Edge-Epitaxial Growth of 2D NbS$_2$-WS$_2$ Lateral Metal-Semiconductor Heterostructures

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2D metal-semiconductor heterostructures based on transition metal dichalcogenides (TMDs) are considered as intriguing building blocks for various fields, such as contact engineering and high-frequency devices. Although, a series of p–n junctions utilizing semiconducting TMDs have been constructed hitherto, the realization of such a scheme using 2D metallic analogs has not been reported. Here, the synthesis of uniform monolayer metallic NbS$_2$ on sapphire substrate with domain size reaching to a millimeter scale via a facile chemical vapor deposition (CVD) route is demonstrated. More importantly, the epitaxial growth of NbS$_2$-WS$_2$ lateral metal-semiconductor heterostructures via a “two-step” CVD method is realized. Both the lateral and vertical NbS$_2$-WS$_2$ heterostructures are achieved here. Transmission electron microscopy studies reveal a clear chemical modulation with distinct interfaces. Raman and photoluminescence maps confirm the precisely controlled spatial modulation of the as-grown NbS$_2$-WS$_2$ heterostructures. The existence of the NbS$_2$-WS$_2$ heterostructures is further manifested by electrical transport measurements. This work broadens the horizon of the in situ synthesis of TMD-based heterostructures and enlightens the possibility of applications based on 2D metal-semiconductor heterostructures.
metal-semiconductor heterostructure maybe also be promising in high-speed integrated circuits and microwave technologies, considering its high-frequency characteristics. Additionally, the ultrathin body thickness of 2D configuration can bring metallic TMDs high mechanical flexibility, which makes the pliable/wearable device systems capable. Hence, the direct synthesis of 2D metal-semiconductor TMD heterostructures is crucial for the practical applications of TMD-based electronic and optoelectronic devices.

Bulk metallic TMD crystals are commonly synthesized via chemical vapor transport techniques\cite{16-38} and their thin flakes are obtained by mechanical exfoliation method.\cite{19} Very few reports about the uniform and controllable growth of monolayer metallic TMDs have been made so far by chemical vapor deposition (CVD) method.\cite{17,20,39} Although lots of interesting physics and electronic properties have been explored from 2D TMD semiconductors and its heterostructures obtained via one-step, two-step, and even multistep growth processes,\cite{40-47} the synthesis of 2D metallic TMDs and establishment of Van der Waals (vdW) heterostructures between metallic and semiconductor TMDs are sparsely reported.\cite{48,49} These have not only hindered the exploration of their electronic/magnetic properties but also greatly impeded their practical applications in electronic devices.

Having in mind the astonishing research progress on CVD grown high-quality and large domain MoS$_2$, WS$_2$ flakes, etc.,\cite{50-52} and also speculating the similar structure of NbS$_2$ with a complementary electronic properties, it is reasonable to hypothesize that the rational synthesis of NbS$_2$-WS$_2$ heterostructures could lead us one step forward in the area of 2D materials. In this study, we present a direct synthesis of monolayer NbS$_2$ with a large domain size via an ambient pressure CVD (APCVD) method. More importantly, we realize a controllable epitaxial growth of NbS$_2$-WS$_2$ lateral heterostructures via a facile “two-step” CVD route. Transmission electron microscopic studies show perfect atomic structures and clear chemical modulation with distinct interfaces. Moreover, Raman and photoluminescence (PL) spectroscopic characterizations reveal the controlled spatial modulation within the concentration features with well-defined rectification, which indicate the potential application in electronic devices. We believe that the findings in our work pave a promising way for the property investigations and application developments of 2D metallic materials and 2D metal-semiconductor TMD heterostructures.

