Modulating Electronic Structure of Monolayer Transition Metal Dichalcogenides by Substitutional Nb-Doping

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Abstract: Modulating electronic structure of monolayer transition metal dichalcogenides (TMDCs) is important for many applications, and doping is an effective way toward this goal, yet is challenging to control. Here, the in situ substitutional doping of niobium (Nb) into TMDCs with tunable concentrations during chemical vapor deposition is reported. Taking monolayer WS2 as an example, doping Nb into its lattice leads to bandgap changes in the range of 1.98–1.65 eV. Noteworthy, electrical transport measurements and density functional theory calculations show that the 4d electron orbitals of the Nb dopants contribute to the density of states of Nb-doped WS2 around the Fermi level, resulting in an n- to p-type conversion. Nb-doping also reduces the energy barrier of hydrogen absorption in WS2, leading to an improved electrocatalytic hydrogen evolution performance. These results highlight the effectiveness of controlled doping in modulating the electronic structure of TMDCs and their use in electronic related applications.

1. Introduction

2D transition metal dichalcogenides (TMDCs) have been considered promising candidates for high-performance electronics, optoelectronics, and electrocatalysis,[35–38] however, the controlled modulation of the electronic structure is a key challenge. It is known from silicon that the carrier type and structure can be changed by doping with boron (p-type) or phosphorus (n-type) with well-controlled concentrations.[7] Therefore, the doping of heteroatoms into TMDCs may effectively modulate their electronic structure such as carrier type,[8] which determines their physicochemical properties.[9–12] Meanwhile, for electrocatalysts, changing the local atomic configurations of electrocatalysts by doping may also improve reactions such as the hydrogen evolution reaction (HER)[13] and the oxygen evolution reaction.[14]

Great efforts have recently been made to tune the electronic structure of TMDCs, including charge transfer induced by the absorption of other molecules or functional groups,[15–17] plasma treatment,[18–20] and cation doping during the chemical vapor transport (CVT) growth of TMDCs.[21,22] Note that these methods have some deficiencies. For example, charge transfer doping is usually unstable with time; plasma treatment may damage the original structure of the TMDCs; and CVT is time consuming and only bulk materials can be grown. Chemical vapor deposition (CVD) has been considered a more suitable approach for incorporating heteroatoms into 2D TMDCs during the growth process to overcome these problems, facilitating the steady, damage-free, and efficient preparation of monolayer TMDCs with a controlled doping concentration. Indeed, the doping of different metal or chalcogen atoms into TMDCs during CVD growth has been reported in several systems.[23–29] For instance, Qin et al. have grown Nb-doped WS2 by using liquid phase precursors in CVD method, while the as-grown samples have nonuniform distributions of photoluminescence (PL) intensity.[10] Li et al. reported doping Se into MoS2, where Se and S are from the same group and provide limited modulation of the intrinsic properties of the TMDCs.[11] It is clear that more effort is needed in exploring the effective doping and related applications of TMDCs.

Here, we use a one-step CVD method for the doping of Nb atoms into the lattice of a monolayer TMDC to achieve controllable modulation of its electronic structure. We show that the bandgaps of monolayer WS2 can be changed from 1.98 to 1.65 eV by the addition of a controlled concentration of Nb dopant from 0.3 to 4.7 at%. The Nb-doped WS2 has a high crystallinity, a tunable composition and property, as well as good uniformity. Electrical transport measurements show that Nb-doping converts n-type WS2 into p-type, which has a lower overpotential for HER than pure WS2, i.e., 90 mV at 10 mA cm−2 and 320 mV at 1000 mA cm−2. Such a change in the electronic properties and device characteristics is explained by density.
functional theory (DFT) calculations, showing that the 4d electron orbitals of Nb dopant atoms contribute to the density of states (DOS) around the Fermi level in Nb-doped WS$_2$. These results together show the importance of substitutional doping in changing the properties of 2D TMDCs and expanding their applications that involve the electronic structure.

