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Realization of 2D crystalline metal nitrides via selective atomic substitution

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Two-dimensional (2D) transition metal nitrides (TMNs) are new members in the 2D materials family with a wide range of applications. Particularly, highly crystalline and large area thin films of TMNs are desirable for applications in electronic and optoelectronic devices; however, the synthesis of these TMNs has not yet been achieved. Here, we report the synthesis of few-nanometer thin Mo$_5$N$_6$ crystals with large area and high quality via in situ chemical conversion of layered MoS$_2$ crystals. The versatility of this general approach is demonstrated by expanding the method to synthesize W$_3$N$_4$ and TiN. Our strategy offers a new direction for preparing 2D TMNs with desirable characteristics, opening a door for studying fundamental physics and facilitating the development of next-generation electronics.

INTRODUCTION

Transition metal nitrides (TMNs) are well-known for their high melting points, hardness, and chemical inertness (1, 2). The successful preparation of two-dimensional (2D) MXenes through selectively etching the “A” layer of bulk MAX phase triggered the study of 2D metal carbides and nitrides since 2011 (3–6). Although a variety of carbide MXenes have been synthesized using this method, the synthesis of nitrides MXenes is limited to Ti$_3$N$_2$ and Ti$_3$N (7, 8), due to the low availability of bulk MAXs for corresponding 2D metal nitrides. Urbankowski et al. (9) further reported the synthesis of multilayer molybdenum and vanadium nitrides by ammoniation of carbide MXenes synthesized using the selective etching method. Currently, as-synthesized 2D TMNs are either in solution phase or in powder form, and the lateral sizes of the flakes are usually small (<10 μm) (10–15). In addition, samples prepared by selective etching suffer from defects generated during the etching process and large thickness distributions (16, 17). These types of 2D TMNs are not suitable for high-performance electronic and optoelectronic device applications, which often require 2D crystals with decent area (>10 μm of lateral size), quality, and deposition on solid-state substrates (18, 19). Conventional 2D materials such as graphene and transition metal dichalcogenides (TMDs) produced using chemical vapor deposition (CVD) have made substantial progress in advancing the development of electronic devices (20–22). In contrast to many conventional 2D materials with strong in-plane covalent bonds and weak out-of-plane van der Waals interactions between the layers, the van der Waals gap is absent in bulk TMN crystals. Instead, covalent bonding extends in 3D frameworks of TMNs. Thus, conventional methods such as top-down mechanical exfoliation and bottom-up CVD, which take advantage of the weak interlayer van der Waals interaction and self-limited in-plane growth, are ineffective for the synthesis of large-area and ultrathin 2D TMNs. Therefore, developing effective routes to synthesize 2D TMN crystals with desired morphology and quality is essential to realize the potential for applications toward electronic devices.

Using nitriding reaction of metal oxides, TMDs, and transition metal carbides (TMCs) to synthesize bulk TMNs is an established process (23–28). Recently, transformation of 2D MoS$_2$ and TMCs to 2D TMNs while retaining crystal structure was demonstrated in an ammonia atmosphere (9, 27). This transformation method is promising for large-area synthesis of 2D TMNs, considering the well-established preparation methods of TMD thin films with controlled thickness and various lateral dimensions ranging from micrometer size to wafer scale (22, 29, 30). However, the precursors used in the reported work for the transformation are either multilayered carbide MXenes or powder TMDs (9, 27). The obtained 2D TMNs are still marred by large thickness distributions, defective structures, and small lateral sizes passed on from the precursors. Moreover, an atomic-level investigation of the transformation, which is the key to evaluate the potential of the strategy for producing high-quality and large-area 2D TMN crystals, is lacking.