Uniform monolayer metallic NbS$_2$ triangles were grown on sapphire (Al$_2$O$_3$(0001)) substrates via an APCVD system in a three-zone furnace. Niobium pentoxide (Nb$_2$O$_5$) and Sulfur (S) powder were chosen as the reaction precursors. The Nb$_2$O$_5$ powder, mixed with a little amount of Sodium chloride (NaCl), was placed at the center of quartz tube onto which the growth substrate (sapphire(Al$_2$O$_3$(0001))) was laid facing down. The sulfur powder was then placed at the upstream region. The reaction condition was set in such a way that the temperature of the upstream region was raised to 150–200 °C, and the sulfur vapor was carried by Ar gas flow (mixed by H$_2$) toward the center to react with Nb$_2$O$_5$ at 790 °C and deposit NbS$_2$ on sapphire. More details of the growth experiments are provided in the Experimental Section and Supporting Information (Figure S1). Figure 1a schematically depicts the typical structure model of monolayer NbS$_2$ seen from top and side views, which is similar to that of MoS$_2$.\cite{9} A typical scanning electronic microscopy (SEM) image in Figure 1b demonstrates the achievement of uniform NbS$_2$ triangles on sapphire. And the maximum edge length of the as-grown NbS$_2$ triangle can be as large as 100 µm, confirmed by the inset optical image. Furthermore, X-ray photoelectron spectroscopy (XPS) results and Raman spectra of as-grown monolayer NbS$_2$ were also obtained and supplemented in Figures S2 and S3 (Supporting Information), fully confirming its chemical component. Figure 1c gives a representative atomic force microscopy (AFM) image and demonstrates that the thickness of as-grown NbS$_2$ triangles is ≈1.0 nm, indicating its monolayer nature. Besides, the as-grown NbS$_2$ is proved to be air-stable (Figure S4, Supporting Information). Afterward, the NbS$_2$-WS$_2$ lateral heterostructure was fabricated by sequentially growing each components on sapphire (Al$_2$O$_3$(0001)) substrates through a “two-step” CVD route, as schematically illustrated in Figure 1d. In the first step, large-scale monolayer WS$_2$ triangles were synthesized on the sapphire substrate via an APCVD method. Briefly, WO$_3$ powder, mixed with a little amount of NaCl powder, was used as growth precursor and sulfurized by sulfur vapor to obtain a large scale WS$_2$ monolayer at 730 °C (details of the growth process are elaborated in Figure S5 in the Supporting Information and the Experimental Section). Subsequently, monolayer WS$_2$ triangles supported by sapphire substrate were in turn utilized for the preparation of NbS$_2$ layers. In the second growth step, the APCVD method for the NbS$_2$ growth (mentioned above) was again adopted to eventually realize the epitaxial growth of NbS$_2$. Notably, there exists a short interruption before the second growth step for material transition. Generally, the edges or grain boundaries of primary synthesized WS$_2$ are easily passivated by some impurities under an ambient condition. Merely, the absorbent molecules can be removed by the NbS$_2$ growth process at a relatively high growth temperature (~790 °C) under the S atmosphere. So no additional treatment is necessary between the two-step growth processes. Figure 1e shows SEM image of monolayer WS$_2$ triangle obtained from the first step growth. The XPS and AFM results are shown in Figures S6 and S7 (Supporting Information). The morphology of the lateral heterostructure grown as triangular NbS$_2$-WS$_2$ on sapphire substrate can be clearly visualized from the SEM image in Figure 1f. These two concentric triangular regions with a slightly different image contrast marked by yellow and blue triangles reveal a transparent interface between WS$_2$ (centric) and NbS$_2$ (peripheral) (the elements’ distribution is presented in Figure S16, Supporting Information). The AFM image (inset of Figure 1f) indicates that the heterostructure possesses a smooth surface with a thickness of 10 nm for NbS$_2$ and a height of ≈1.0 nm for WS$_2$. Notably, by controlling the growth parameters, the thickness of NbS$_2$ within the heterostructure can be as thin as about ≈5 nm, shown in Figure S9 (Supporting Information). Furthermore, the chemical composition of NbS$_2$-WS$_2$ lateral heterostructure
was determined by X-ray photoelectron spectroscopy (XPS) characterization (Figure 1g). It is apparent that the heterostructure constitutes elements of Nb, W, and S. The chemical states of Nb 3d 5/2 and 3d 3/2 can be identified from the peaks at binding energies of 203.5 and 207.5 eV, respectively. The 4f 7/2 and 4f 5/2 states of W are corroborated from the peaks at binding energies ≈32.0 and 34.3 eV whereas those at binding energies ≈161.5 and 162.5 eV are meant for 2p 3/2 and 2p 1/2 states of S, respectively, which are in agreement with the spectra of NbS2 and WS2.[41] Besides, by further designing and controlling the growth parameters, NbS2/WS2 vertical heterostructures were also successfully obtained via Van der Waals epitaxial growth. And the coverage of upper NbS2 film can be efficiently controlled by tuning the growth condition. Much more detailed information about their morphologies and optical properties of the NbS2/WS2 lateral heterostructures is shown in Figure S10–S12 (Supporting Information). In brief, these results demonstrate that we realize the epitaxial growth of NbS2-WS2 heterostructures in both lateral and vertical ways via a “two-step” CVD method.