2. Results and Discussion

We first studied the bandgap engineering of TMDCs by changing the doping concentration, using Nb-doped monolayer WS$_2$ as an example. It is known that both WS$_2$ and NbS$_2$ have the 2H-phase crystal structure with similar lattice constants (WS$_2$ [a, b, c] = [3.16, 3.16, 12.47] Å, NbS$_2$ [a, b, c] = [3.32, 3.32, 11.94] Å), and the covalent radii of W (137 pm) and Nb (134 pm) are very close. These features suggest the possible substitutional doping of Nb into WS$_2$ with a few defects, and the top and side view structures of Nb-doped WS$_2$ are shown in Figure 1a. The DFT results show that when Nb-doping concentrations in WS$_2$ reach 2.0 and 4.0 at%, corresponding to one Nb substitutional dopant atom in a 2D 7-by-7 and 5-by-5 superlattices, respectively, they induce hole doping and increase the energy level of the valence band maximum (VBM) of WS$_2$ (Figure 1b). The positions of the Fermi level ($E_F$) taking the VBM energy level change with the Nb-doping concentration according to the DFT calculations (Figure 1c). Therefore, the substitutional doping of Nb atoms in monolayer WS$_2$ changes its electronic structure.

Motivated by the DFT results, we prepared monolayer Nb-doped WS$_2$ with different doping concentrations using an in situ substitutional doping method based on CVD. Briefly, mixtures of WO$_3$, NbCl$_5$, and NaCl, as well as sulfur were used to grow Nb-doped WS$_2$ at 780 °C (Figure 2a; see details in the “Experimental Section”). The Nb-doped WS$_2$ has a triangular shape with a grain size of ~30 µm and a thickness of 0.62 nm (Figure 2b,c), showing the formation of monolayer samples. Pure WS$_2$ has a strong PL peak at 1.98 eV while the Nb-doped WS$_2$ with the highest Nb concentration of 4.7 at% has a weak peak at 1.65 eV, which is redshifted by 330 meV compared with the pure WS$_2$ (Figure 2d,e). The Raman spectra (Figure 2f) of the Nb-doped and pure WS$_2$ show the same peaks at $E_{2g}^1$ and $A_{1g}$. Similar phenomena in terms of quenched PL and unchanged Raman spectra are shown in Nb-doped MoS$_2$ systems (Figure S1a,b, Supporting Information). We obtained PL and Raman intensity maps ($E_{2g}^1$ and $A_{1g}$ peaks) of Nb-doped WS$_2$ (Figure 2g–i) as well as Nb-doped MoS$_2$ (Figure S1c–f, Supporting Information), and they showed good homogeneity. X-ray photoelectron spectroscopy (XPS) shows peaks associated with the Nb 3d core levels at 209.5 and 206.8 eV in the Nb-doped WS$_2$ (Figure 2j), and the core-level peaks of W and S show a shift to lower binding energies compared with the

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**Figure 1.** a) Top and side view structures of Nb-doped WS$_2$. b) DFT calculations of the DOS in pure WS$_2$ (bottom panel), 2.0 at% Nb-doped WS$_2$ (middle panel), and 4.0 at% Nb-doped WS$_2$ (top panel). The energy of the VBM is taken as the Fermi level denoted by gray dashed lines. c) The relationship between the position of the Fermi level for different Nb-doping concentrations.
pure WS$_2$ (Figure 2k,l), indicating that the Fermi level of the Nb-doped WS$_2$ is shifted toward the VBM.$^{[21,32]}$ Overall, these results show that the Nb-doped WS$_2$ is homogeneous, and its electron structure can be modified in a controlled manner by changing the amount of Nb dopant.

We then characterized the microstructures of the monolayer Nb-doped WS$_2$ by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Compared with the pure WS$_2$ (Figure 3a), the darker contrast at the cation sites indicates substitutional Nb atoms due to their much smaller atomic number than W (Figure 3b–d). W vacancies can also be differentiated from the Nb dopant due to the almost absent contrast. The intensity ratio of Nb/W is $\approx 0.4$, as indicated by the experimental intensity profiles and agreed well
with the simulation results (Figure 3e). The doping concentrations of Nb are calculated using atom-by-atom quantitative intensity mapping (Figure 3f–h). By increasing the amount of Nb precursor, the doping concentration of Nb increased from 0.3 to 4.7 at%. Energy-dispersive X-ray spectroscopy (EDX) shows that the Nb dopant atoms are incorporated in the WS$_2$ lattice (Figure S2, Supporting Information). These results show that substitutional doping of Nb in WS$_2$ with different concentrations has been achieved.