Here, beginning with a precursor layer of MoS$_2$, an in situ transformation from MoS$_2$ to ultrathin Mo$_5$N$_6$ is achieved. Optical and scanning electron microscopy (SEM) images show that the geometry and morphology of the crystals are retained during the transformation. The obtained Mo$_5$N$_6$ exhibits high crystallinity over the entire area. In situ transformations of various MoS$_2$ flakes down to four layers for Mo$_5$N$_6$ flakes with different thicknesses are achieved. Atomic force microscopy (AFM) analysis shows that the thickness of most of MoS$_2$ flakes is reduced by about two-third after the transformation. Electrical measurements show the high conductivity of metallic Mo$_5$N$_6$ samples. We further demonstrate that this strategy can be applied to other TMDs such as WS$_2$ and TiS$_2$ for preparing their corresponding TMNs. This work opens a new direction for preparing 2D TMNs with desired quality that are previously inaccessible.

RESULTS

Figure 1 shows a schematic illustration of the typical reaction process. The conversion was performed in a horizontal tube furnace
MoS$_2$ flakes with different thicknesses were prepared using mechanical exfoliation and transferred onto a SiO$_2$/Si substrate, which was then placed at the center of the furnace. A crucible filled with urea was placed in the upstream zone of the furnace, serving as the ammonia gas source, which was released from the thermolysis of urea at 200°C (31, 32). Ar gas (100 sccm) was used as carrier gas. The temperature in the center of the furnace was set at 750° to 800°C for the chemical reaction between gaseous ammonia and MoS$_2$ flakes (23, 27). Apart from Mo$_5$N$_6$, which was the solid product, the other two side products, H$_2$S and N$_2$, were in gaseous phase and carried away by the Ar gas (23, 27), leaving clean Mo$_5$N$_6$ products with minimum contaminants.

Figure 2 (A and B) shows optical images of a 12.9-nm MoS$_2$ flake before and after the reaction. The optical contrast of the flake changed markedly after the reaction, but the morphology and shape of flakes are retained. Conversion results of more MoS$_2$ flakes with different thicknesses ranging from ~3 nm to tens of nanometers are shown in fig. S1. All MoS$_2$ flakes displayed notable changes of optical contrast after conversion. Absorption spectra (fig. S2) of the flake before (MoS$_2$) and after (Mo$_5$N$_6$) the conversion suggest that such change originated from the distinct optical properties, consistent with the distinct electronic band structures of the two materials (15, 33). More evidence supporting the successful conversion of MoS$_2$ to Mo$_5$N$_6$ is reported in later sections. AFM images show the atomically smooth surface of the flakes after conversion (fig. S3), suggesting a mild conversion process during which the reaction is confined within the surface of the flakes after conversion (fig. S3), suggesting a mild conversion process during which the reaction is confined within the surface of the flakes after conversion. Raman mapping results (fig. S5) on a thick Mo$_5$N$_6$ flake, which provides better signal-to-noise ratio of EDS signal. Dark-field STEM image shows the inhomogeneous contrast of the thick Mo$_5$N$_6$ flake (fig. S5), which is probably due to strong local strain during the conversion process. EDS maps of N K peak and Mo L peak (fig. S5) show uniform distribution of Mo and N elements in the flake. TEM characterization performed on the converted flake globally. Corresponding PL mapping results are shown in fig. S4.

