and the ligands, and thus they can act as surface charge-transfer donors and acceptors. Two thiol-terminated molecules containing NH2 or fluorine-rich groups were used to modulate the electrical properties of v-MoS2 in this study, as depicted in Figure 2b. Because of the lone pair of electrons present in the NH2 group, it is expected that mercaptotethylamine (NH2-terminated thiol, MEA) can donate electrons to v-MoS2, consequently leading to an n-doping effect. In contrast, 1H,1H,2H,2H-perfluorodecanethiol...
(CF3-terminated thiol, FDT) can withdraw electrons from v-MoS2 because of the high electronegativity of fluorine atoms and can provide a p-doping effect.37 MEA and FDT have the same spacer group composed of two carbon atoms, and the length of two carbon atoms as a spacer group is short enough to transfer charge between the functional group and the MoS2 surface, as also reported in previous studies.26,37,44,45 MEA-treated (MEA-MoS2) and FDT-treated (FDT-MoS2) samples were immersed in ethanol and tetrahydrofuran (THF) for 12 h in order to completely remove the residual unbound molecules, which are only weakly physisorbed on v-MoS2 sheets. After the molecule-attachment and washing process, the chemical states of v-MoS2, MEA-MoS2, and FDT-MoS2 were investigated by XPS to confirm the secure binding of thiol-terminated molecules on MoS2. The splitting of C 1s spectra indicates the presence of C–N bonds on MEA-MoS2 and C–F bonds on FDT-MoS2, respectively (Figure 2c). The entire C 1s peak of MEA-MoS2 and FDT-MoS2 shifted slightly toward higher binding energy compared to that of v-MoS2. As shown in Figure 2d, Mo 3p3/2 peaks at 395.1 eV were observed for all samples, while only MEA-MoS2 has clear N 1s peaks. In contrast, the F 1s peak was obtained for only FDT-MoS2 due to the CF2 and CF3 groups in FDT (Figure 2e). These XPS analysis results led to the conclusion that MEA and FDT molecules were tightly bound on the surface of MoS2 after the repeated washing processes.

We also characterized the surface topography of MEA-MoS2 and FDT-MoS2 by AFM before (Figure 3a and 3b) and after the doping process (Figure 3c and 3d) to further confirm the binding of thiol molecules. The surface roughness of the silica substrate after MEA and FDT treatments (blue circle) did not change significantly because the weak binding of SiO2 and thiol groups may not be sufficient to prevent detachment of the molecules during the washing process. However, the surface roughness of MEA-MoS2 and FDT-MoS2 (yellow circle) was increased from 0.0865 to 0.2815 nm and from 0.107 to 0.3905 nm, respectively, suggesting the existence of the molecules after the washing process. These AFM scanning results suggest that the thiol-terminated molecules were tightly absorbed only on v-MoS2.

In order to investigate the surface charge transfer effect between the functional groups of thiol molecules and v-MoS2, we also performed photoluminescence (PL) measurement because the n-doping and p-doping effects of the molecules can induce red-
blue-shift of the PL peaks, respectively. To minimize the effect of spatial inhomogeneity, the PL spectra were measured within the channel region after fabricating MoS2 FETs. We confirmed that the PL and Raman spectra obtained from the channel region have consistent peak positions, as shown in Figure S5c and S5d. If MEA donates electrons to v-MoS2, these excess electrons would be bound with photoexcited electron–hole pairs to form trions.46 Figure 3e depicts that the measured PL spectra of MEA-MoS2 was red-shifted and noticeably weakened, which is an indication of n-doping. On the other hand, the PL spectra of FDT-MoS2 were blue-shifted and more intensified because of the p-doping effect by F-containing groups and the resultant enhancement of the PL from excitons (Figure 3f). These PL characterization results reveal that various functional groups can be combined with the thiol-termination group to induce surface charge transfer and attached molecules can consequently act as a dopant for modulating the electrical properties of v-MoS2.

