# **Inorganic Chemistry**

## Synthesis of Semiconducting 2H-Phase WTe<sub>2</sub> Nanosheets with Large Positive Magnetoresistance

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Cite This: https://dx.doi.org/10.1021/acs.inorgchem.0c02049

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**ABSTRACT:** Tungsten ditelluride (WTe<sub>2</sub>) is provoking immense interest because of its unique electronic properties, but studies about its semiconducting hexagonal (2H) phase are quite rare. Herein, we report the synthesis of semiconducting 2H WTe<sub>2</sub> nanosheets with large positive magnetoresistance, for the first time, by a simple lithium-intercalation-assisted exfoliation strategy. Systematic characterizations including high-resolution transmission electron microscopy, X-ray diffraction, and Raman and X-ray photoelectron spectroscopies provide clear evidence to distinguish the structure of 2H WTe<sub>2</sub> nanosheets from the orthorhombic (Td) phase bulk counterpart. The corresponding electronic phase transition from metal to semiconductor is also confirmed by density of states calculation, optical absorption, and electrical transport property measurements. Besides, the 2H WTe<sub>2</sub> nanosheets exhibit large positive magnetoresistance with values of up to 29.5% (10 K) and 16.2% (300 K) at 9 T. Overall, these findings open up a promising avenue into the exploration of WTe<sub>2</sub>-based materials in the semiconductor field.

wo-dimensional (2D) materials with ultrathin thickness and scalability have attracted much attention from scientists because of their unique structure advantages.<sup>1-5</sup> Triggered by the experimental discovery of graphene, tremendous efforts have thus been made to develop inorganic graphite analogues with weak van der Waals forces between layers, which can be easily exfoliated into ultrathin nanosheets.<sup>6–12</sup> Among all of these materials, transition-metal dichalcogenides (TMDs)  $MX_2$  (M = Mo or W; X = S, Se, or Te) are especially unusual layered materials because they can exist in several phases including 2H, 1T, and Td (also called 1T'), depending on the coordination environment of metal atoms.<sup>13-18</sup> Each phase has a different crystal structure and electronic properties; for instance, 2H-phase MX<sub>2</sub> is usually a semiconductor with a hexagonal crystal structure, while metallic 1T- and Td-phase MX<sub>2</sub> possess monoclinic and orthorhombic structures, respectively.<sup>19-21</sup> Therefore, 2D TMD materials have caused great interest for electronic and optoelectronic applications that are related to the sample thickness and crystalline structure.

Among TMDs, WTe<sub>2</sub> has become an important synthetic target since the discovery of its nonsaturating extremely large positive magnetoresistance effect at low temperatures, which has not been observed in other TMDs.<sup>22–25</sup> However, to our best knowledge, almost all of the previous reports on the studies of WTe<sub>2</sub> were focused on its naturally formed Td phase with a semimetallic electronic property,<sup>26–29</sup> whereas negligible success has been achieved in the semiconducting 2H phase, which greatly hampered its application in the semiconductor field. Therefore, it is of great significance to design a simple and feasible chemical route to obtain semiconducting 2H-phase WTe<sub>2</sub>.

Herein, we synthesize semiconducting 2H-phase  $WTe_2$  nanosheets for the first time by using a simple lithium-intercalation-assisted exfoliation strategy, which is supported

by both experimental measurements and theoretical calculations. Moreover, from the analysis results of Raman spectroscopy, we suspect that the lithium-intercalated process may cause the movement of Te atoms, which bring about a change of the coordination environment for W atoms between bulk and nanosheets, resulting in a structural phase transition from Td to 2H. Furthermore, the as-obtained 2H WTe<sub>2</sub> nanosheets exhibit large positive magnetoresistance with a value of up to 29.5%. We anticipate that this work would open a new door for the development of WTe<sub>2</sub> in the semiconductor field.