To investigate the effect of Nb-doping on changing the electronic structure of WS$_2$, we fabricated and measured the properties of field-effect transistors (FETs) based on Nb-doped WS$_2$. The devices were fabricated by a direct laser writing technique followed by the deposition of Cr/Au as the drain and source contacts (details in the “Experimental Section”). A pure WS$_2$-based FET shows n-type conduction (black curve, Figure 4a), which is consistent with previous studies.$^{[20,24]}$ Note that the FET based on Nb-doped WS$_2$ with a low doping concentration (2.5 at% Nb)

![Image](image-url)

**Figure 3.** Microstructural characterization of the Nb-doped WS$_2$. a–d) HAADF-STEM images of the pure and Nb-doped WS$_2$ with different doping concentrations. e) Comparison of the experimental and simulated intensity profiles taken from the red box in panel (b), showing the typical W–Nb–W configuration. f–h) Corresponding atom-by-atom maps show the positions of W (blue), Nb (pink), and S (yellow) atoms in Nb-doped WS$_2$.

![Image](image-url)

**Figure 4.** Transport properties of the Nb-doped WS$_2$. a) Transfer characteristics of FETs fabricated using pure WS$_2$, 2.5 at% Nb-doped WS$_2$, and 4.7 at% Nb-doped WS$_2$. b) Relationship between carrier concentration and Nb-doping concentration. c) Relationship between $V_{th}$ and Nb-doping concentration.
shows ambipolar conduction behavior (blue curve, Figure 4a). For a high doping concentration (4.7 at% Nb), it shows p-type conduction behavior (red curve, Figure 4a). The carrier concentrations ($n$) and threshold voltages ($V_{th}$) of these devices were also investigated based on the transfer curves (Figure S3, Supporting Information) and the electron concentration ($n_e$) changed from $4.92 \times 10^{11}$ to $6.16 \times 10^{11}$ to $8.00 \times 10^{10}$ cm$^{-2}$ at $V_g = 80$ V, the hole concentration ($n_h$) changed from $1.03 \times 10^{12}$ to $6.62 \times 10^{12}$ cm$^{-2}$ at $V_g = -80$ V (Figure 4b), and the threshold voltage ($V_{th}$) changed from 67, 65, to 14 V (Figure 4c; see the “Experimental Section” for the details of how these values were obtained). DFT calculations were used to understand these changes in electrical properties, and showed that the valence electronic states of pure WS$_2$ primarily originate from hybridization of the 5d orbitals from W and the 3p orbitals from S (bottom panel in Figure 1b). When Nb atoms are doped into the WS$_2$ lattice, they induce additional sharp defect states above the VBM of pure WS$_2$ (middle and top panels in Figure 1b), which serve as a shallow acceptor level. Overall, the results show that modulating the electronic structure of WS$_2$ contributes to the n- to p-type conversion.

To further explore the effect of Nb-doping on changing the electronic structure of WS$_2$, we also checked the HER activity of Nb-doped WS$_2$ using a microreactor design. After two rounds of electron beam lithography, Cr/Au was deposited to serve as the drain and source contacts (Figure 5a; Figure S4, Supporting Information; details in the “Experimental Section”). Linear sweep voltammograms (LSVs) were obtained on the pure and 4.7 at% Nb-doped WS$_2$ (Figure 5b), and the corresponding results of the overpotential at different current densities are summarized in Figure 5c, showing overpotentials of 90 mV at 10 mA cm$^{-2}$ and 320 mV at 1000 mA cm$^{-2}$. Obviously, Nb-doped WS$_2$ is more active for HER than pure WS$_2$. Here, the HER performance of Nb-doped WS$_2$ at both low and high current densities is comparable to the $2H$ Nb$_{1.35}$S$_2$ catalyst, which possesses one of the best HER performances reported so far [34]. Then, the Gibbs free energy of hydrogen adsorption ($\Delta G_H$) was calculated as an indicator for HER performance [35]. Taking all the active sites into consideration (Figure S5, Supporting Information), our DFT results show that hydrogen adsorption at the in-plane center of the hexagonal ring next to the Nb dopant (the most preferable site, denoted as “hollow-in”) has the lowest energy barrier ($\approx 0.11$ eV) (Figure 5d–f). In addition, the 4.7 at% Nb-doped WS$_2$ reduces the energy barrier for valence states interacting with H$^+$, thus enhancing H$_2$ adsorption. Overall, these results show that modulating the electronic structure of WS$_2$ plays an important role in fast HER kinetics. In addition, we compared our work with others as shown in Table S1 (Supporting Information), especially on tuning the properties of the doped TMDCs. The FET and HER measurements show the ability to modulate device behavior and performance of WS$_2$ via Nb-doping, where the localized and delocalized electrons play important roles.