We now demonstrate how the surface charge transfer doping affected the performance of the FET devices, as schematically illustrated in Figure 4a and 4b. Figure 4c presents the transfer curve of v-MoS2 FET doped with MEA. The measurement was carried out in a glovebox and with a drain-source voltage (VDS) of 0.5 V. The variations of the threshold voltage (Vth) obtained from the transfer curves after doping and thermal annealing are summarized in Table 1. MEA-treatment on v-MoS2 led to a negative shift of Vth and a slight increase of the drain current (IDS), which implies n-doping of v-MoS2. Nevertheless the degree of change observed upon doping via attachment of MEA molecules is relatively small, and it may be attributed to the adsorbed H2O and O2 acting as a p-dopant for MoS2.43 In addition to adsorption on the MoS2 surface, the hydrophilic NH2 group can absorb a large quantity of H2O molecules. Thus, to remove physisorbed H2O and O2, the doped MoS2 samples were annealed at 150 °C for 10 min, and additional FET characterization was carried out to tell apart the original doping effect by thiol-terminated molecules from the parasitic effects from H2O and O2. A significant negative shift of Vth and a marked increase of IDS were observed after the annealing process, as shown in Figure 4c. On the other hand, even without additional thermal treatment, a clear positive shift of Vth and a substantial decrease of the overall current were obtained upon binding of FDT, indicating significant p-doping of v-MoS2 (Figure 4d). In order to eliminate the additional contribution caused by the adsorption of H2O and O2 molecules, we performed the same annealing treatment as applied to MEA-MoS2. Despite the decreased p-doping effect caused by the removal of H2O and O2, the IDS of the FDT-MoS2 FET device remained lower than that of v-MoS2, indicating that its n-concentration is still significantly lower than that of v-MoS2. In addition, its Vth was also larger compared to that of the v-MoS2 FET device. Both observations confirm the p-doping effect by the attached FDT molecules. These transfer characteristics of the devices based on MEA and FDT-treated MoS2 are consistent with the PL analysis results shown above.
Figure 4. Electrical characterizations of FET devices based on the functionalized MoS2. (a, b) Schematic illustration presenting charge transfer doping of a back-gated MoS2 FET with MEA and FDT molecules, respectively. (c, d) Transfer characteristics of MEA-MoS2 and FDT-MoS2 obtained with \( V_{GS} = 0.5 \) V; before doping (black line), after doping (blue line), after doping and annealing (red line). (e) Changes in carrier density before and after doping process (measured at \( V_{GS} = 0 \) V).

**TABLE 1. Variation in Threshold Voltage \( (V_{th})^a \) of MEA-MoS2 and FDT-MoS2 FET Devices**

<table>
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<tr>
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<th>MEA-MoS2</th>
<th>FDT-MoS2</th>
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<tr>
<td>( V_{th} ) [V]</td>
<td>undoped</td>
<td>doped</td>
</tr>
<tr>
<td></td>
<td>-25</td>
<td>-38.5</td>
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* \( V_{th} \) was defined at \( V_{DS} \) having a drain current of 1 nA (constant current method).

From these transfer curves, we calculated the carrier density \( n_{2D} \) to quantitatively compare the doping levels of MEA-MoS2 and FDT-MoS2 using the equation \( n_{2D} = \frac{1}{2LW} \frac{dI_D}{dV_{GS}} \), where \( q \) is the electron charge, \( L \) and \( W \) are the channel length and width, respectively, and \( \mu \) is the mobility at \( V_{GS} = 0 \). The mobility was extracted using the following equation with the gate capacitance \( (C) \) of \( 1.15 \times 10^{-8} \) F/cm\(^2\) (SiO\(_2\) 300 nm).

\[
\mu = \frac{\partial I_D}{\partial V_{GS}} \frac{L}{WC_{V_{DS}}}
\]