To determine the phase and crystal structure of the flake, we performed transmission electron microscopy (TEM) characterization on an as-prepared sample. The low-magnification TEM image in Fig. 3A shows the smooth surface of the flake where the small variations of the contrast are due to the wrinkles generated during the transfer process. The selected-area electron diffraction (SAED) pattern in Fig. 3B (see also fig. S5) indicates the high crystallinity of the sample. Same SAED pattern was observed when measuring on different regions of the flake. The hexagonal diffraction pattern is consistent with the crystal structure of the Mo$_5$N$_6$ (15). The experimental and simulated SAED patterns (fig. S5) of Mo$_5$N$_6$ match well with each other. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image is shown in Fig. 3C, where Mo atoms and atomic lattice are seen and no obvious defect is found in the sample. N atoms are invisible under our STEM condition due to the small atomic number compared to Mo atoms. In addition, the distance of 0.239 nm between the lattice planes is consistent with the d-spacing of (110) planes in Mo$_5$N$_6$ crystal, which matches with the SAED pattern. We also noticed that the obtained Mo$_5$N$_6$ crystal had an enhanced stability under 200-keV electron beam compared to MoS$_2$ flakes (37, 38), where Mo$_5$N$_6$ flakes on TEM grid remained stable without noticeable change after being exposed under electron beam for 30 min (fig. S6), providing an additional advantage for future applications in electronic devices. STEM imaging and energy-dispersive spectroscopy (EDS) mapping were performed (see fig. S5) on a thick Mo$_5$N$_6$ flake, which provides better signal-to-noise ratio of EDS signal. Dark-field STEM image shows the inhomogeneous contrast of the thick Mo$_5$N$_6$ flake (fig. S5), which is probably due to strong local strain during the conversion process. EDS maps of N K peak and Mo L peak (fig. S5) show uniform distribution of Mo and N elements in the flake. The TEM characterization confirmed that a highly crystalline Mo$_5$N$_6$ flake was successfully obtained through the chemical transformation.

The chemical composition and oxidation states of the elements in sample Mo$_5$N$_6$ were characterized using x-ray photoelectron spectroscopy (XPS) and EDS analyses. Figure 3D shows the XPS wide scan survey spectrum of the sample, where notable Mo and
N signals are observed and no signal from S appeared, indicating complete conversion of MoS$_2$ to Mo$_5$N$_6$. Other elements such as O, Si, and C are from the SiO$_2$/Si substrate and the chamber environment. Similar results were obtained from EDS characterization (fig. S7).

High-resolution XPS spectra deconvolution for N 1s, Mo 3p, and Mo 3d regions are shown in Fig. 3 (E and F). The N 1s peak at 397.9 eV and Mo 3p$_{3/2}$ at 395.3 eV (Fig. 3E) suggest that chemical bond formed between Mo and N (15). In the Mo 3d region (Fig. 3F),
the peaks at 233.0 and 229.8 eV were assigned to the binding energies of Mo 3d_{3/2} and Mo 3d_{5/2}, respectively (39), with a spin-orbit splitting of 3.2 eV. This characteristic doublet of core-level Mo 3d_{5/2} and 3d_{3/2} indicates that Mo (+4) oxidation state dominates in Mo_3N_6 (25). Nevertheless, the binding energy of 229.8 eV is slightly smaller than the reported value at 230.0 eV for Mo (+4) oxidation state (15), suggesting the coexistence of Mo (+3) oxidation state in the sample. No peaks corresponding to higher oxidation states of Mo from MoO_x were observed in the Mo 3d region (40), ruling out the possibility of the formation of MoO_x.