**Figure 5.** Improved HER performance of the Nb-doped WS$_2$. a) The typical picture of the HER-microreactor device. b) LSV curves of the microreactor devices based on pure WS$_2$ and 4.7 at% Nb-doped WS$_2$. c) Summary of the overpotential at different current densities. d) The charge density variance of WS$_2$ after substitutional Nb-doping. e) $\Delta G_H$ versus the reaction coordinates for the most preferable H$^+$ adsorption sites in the pure and Nb-doped WS$_2$. f) Corresponding schematic structures of these two most preferable sites. The blue, yellow, pink, and green spheres, respectively, denote W, S, Nb atoms, and H$^+$ ions.
3. Conclusion

We have modulated the electronic structure of monolayer TMDCs by the substitutional doping of Nb during the CVD process. Systematic characterization of the doped materials shows tunable compositions from 0.3 to 4.7 at% and a redshift of the optical bandgap from 1.98 to 1.65 eV. Moreover, the Nb-doped WS2 shows an n- to p-type conversion behavior and a low overpotential for HER electrocatalysis (90 mV at 10 mA cm−2 and 320 mV at 1000 mA cm−2). Theoretical studies indicate that the 4d electron orbitals of Nb-dopant atoms contribute to the DOS around the Fermi level in Nb-doped WS2. Nb-doping also reduces the energy barrier of hydrogen adsorption, leading to an improved HER performance. The study sheds light on the mechanism of bandgap engineering, which opens up further applications based on 2D TMDCs.

4. Experimental Section

Materials and Chemicals: Sulfur powder (99.95%, Alfa Aesar, USA), niobium(V) chloride (NbCl5, 99.9%, Shanghai Macklin Biochemical Co., Ltd., China), tungsten(VI) oxide powder (WO3, 99.99%, Alfa Aesar, USA), molybdenum(VI) oxide powder (MoO3, 99.99%, Alfa Aesar, USA), sodium chloride (NaCl, 99.5%, Shanghai Macklin Biochemical Co., Ltd., China), potassium hydroxide (KOH, 90%, Shanghai Macklin Biochemical Co., Ltd., China), sulfuric acid (H2SO4, 98 wt%, Shanghai Macklin Biochemical Co., Ltd., China), polyethylene oxide (PEO), polyvinyl alcohol (PVA), acetonitrile, and isopropanol alcohol (IPA). Analytical Reagent, Shanghai Macklin Biochemical Co., Ltd., China) were used as received.

CVD Growth of Nb-Doped WS2, Nb-Doped MoS2, Pure WS2, and Pure MoS2: The growth was conducted in a homemade two-zone CVD setup with a 1 in. diameter quartz tube (TF55035C-1, Lindberg/Blue M, Thermo Fisher Scientific, USA). Sulfur powder (100 mg) was placed in the first zone at upstream, WO3 mixed with NaCl (mass ratio = 6:1), and NbCl5 with different masses (1, 2, and 10 mg) with a facedown SiO2/Si substrate were placed downstream (8–10 cm) for the growth of the Nb-doped WS2. The tube was flushed with Ar for 30–40 min to remove the air, and the furnace was then heated to 780 °C with a heating rate of 40 °C min−1 and kept at this temperature for 1–5 min for the growth of Nb-doped WS2 before being cooled to room temperature. A flow of 100 sccm of Ar was introduced during the whole process. The Nb-doped MoS2, pure WS2, and MoS2 were grown using the same method, using MoO3 mixed with NaCl (mass ratio = 6:1), and NbCl5 with different masses (2 and 10 mg), WO3 and NaCl (mass ratio = 6:1), MoO3 and NaCl (mass ratio = 6:1) as the respective precursors.

Direct Transfer of Nb-Doped WS2 onto a TEM Grid: Schematics of whole processes are shown in Figure S6 (Supporting Information). IPA was dropped on the sample which was covered by a transmission electron microscopy (TEM) grid and was then baked at 70–80 °C for 10 min. HF:H2O (1:6, volume ratio) was used to etch away the SiO2/Si substrate. After etching, the WS2/TEM grid was washed in deionized water and dried for TEM characterization.