The estimated \( n_{2D} \) values of MEA-MoS2 and FDT-MoS2 are presented in Figure 4e. The carrier density was increased from \( 9.4 \times 10^{11} \) cm\(^{-2}\) to \( 1.4 \times 10^{12} \) cm\(^{-2}\) \((\Delta n = 4.6 \times 10^{11} \text{ cm}^{-2})\) by the MEA treatment on \( v\)-MoS\(_2\). After thermal annealing, significant enhancement of the carrier density \( (\Delta n = 3.7 \times 10^{12} \text{ cm}^{-2})\) was observed, due to the removal of adsorbed molecules. In the case of FDT-MoS2, the estimated carrier density changes \( (\Delta n_{2D}) \) were \(-7.0 \times 10^{11} \text{ cm}^{-2}\) after doping with FDT and \(-1.8 \times 10^{11} \text{ cm}^{-2}\) after postdoping annealing. These doping concentrations are comparable with recently reported values of n-doping with potassium and benzyl viologen \((-1 \times 10^{13} \text{ cm}^{-2})\)\(^{31,32}\) and p-doping with octadecyltrichlorosilane (OTS) \((-1.4 \times 10^{11} \text{ cm}^{-2})\).\(^{35}\) Furthermore, we also confirm the p-doping effect using 2,2,2-trifluoroethanithiol (TFET) with three fluorine atoms (in Figure S6a) with a much smaller number of fluorine atoms per molecule compared to FDT with 21 fluorine atoms. The overall length of TFET is much shorter than that of FDT and is comparable with that of MEA. As shown in Figure S6b, TFET also provides a p-doping effect, although TFET-MoS2 demonstrates a relatively smaller decrease of drain current than the case of the FDT-doped FET device. Also, the change of carrier density \( (\Delta n = -1.85 \times 10^{11} \text{ cm}^{-2})\) and the shift of threshold voltage \( (\Delta V_{th} = 4.7 \text{ V})\) were smaller than those \( (\Delta n = -7.0 \times 10^{11} \text{ cm}^{-2} \text{ and } \Delta V_{th} = 8.5 \text{ V})\) of FDT-MoS2, as depicted in Figure S6c, which can be explained by the different number of fluorine atoms in the functional groups. This suggests that the surface charge transfer effect dominates the doping effect and can be modulated quantitatively by choosing appropriate functional groups.

The n-doping with MEA and p-doping with FDT were also confirmed by high-resolution XPS spectra of Mo 3d and S 2p, as shown in Figure S7. The Mo 3d and S 2p peaks shifted to higher binding energy, which is caused by a reduction of the work function after the charge transfer.\(^6\) In contrast, the FDT treatment would increase the work function of v-MoS\(_2\) due to the charge transfer from v-MoS\(_2\) to FDT, which was confirmed by the negative shift of the Mo 3d and S 2p peaks.

The doping effect by the chemisorbed molecules also influenced the output characteristics of MoS\(_2\) FETs. As the n-doping effect increases, the channel conductivity, the relative contribution from contact to total resistance rises, and thus more nonohmic behavior is observed in the output characteristics of MEA-MoS\(_2\) (Figure S8a). On the other hand, in the case of FDT-MoS\(_2\), due to the decreased channel conductivity resulting from the p-doping effect, the channel resistance was relatively more dominant in the total...
resistance, leading to more ohmic-like characteristics (Figure S8b).

To investigate the effect of the MoS2 thickness on doping density, we compared 2-layer, 4-layer, and bulk MoS2 using MEA, as shown in Figure S9. The trend of the n-doping effect upon the molecular MEA-functionalization and thermal annealing is similar to the results obtained with a 4-layer MoS2 FET, as shown in Figure S9a and S9b. The change of carrier density increased with a decreasing number of layers, as presented in Table S1. The double-layer MoS2 FET showed the highest enhancement of current at $V_{GS} = 0\, \text{V}$ (about a 19.7-fold increase) and carrier density changes ($\Delta n = 7.6 \times 10^{12} \, \text{cm}^{-2}$) after thermal annealing in a glovebox, consistent with previous studies.\(^{36,47}\)

Furthermore, we measured the transfer curve of MEA-MoS2 in ambient conditions to confirm the air stability of the doping effect. Because our v-MoS2 obtained by annealing at 250 °C has abundant sulfur vacancies, H$_2$O and O$_2$ molecules are easily absorbed on the vacancy sites in ambient conditions, and thus the current level is lower than that measured in a glovebox (Figure 5a, plotted in a semilog scale). After doping with MEA and subsequent annealing at 150 °C for 10 min, the transfer curve measured in ambient conditions (Figure 4c) is similar to the results obtained in a glovebox, as shown in Figure 5b. However, the current level significantly decreased after storage in air for 7 days due to the adsorption of H$_2$O and O$_2$ on MEA-MoS2 (Figure 5c). Thus, the total resistance ($R_{tot}$) of this sample underwent a 10$^3$-fold increase at $V_{GS} = -40\, \text{V}$ ($R_{tot}$ of the first annealed MEA-MoS2 sample = $4.4 \times 10^5\, \Omega$; $R_{tot}$ after 2 days in air = $1.23 \times 10^8 \, \Omega$; $R_{tot}$ after 7 days in air = $5.11 \times 10^8 \, \Omega$, as shown in Figure 5d. However, the second annealing at 150 °C for 10 min restored the current level to that of the first annealed sample, and consequently the total resistance was also recovered. Moreover, this low resistance state was maintained during additional storage (4 days) in a glovebox. This behavior reveals that the thiol molecules bound with MoS2 were not degraded during the long storage in an air environment and thermal annealing at 150 °C, suggesting this doping method lends excellent stability.