In this work, detailed processes for preparing 2H WTe<sub>2</sub> nanosheets are illustrated in Figure 1. Briefly, bulk Td WTe<sub>2</sub> powder (Figure S1) existing in distorted WTe<sub>6</sub> octahedral layers was first prepared through a simple high-temperature solid reaction between tungsten and tellurium powders in an evacuated quartz tube. Then, after a lithium-intercalated process between the synthesized bulk powders with *n*-butyllithium (*n*-BuLi) in hexane, a layered  $\text{Li}_x$ WTe<sub>2</sub> intermediate with an expanded interlayer distance was fabricated. Subsequently, WTe<sub>2</sub> nanosheets that adopt hexagonal crystal structures were obtained by liquid exfoliation of the layered  $\text{Li}_x$ WTe<sub>2</sub> intermediate.

The morphology of the as-obtained nanosheets was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As seen from the SEM image in Figure S2 and the TEM image in Figure 2a, the product

Received: July 10, 2020



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Figure 1. Schematic illustration of the formation process of the 2H  $\rm WTe_2$  nanosheet.



**Figure 2.** Characterization of 2H WTe<sub>2</sub> nanosheets: (a) TEM image; (b) HRTEM image (inset: corresponding FFT image); (c) IFFT image; (d) HAADF image; (e and f) elemental mapping images.

possesses a free-standing nanosheet morphology with sizes of about several hundreds of nanometers. High-resolution TEM (HRTEM) was conducted to study the structural information on the nanosheet. As displayed in Figure 2b, the WTe<sub>2</sub> nanosheet with a hexagonally atomic arrangement can be clearly observed, in which the distance of 0.307 nm corresponds to the interplanar spacing of the {001} planes. Furthermore, from the corresponding fast Fourier transform (FFT; Figure 2b, inset) and inverse FFT (IFFT) images (Figure 2c), its typical hexagonal symmetry can be further confirmed, which is in contrast to reports on bulk WTe<sub>2</sub> with an orthorhombic phase (Figure S3).<sup>30,31</sup> Moreover, the highangle annular dark field (HAADF) and elemental mapping images (Figure 2d–f) show the homogeneous distribution of W and Te atoms throughout the whole nanosheet.

Structural information on the 2H WTe<sub>2</sub> nanosheets was further investigated by X-ray diffraction (XRD) and Raman spectroscopy. As shown in Figure 3a, the XRD pattern of the bulk material matches well with the pure orthorhombic WTe<sub>2</sub>, revealing its high purity. By comparison, both the XRD patterns of experimental 2H WTe<sub>2</sub> nanosheets and the simulated bulk 2H phase shift to lower angles. Moreover, only the lattice planes with integer multiple indexes of (002) for the 2H WTe<sub>2</sub> nanosheets are detected, indicating the high [001] orientation.<sup>17</sup> In Figure 3b, the Raman peaks at 110.7, 122.3, 141.9, 163.5, and 210.3 cm<sup>-1</sup> for bulk WTe<sub>2</sub> agree well with the previous reports for the Td bulk counterpart, which can be assigned to the  $A_2^4$ ,  $A_1^9$ ,  $A_1^6$ ,  $A_1^5$ , and  $A_1^2$  modes, respectively.<sup>31,32</sup> Compared with the bulk sample, the first four



Figure 3. Structural characterization of the 2H WTe<sub>2</sub> nanosheets and bulk Td WTe<sub>2</sub>: (a) XRD patterns; (b) Raman spectra; (c) XPS W 4d spectra; (d) XPS Te 3d spectra.