To address the mechanism by which the lattice changed during the atomic substitution from MoS_2 to Mo_3N_6, we investigated thickness changes of flakes before and after chemical conversion. The crystal structure models of MoS_2 and Mo_3N_6 (Fig. 4, A and B) predict that the van der Waals gap between MoS_2 layers will disappear during the transformation to Mo_3N_6 crystals, leading to the reducing of the thickness from MoS_2 to Mo_3N_6. The distance between two Mo layers in MoS_2 is 7.66 Å (41), while it is 2.77 Å in Mo_3N_6 (42); therefore, the thickness of the flake can be predicted to decrease to 36% when transforming from MoS_2 to Mo_3N_6. To test this hypothesis, we performed AFM to extract the thickness of flakes. As expected, we observed that the thickness was reduced after chemical transformation. Figure 4 (C and D) shows typical AFM images of MoS_2 and corresponding Mo_3N_6 flake, where they have nearly the same morphology and both surfaces are smooth. However, the thickness of the flake decreased from 9.5 nm for MoS_2 to 3.5 nm for Mo_3N_6 (Fig. 4E), where Mo_3N_6/MoS_2 thickness ratio is 37%. Furthermore, we performed this comparison for ~30 flakes with MoS_2 thickness ranging from a few nanometers to ~35 nm. Reduced sample thickness was observed for all flakes after conversion (Fig. 4F). The average Mo_3N_6/MoS_2 thickness ratio is 56% based on the slope of linear fitting curve, but for MoS_2 flakes with the thickness of 5 to15 nm, the ratio is around 40%, matching well with the expected value. For thinner flakes, the ratio is larger, probably because the termination groups on the surface are non-negligible at this size range (3, 5) or the substrate roughness introduces a large uncertainty for the measurement. Figure S8 shows that a four-layer MoS_2 flake (3.4 nm) turned to a 2.1 nm Mo_3N_6 flake after conversion. Note that we found that the morphology and quality of the flake remain well at such thin level. On the basis of the morphology retaining and thickness depression phenomena observed in our experiments, we propose the following mechanism of the chemical transformation from MoS_2 to Mo_3N_6. When NH_3 gas diffuses into the van der Waals gaps of the MoS_2 flake, one N atom will replace two S atoms sandwiched by two adjacent Mo layers. When Mo—S bonds around a Mo atom are broken, six binding sites on the Mo atom will be released. Each N atom will then bond with six Mo atoms to form Mo_3N_6, where adjacent Mo layers are bridged by the N atoms, leading to the vanishing of the van der Waals gaps that originally exist in MoS_2. In this process, breaking Mo—S bonds and forming Mo—N bonds do not require large rearrangements of Mo atoms, although small shift of positions of Mo atoms may be necessary to compensate the bond length difference between Mo—S and Mo—N. Despite the layered structure of MoS_2 (point group, D_{6h}; space group, P6_3/mmc) (41) and nonlayered nature of Mo_3N_6 (point group, C_{6h}; space group, P6_3/m) (42), the Mo layers in these two materials are both in hexagonal pattern. This similarity in structure allows gentle transformation without structural collapse, leading to the morphology retaining of samples before and after chemical transformation.

To further investigate the transformation process, we performed the reaction under varying conditions. We found that excess amount of urea, which provided sufficient NH_3 gas in the chamber, was a

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**Fig. 4. Thickness characterization and analysis of samples before (MoS_2) and after conversion (Mo_3N_6). (A and B) Side view of crystal structures labeled with distance between adjacent Mo layers in MoS_2 and Mo_3N_6. (C and D) AFM images of the same flake before [MoS_2 (C)] and after conversion [Mo_3N_6 (D)]. The white dashed lines indicate the location where we measured the thickness of the flakes. (E) AFM height profiles of the flake before [MoS_2 (C)] and after conversion [Mo_3N_6 (D)]. (F) Correlation plot of the thickness of MoS_2 and converted Mo_3N_6 (in black). Data points in red show the corresponding thickness ratios of Mo_3N_6/MoS_2.**
key factor for the success because it ensured a reducing environment to prevent MoS2 from oxidation (fig. S9). In addition, the degree of conversion could be tuned by changing the reaction temperature and time. A complete transport occurs within 5 min when the reaction temperature varied from 750° to 800°C (fig. S9). However, at 700°C, the conversion was only partially complete even after 60 min, where only the edge area was converted and no Mo5N6 was observed in the central region of the flake (fig. S10), indicating that the conversion started from the edge of the MoS2 flake. Because of the partial conversion, we realized a lateral heterostructure between MoS2 and Mo5N6 through a simple partial conversion. The successful synthesis of this heterostructure offers a great platform for future study on the junction properties and applications. Moreover, the converted Mo5N6 showed excellent stability, where the crystal structure remained intact after 6 months and survived in acetone, deionized (DI) water, and 1 M H2SO4 solution for at least 2 hours without noticeable changes from optical images and Raman spectra (fig. S11). This is advantageous to be compatible with future device fabrication process.