**CONCLUSIONS**

In summary, we have demonstrated a highly effective and stable surface charge transfer doping mechanism based on thiol-based molecular functionalization. We showed that the vacancy sites of MoS2 can be artificially created by thermal annealing and can act as the binding sites for thiol-terminated molecules. As a demonstration, we showed that amine-containing MEA and F-containing FDT molecules can be selectively chemisorbed and tightly bound on sulfur vacancies via the strong interaction between the thiol and the S-vacancy. Surface charge transfer between MoS2 and functional groups of bound molecules and a consequent doping effect were confirmed by systematic characterizations using XPS, PL spectroscopy, Raman spectroscopy, and electrical measurements on FET devices. Significant enhancement ($\Delta n = 3.7 \times 10^{12} \, \text{cm}^{-2}$; MEA-treated and thermal-annealed) or reduction ($\Delta n = -1.8 \times 10^{11} \, \text{cm}^{-2}$; FDT-treated and thermal-annealed) of the carrier density was obtained.
METHODS

Materials. Molybdenum disulfide (MoS₂) was purchased from 2D SEMICONDUCTORS, INC. 2-mercaptoprothanolamine (NH₂-terminated thiol, MEA), 1H,1H,2H,2H-perfluorodecanethiol (CF₃-terminated thiol, FDT) and 2,2,2-trifluoroethanthiol (TFET) were purchased from Sigma-Aldrich. AZ5214E photoresist, AZ300-MIF developer, and AZ400T lift-off solution used in photolithography were purchased from Microchemical, INC.

Preparation and Doping of Vacancy-Containing MoS₂. Few-layer MoS₂ was mechanically exfoliated from bulk MoS₂ using a Scotch tape method and was placed onto 300 nm-thick SiO₂ on a heavily p-doped Si substrate. Optical microscopy was used to identify the thickness and location of MoS₂ sheets. The samples were placed in the middle of a tube furnace and annealed at 250 °C for 1 h. For the monolayer formation of MEA and FDT molecules on v-MoS₂ samples, the samples were soaked in a solution of 1/40 (v/v) MEA/ethanol and FDT/THF for 72 h. They were then rinsed with ethanol and THF. Blown dry with N₂ and baked at 100 °C for 30 min in a dry glovebox. After being baked, the MEA treated and FDT treated samples were immersed in ethanol and tetrahydrofuran (THF) for 12 h to remove unbound molecules.

Characterization of Doped/Undoped MoS₂. The thickness and the surface roughness of the v-MoS₂ samples were obtained using atomic force microscopy (AFM, XE-70, Parksystems). All AFM images were collected with 10 × 10 um scan size and a 0.1 Hz scan rate. Raman spectroscopy and photoluminescence (PL) analyses were performed using a LabRAM ARAMIS system (Horiba scientific) with a 514 nm excitation laser under ambient conditions (scan range: 350 to 450 cm⁻¹ for Raman analysis and 580 to 720 nm for PL measurement). An X-ray photoelectron spectroscopy (XPS) analysis was carried out using a multipurpose X-ray photoelectron spectrometer (Sigma Probe, Thermo VG Scientific).

Fabrication and Characterization of MoS₂ FET Devices. Back-gated MoS₂ FETs were fabricated using conventional photolithography. To pattern the source and drain electrodes, we used a photore sist (AZ5142E) and a mask aligner (MDA-8000B) followed by a development process using AZ300MIF developer. A Ti/Au (20 nm/80 nm) electrode was deposited by electron beam evaporation followed by a lift-off process with AZ400T. All devices were then annealed at 200 °C in H₂/Ar for 1 h to improve the contact of the MoS₂/Ti interface. The aforementioned doping process was performed after fabricating the FET devices. Electrical properties (transfer and output characteristics) of the FET devices were measured using a HP4156A semiconductor parameter analyzer in a nitrogen-filled glovebox. To remove the H₂O and O₂ absorbed on v-MoS₂ during the doping process, the doped v-MoS₂ FETs were annealed at 150 °C for 10 min in a glovebox before characterization.

Conflict of Interest: The authors declare no competing financial interest.

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REFERENCES AND NOTES