Characterization of the Samples: An optical microscope (Carl Zeiss, Germany) and an atomic force microscope (Cypher ES, Asylum Research, USA) were used to observe the morphology and thickness of the TMDCs. Raman spectroscopy and PL spectroscopy were performed using a 532 nm laser excitation (Horiba LabRam Evolution, Japan). The step size of Raman and PL maps was =0.8 µm. All the peaks were calibrated using the Si peak at 520.7 cm−1. Chemical analyses of the samples were performed by XPS (Thermo Scientific K-Alpha XPS, using Al (Kα) radiation as a probe, USA). Microstructure characterization of the samples was performed using an STEM (FEI Titan Themis G2 double aberration corrected TEM with a super energy-dispersive X-ray spectroscopy detector, USA) operated at an acceleration voltage of 60 kV.

FET Devices’ Fabrication and Measurements: The Nb-doped WS2 was coated with a PMMA thin film by spin-coating at 3000 rpm for 1 min followed by baking at 125 °C for 30 min. The baked sample was soaked in KOH (1 m) to detach the PMMA/Nb-doped WS2 film from the SiO2/Si substrate, and the detached film was then attached to a fresh 300 nm thick SiO2/Si substrate and baked at 80 °C for 30 min to promote the adhesion of the Nb-doped WS2 to the substrate. The PMMA film was removed by soaking in acetone overnight. Finally, source and drain electrodes (5/50 nm Cr/Au) were fabricated on the Nb-doped WS2 using a direct laser writing system (miDAlIX, DaLi, Slovenia) followed by e-beam evaporation (ebeam) and lift-off processes. The FETs were measured using a semiconductor analyzing system and probe station with vacuum at a base pressure of 10−5 mbar at room temperature (Keithley 4200A-SCS, USA; LakeShore, USA). According to the electrical measurements, carrier concentration (n) and threshold voltage (Vth) were calculated using the following formulas:

\[
\begin{align*}
 n &= \frac{I_d}{qWV_d} \\
 \mu &= \frac{L}{WV_d}\frac{dI_d}{dV_g}
\end{align*}
\]

where \( q \) is the unit electron charge, \( I_d \) is the channel current, \( V_d \) is the drain voltage, \( \mu \) is the carrier mobility, \( L \) and \( W \) are the length and width of the channel, respectively.

HER/Microreactor Fabrication and Measurements: The microreactor was fabricated using two rounds of standard electron beam lithography on the Nb-doped or pure WS2, and Cr/Au source/drain contacts (5/50 nm Cr/Au) were deposited by ebeam. The HER measurements were performed using a three-electrode electrochemical system in a 0.5 m H2SO4 (aq) electrolyte. An Ag/AgCl electrode was used as the reference microelectrode and a Pt wire (diameter of 1 mm) served as the counter electrode. A gold electrode connected to the Nb-doped WS2 or pure WS2 was used as the working electrode. An electrochemical workstation (Biological VNP300, France) was used for the LSV tests with a scan rate of 0.5 mV s−1 to avoid non-Faradic currents. Before testing, the electrolyte was bubbled with Ar for 30–45 min to remove any dissolved oxygen, and the H2SO4 electrolyte (50 µL) was then dropped onto the device for further measurements. All results were without iR compensation.

DFT Calculations: First-principles DFT calculations were performed using the Vienna ab-initio simulation package (VASP) [36,37], where the ion–electron interactions and the exchange correlations were treated by the projected-approximate wave method [38,39] and the Perdew–Burke–Ernzerhof functional [40] for the generalized gradient approximation. A vacuum layer greater than 10 Å thick was used to keep interactions from the neighboring van der Waals layers negligible, while a superlattice thickness larger than 5 × 5 unit cells was adopted to minimize the influence of neighboring dopants. The cut-off energy was set at 400 eV, while the criteria for energy and force convergence were 10−6 eV and 0.01 eV Å−1, respectively. A DFT-D3 method with Becke–Johnson damping [41] was used to treat the van der Waals interaction. The zero-point energy and entropy were also considered in calculating the Gibbs free energy difference.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements

The authors acknowledge the supports by the National Natural Science Foundation of China (Grant Nos. 51722206, 51920105002, 51991340, and 51991343), the Youth 1000-Talent Program of China, the National Key R&D Program (2018YFA0307200), Guangdong Innovative and Entrepreneurial Research Team Program (Program No. 2017ZT07C341), the Bureau of Industry and Information Technology of Shenzhen for the “2017 Graphene Manufacturing Innovation Center Project” (Project No. 201901171523). This work was also assisted by SUSTech Core Research Facilities, especially technical support from Pico-Centre that receives support from Presidential fund and Development and Reform Commission of Shenzhen Municipality.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, bandgap, doping, electronic structure, TMDCs

Received: August 16, 2020
Revised: September 23, 2020
Published online: October 27, 2020