To examine the electrical property of the converted Mo5N6 sample, we fabricated a back-gate transport device on a 9.5 nm-thick Mo5N6 flake (Fig. 5A and fig. S13). The gate dependence of the transport current shows that the drain-source current (Ids) remained constant as the gate voltage scanned from −20 to 20 V, and variations of Ids was still negligible even when noise signal became visible, featuring metallic behavior of the as-synthesized Mo5N6 sample (Fig. 5B). We further performed the temperature-dependent transport measurement down to 77 K to investigate the electrical conductivity of the sample. Fig. 5C shows the output current-voltage relation (I-V) characteristics through a four-probe measurement, where the slope of the I-V curves increases very slowly as the temperature increases from 77 to 240 K (Fig. 5C, inset). The sheet resistances of Mo5N6 at different temperatures were extracted from the slope of I-V curves and the dimension of the transport device (Fig. 5D), using the formula $R_s = R \times (W/L)$. R is the total electrical resistance of the device, and W and L are the effective width and length of the measurement area, which are measured as 3.4 and 6.1 μm, respectively, from the optical image. Low sheet resistances of Mo5N6 ranging from 114.4 to 117.8 ohm square−1 were obtained under different temperatures, which is in the same order of magnitude of CVD graphene (43). The fact that the sheet resistance of Mo5N6 is not sensitive to the temperature change from 77 and 240 K is consistent with the trend of TMNs reported in the literature (9).

We further applied this strategy to the conversion from WS2 and TiS2 to their corresponding nitrides (see Materials and Methods for details of the synthetic conditions). Figure 6 shows a typical conversion result on a 5.6 nm WS2 and a ~100 nm TiS2 flake. As shown in Fig. 6 (A to H), distinct optical contrast change was observed from WS2 and W5N6 as well as from TiS2 to TiN. Similar to the case of MoS2 to Mo5N6 conversion, the morphology of the flakes was retained. Raman characterization showed that the Raman signatures from WS2 and TiS2 disappeared completely (44, 45). Instead, new peaks that correspond to the phonon modes of W5N6 (e.g., ~258 cm−1) and TiN (e.g., ~154 and 620 cm−1) (46, 47) appeared (Fig. 6, I to J), indicating a successful chemical conversion. The Raman mapping results show that the conversion is thorough and uniform. More optical and corresponding SEM images of W5N6 (fig. S12) and TiN (fig. S12) corroborate uniform surface of converted samples. Phase and crystallinity of W5N6 are characterized by HRTEM and EDS analyses (fig. S14) (48). Similar to Mo5N6, W5N6 and TiN also exhibit

### Fig. 5. Electrical transport measurements of Mo5N6.

(A) Schematics of a back-gate device together with electrical connections. (B) Transfer curve of Mo5N6 transport device for both forward and reverse Vg bias with back-gate modulations. Inset: Zoomed-in image of the area indicated by the black rectangle. Negligible gate dependence of the Ids is observed in Mo5N6 transport device. (C) Output I-V curve of Mo5N6 transport device under different temperatures at zero gate voltage. Inset: Zoomed-in region of the I-V curve indicated by the red square. (D) Temperature dependence of the sheet resistance of the Mo5N6 sample.
excellent stability against acetone, DI water, and 1 M H₂SO₄ for at least 2 hours (fig. S11).

DISCUSSION
We demonstrate a versatile conversion strategy from layered TMDs to their corresponding ultrathin nitrides through atomic substitution from chalcogen to nitrogen. This method facilitates the production of 2D crystalline TMNs including Mo₅N₆, W₅N₆, and TiN, offering a pathway toward an important class of 2D materials that previously are inaccessible. The investigation of the in situ transformation from MoS₂ layers to 2D Mo₅N₆ crystals shows reduced thickness after conversion. 2D Mo₅N₆ crystal as thin as 2.1 nm is achieved by converting a four-layer MoS₂. The electrical measurement shows that the converted Mo₅N₆ is metallic with high conductivity, where the sheet resistance is as low as 100 ohm square⁻¹. By controlling the reaction rate, we achieve a Mo₅N₆-MoS₂ lateral heterostructure, demonstrating the advantage of our method in integrating 2D materials together for basic building blocks (e.g., metal-semiconductor junction) for future applications in electronic devices. Building on the success of the TMDs synthesis in the field (21, 22, 30), we anticipate that the strategy we report here will lead to effective synthesis of large-area and high-quality 2D TMNs that satisfy the needs for high-performance electronic and optoelectronic devices.