Atomic resolution transmission electron microscope (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were further performed on transferred samples to investigate the detailed atomic structures of monolayer NbS2 and NbS2-WS2 lateral heterostructure. Figure 2a shows a high-resolution TEM (HRTEM) image of NbS2, displaying a perfect atomic arrangement. The (100) lattice plane spacing (d 100) extracted from Figure 2a can be revealed as ≈0.291 nm; thus the in-plane lattice constant (a 0) should be ≈0.336 nm. Figure 2b shows the corresponding selective area electron diffraction (SAED) pattern with only one set of diffraction spots, revealing the single crystalline nature of NbS2 and its high crystal quality. On the basis of SAED study, we can also determine the (100) lattice plane spacing of NbS2 to be 0.291 nm, consistent with the one observed from the HRTEM result. Energy-dispersive spectroscopy (EDS) mapping was also employed along with TEM on the transferred samples to identify the chemical composition. Figure 2c,d clearly exhibits the spatial distribution of Nb and S atoms on the triangular corner area and the compositional uniformity of the synthesized NbS2.
nanosheet by the uniform color contrasts. Depth insight into the atomic structure and heterointerfaces of NbS2-WS2 lateral heterostructure can be gleaned from Figure 2e in which a low-magnification TEM image of a triangular NbS2-WS2 lateral heterostructure is clearly visible. A more distinct feature of the two components (yellow dashed line) between WS2 (left) and NbS2 (right) is apparent from the HRTEM image displayed in Figure 2f. A grain boundary can be seen at the heterointerface. Corresponding TEM-SAED spots obtained from the heterointerface exhibit two sets of hexagonal diffraction pattern spots with no rotation as shown in Figure 2g, highly indicative of the same crystal orientation and an edge-epitaxial growth of NbS2-WS2 lateral heterostructure. Thus, HAADF-STEM was further utilized to reveal the atomic structure and heterointerface. The STEM images taken from regions 1 and 2 away from the heterointerface, as shown in Figure 2h,i, demonstrate the individual WS2 and NbS2 regions with perfect hexagonal arrangements, confirming the high crystalline quality of our CVD-grown materials. The extracted (100) lattice plane spacings of 0.277 and 0.291 nm are in agreement with the values for pure WS2 and NbS2, respectively. And corresponding fast Fourier transformation (FFT) analysis of each side shows only one set of hexagonally arranged spot, respectively, verifying the individual chemical component of WS2 (left) and NbS2 (right) (Figure S13, Supporting Information). Figure 2j exhibits a smooth atomic arrangement at the interface between WS2 and NbS2 (Figure S14, Supporting Information). The corresponding atomic model in Figure 2k also schematically simulates the distinct interface connection between NbS2 and WS2. Together, these TEM studies reveal the explicit chemical modulation in our NbS2-WS2 lateral heterostructure with a well-defined heterointerface.
Raman and PL spectra were further conducted to examine the sequential distribution of the chemical composition as well as the local optical properties within the NbS₂-WS₂ lateral heterostructures. Figure 3a shows the Raman spectra acquired at different regions within NbS₂-WS₂ heterostructure domain as marked by black and red dots in the SEM image (inset of Figure 3a). The Raman spectrum from the central part presents two characteristic peaks at 352 cm⁻¹ (E₂g) and 417 cm⁻¹ (A₁g) (black line in Figure 3a), in agreement with that of monolayer WS₂. Interestingly, the peripheral part (red line in Figure 3a) exhibits quite different features, whose two Raman modes located at 332 cm⁻¹ (E₂g) and 378 cm⁻¹ (A₁g) correspond to the typical Raman modes of NbS₂ layers. These Raman spectra indicate high quality of the two materials in concentric triangular domain and emphasize the formation of NbS₂-WS₂ lateral heterostructure without compositional alloying.