MATERIALS AND METHODS
Conversion from TMDs to TMNs
MoS₂, WS₂, and TiS₂ with different thicknesses were prepared using mechanical exfoliation method from their bulk crystals (purchased from HQ Graphene) and transferred onto 300 nm SiO₂/Si substrates. Note that SiO₂/Si substrates were cleaned by sonication in water, acetone, and isopropanol solvents sequentially (each for 10 min), followed by O₂ plasma cleaning before use. Chemical conversions were conducted in a horizontal tube furnace where Ar gas was introduced into the tube and the flow was controlled by a mass flow controller. Samples were placed in a 2.5-cm-diameter quartz tube in the center of the furnace. Excess amount of urea (500 mg) was placed in an Al₂O₃ crucible located upstream of the furnace, serving as nitrogen source. After purging with Ar gas for 10 mins, the tube was heated.
to 800°C with a 30 min ramp. The conversion time for Mo₃N₆ and TiN is 1 and 2 hours for W₅N₆. Throughout the conversion, 100 sccm Ar flow was used to maintain the inert atmosphere. When conversion was completed, the system was cooled down naturally.

Material characterizations

As-prepared TMNs were characterized using Raman spectroscopy, AFM, TEM, STEM, SAED XPS, and EDS. Raman and PL measurements were performed on a Renishaw inVia Raman microscope equipped with a 532 nm laser line. All the spectra in comparison were taken using the same condition. The AFM topography was acquired on a Bruker Dimension system. TEM measurements were performed on a JEOL ARM 200F STEM, operating at 200 keV. XPS measurements were performed using a PHI VersaProbe II.

Fabrication and conductivity measurements

The electrical transport device was fabricated through laser writer lithography and thermal evaporation of 5 nm Cr and 45 nm Au. For lift-off, the sample was soaked in Remover PG at 60°C for 10 min to remove the photore sist and then washed in isopropanol and DI water. Device characterization was performed using a semiconductor parameter analyzer (Keysight B1500A) and a Lakeshore cryogenic probe station with micromanipulation probes and liquid nitrogen cooling. All measurements were performed in vacuum (<3 × 10⁻⁶ torr).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/2/eaax8784/DC1

Fig. S1. Typical optical images of MoS2 and Mo5N6 flakes with different thicknesses.
Fig. S2. Absorption spectra of MoS2 and Mo5N6 samples on quartz substrate.
Fig. S3. AFM images of MoS2 and Mo5N6 flakes in Fig. 2.
Fig. S4. PL intensity maps of MoS2 and Mo5N6 flake.
Fig. S5. Structural and elemental characterizations of Mo5N6.
Fig. S6. TEM images of Mo5N6 sample under 200-keV electron beam.
Fig. S7. EDS spectrum of Mo5N6.
Fig. S8. Optical, AFM, and SEM images of chemical transformation on a four-layer Mo5N6 flake.
Fig. S9. Optical images of Mo5N6 flakes prepared from chemical transformations under different conditions.
Fig. S10. Optical images and Raman spectra of a partially converted flake at 700°C.
Fig. S11. Stability test of Mo5N6, W3N7, and TiN.
Fig. S12. Optical and SEM images of Mo5N6 flakes from Mo5N6 and TiN flakes.
Fig. S13. Optical and AFM images of Mo5N6 transport device.
Fig. S14. TEM and EDS characterizations of W3N7 converted from W5N6.

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