Figure 3b displays the PL spectra collected from WS₂ and NbS₂ regions. The centric WS₂ region exhibits a very strong PL characteristic peak at ≈ 625 nm, in accordance with an exciton emission of monolayer WS₂ (black line in Figure 3b). However, the peripheral NbS₂ has no PL peak (red line in Figure 3b) due to its metallic nature. Note that the emission around 700 nm originates from the sapphire substrate. Hence, PL spectra also confirm the formation of NbS₂-WS₂ lateral heterostructure. In order to further solidify our observations made above, the Raman and PL spectra of as-grown WS₂ and WS₂ after “step 2” in APCVD was studied for comparisons (black line and red line in Figure 3c). The peak positions of two prominent peaks for monolayer WS₂ have no deviation. Raman spectra in Figure 3c reveals the same characteristic peaks of WS₂ with no Raman shifts. Similarly, the typical PL peaks for WS₂ at both conditions also possess the same position and intensity as shown in Figure 3d. These results suggest that WS₂ region in the NbS₂-WS₂ lateral heterostructure domain still maintain its intrinsic structure with no doping possibility by other atoms or damage after “step 2” growth. Figure 3e–h exhibits the Raman maps constructed by integrating correlated Raman peak intensities (378 cm⁻¹ and 332 cm⁻¹ for NbS₂; 351 cm⁻¹ and 417 cm⁻¹ for WS₂). The clear boundaries demonstrate individual NbS₂ and WS₂ regions, highly verifying the formation of NbS₂-WS₂ lateral heterostructures without any alloy phases in the interface. And uniform signals in the Raman mapping images confirm the high crystalline quality and uniform chemical distribution. The PL mapping image of
an NbS₂-WS₂ heterostructure domain in Figure 3i also shows very different PL peaks at 625 nm from the central part while no peak from the out peripheral part, powerfully confirming the sharp interfaces (Figure 3j). In general, the integrated Raman and PL studies of the heterostructures reveal the formation of concentric triangular domains of WS₂ and NbS₂.

To further investigate the transport properties of obtained NbS₂ crystals, electronic devices based on NbS₂ were fabricated on sapphire substrates. Figure 4a shows a typical optical image of constructed device of NbS₂ with a thickness of ≈2 nm (shown as inset AFM image). Figure 4b demonstrates a linear $I_{ds}$–$V_{ds}$ curve of the NbS₂ device collected at room temperature, indicating an Ohmic contact between NbS₂ and electrodes. Figure 4c shows the temperature-dependent resistance for the NbS₂ device, exhibiting a decreasing resistance from 200 to 30 K and then an increasing resistance from 30 to 2 K. The temperature of the minimum resistance ($T_m$) was observed as ≈30 K and higher than that of bulk NbS₂, which may be due to electron–electron interaction enhanced in low dimensional system.[33] These results confirm the metallic nature of NbS₂ crystals, in a good agreement with DFT calculation.[34] The metallic ground state of NbS₂ crystals is also evidenced by the PL spectra without signal (Figure S3, Supporting Information).

Further, to characterize the electrical transport properties and performance of the obtained NbS₂-WS₂ lateral vdW heterostructures, series of FETs were fabricated on Si substrate with SiO₂ of 300 nm. Figure 4d schematically illustrates the process of device construction. First, the concentric triangular NbS₂-WS₂ lateral heterostructure should be etched by reactive ion etching technique, obtaining an NbS₂-WS₂ lateral heterostructure ribbon. Subsequently, Cr/Au thin films were thermally evaporated as electrodes deposited on NbS₂ region and WS₂ region separately. The detailed fabrication procedure is given in the Experimental Section. Figure 4e shows an optical image of our fabricated FET device based on the NbS₂-WS₂ lateral heterostructure (the thickness of NbS₂ part is shown in Figure S15, Supporting Information). The transfer characteristic curve ($I_{ds}$–$V_{gs}$) of this device (Figure 4f) shows a typical n-type behavior with an on–off ratio of $10^5$. The field-effect mobility is calculated to be 0.14 cm² V$^{-1}$ s$^{-1}$ ($L = 9.3 \mu$m, $W = 10.9 \mu$m, $V_{ds} = 1$ V), which is comparable with reported CVD-grown heterostructure result.[38] The corresponding output characteristic ($I_{ds}$–$V_{ds}$) in Figure 4g depicts that the $I_{ds}$ decreases with the $V_{gs}$ varying from 80 to 30 V. Most importantly, the gate-tunable output curves demonstrate explicit current rectification behavior, different from that of pure WS₂ (Figure S16, Supporting Information), highly

Figure 4. Electrical characterization of NbS₂ flakes and as-grown NbS₂-WS₂ lateral heterostructure. a) The OM image of fabricated device based on as-grown NbS₂ on sapphire. Scale bar, 10 µm. The inset is the AFM image of NbS₂ flake, showing a thickness of ≈2 nm. Scale bar, 10 µm. b) The $I_{ds}$–$V_{ds}$ curve of the NbS₂ device collected at room temperature. c) Temperature dependence of the resistance for the NbS₂ device. d) Schematic views of the fabrication processes for the FET device based on NbS₂-WS₂ lateral heterostructure domains. e) An optical image of fabricated NbS₂-WS₂ lateral heterostructure device. Scale bar, 10 µm. f) The transfer characteristic curve of this device, demonstrating n-type behavior. g) The corresponding $I_{ds}$–$V_{ds}$ output characteristics at different backgate voltages.
An APCVD system was used for the NbS$_2$ synthesis. A three-zone WO$_3$ were placed at the center of furnace. The evaporating temperature of S and sapphire (Al$_2$O$_3$) substrates were successively placed downward on the Nb$_2$O$_5$ powder (0.5 g) mixed with a little amount of sodium chloride (NaCl (0.05 g)). Prior to heating, the furnace tube was purged with 400 sccm Ar for 30 min and then with 100 sccm Ar and 1–10 sccm H$_2$ to create a preferable growth atmosphere for the growth. The Nb$_2$O$_5$ growth lasted for 15 min and finally Nb$_2$O$_5$ monolayer was obtained on sapphire substrates.

For the synthesis of NbS$_2$-WS$_2$ lateral heterostructure, monolayer WS$_2$ flakes were first synthesized via APCVD method. S powder was placed at the upstream of furnace, tungsten trioxide (WO$_3$) powder (Alfa Aesar, purity 99%) and sulfur (S) powder (Alfa Aesar, purity 99.9%) were used as precursors. Two quartz boats containing S, Nb$_2$O$_5$, and substrates were loaded into the tube from upstream to downstream with the temperature of 190 and 790 °C, respectively. The substrates were faced downward on the Nb$_2$O$_5$ powder (0.5 g) mixed with a little amount of sodium chloride (NaCl (0.05 g)). Prior to heating, the furnace tube was purged with 400 sccm Ar for 30 min and then with 100 sccm Ar and 1–10 sccm H$_2$ to create a preferable growth atmosphere for the growth. The Nb$_2$O$_5$ growth lasted for 15 min and finally Nb$_2$O$_5$ monolayer was obtained on sapphire substrates.

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The authors declare no conflict of interest.

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