peaks for the 2H WTe<sub>2</sub> nanosheets exhibit identical red shifts of 2 cm<sup>-1</sup> with a shoulder peak at 131.7 cm<sup>-1</sup> of the A<sub>1</sub><sup>8</sup> mode. Furthermore, all peaks for the 2H  $WTe_2$  nanosheets, particularly the  $A_1^9$  mode, are much more intense and broader. To our knowledge, the  $A_2^4$  and  $A_1^5$  modes soften with a red shift as the number of layers decreases, while the  $A_1^8$  and  $A_1^2$ modes stiffen with a blue shift.<sup>32</sup> When the previous literature on the phase transition of TMDs is consulted, 33,34 it is concluded that the Raman shifts in this work not only are related to the sample thickness but also are caused by structural phase transformation. Moreover, the first five Raman modes of the 2H WTe2 nanosheets stem from the relative movements of Te atoms, and the  $A_1^2$  mode is due to the displacement between adjacent W atoms.<sup>32</sup> Considering that the lithium-intercalated reaction can transform 2H MoS<sub>2</sub>/WS<sub>2</sub> to the trigonal 1T phase,<sup>33,34</sup> we thus suppose that the lithiumintercalated process may cause the movement of Te atoms, which brings about a change from distorted octahedral to trigonal-prismatic coordination of W atoms, leading to the structural phase transition from Td to 2H.

We further characterized the 2H WTe2 nanosheets to highlight the differences in their crystal structure compared to the bulk Td phase by X-ray photoelectron spectroscopy (XPS). As displayed in Figure 3c, the XPS W  $4f_{7/2}$  (31.7 eV) and W  $4f_{5/2}$  (33.8 eV) peaks of the 2H WTe<sub>2</sub> nanosheets have a positive shift of 0.3 eV compared to the bulk Td WTe<sub>2</sub>. Interestingly, a similar shift of 0.3 eV to high binding energy is also observed for the XPS Te  $3d_{5/2}$  (573.0 eV) and Te  $3d_{3/2}$ (583.4 eV) peaks of the 2H WTe<sub>2</sub> nanosheets relative to the bulk Td WTe<sub>2</sub> (Figure 3d). This result clearly demonstrates that the two samples have different valence electron densities, which is caused by their crystal forms with different lattice symmetries. Besides, two oxidation peaks that often occur in TMDs at an ambient environment<sup>17,33-35</sup> appear at both XPS W 4f and Te 3d. Compared with the bulk Td WTe<sub>2</sub>, the degree of oxidation for the nanosheets does not increase, and we suppose that the bulk WTe2 has undergone oxidation in air after high-temperature preparation, resulting in the above XPS observation. The above characterizations and analyses show the successful preparation of 2H WTe<sub>2</sub> nanosheets.

Following the analyses above, a density functional theory (DFT) calculation on the density of states (DOS) was performed to study the electronic structure of the 2H WTe<sub>2</sub> nanosheet, of which the unit cell parameters were derived from HRTEM and XRD results (see the DFT Calculation Details section). As displayed in Figure 4a, the calculated DOS of bulk



**Figure 4.** (a) Calculated DOS of the 2H WTe<sub>2</sub> nanosheets and bulk Td WTe<sub>2</sub>. The light-pink shading highlights the DOS contribution near the Fermi level. (b) UV–visible absorption spectra of the 2H WTe<sub>2</sub> nanosheets and bulk Td WTe<sub>2</sub>. (c) Temperature-dependent resistance of the 2H WTe<sub>2</sub> nanosheets. (d) Temperature-dependent magnetoresistance of the 2H WTe<sub>2</sub> nanosheets under different magnetic fields.

Td WTe<sub>2</sub> across the Fermi level, indicating that the bulk material is intrinsically metallic. Conversely, the DOS of the 2H WTe<sub>2</sub> nanosheet near the Fermi level is discontinuous, which suggests semiconductor behavior in the as-exfoliated nanosheet. To validate the theoretical investigation, UV-vis absorption was further measured. As shown in Figure 4b, bulk Td WTe<sub>2</sub> absorbs all frequencies, consistent with no energy gap, while the 2H WTe2 nanosheet exhibits a prominent absorption edge at 596 nm with a band gap of 2.08 eV. Besides, the electrical transport property was also examined by temperature-dependent resistance measurement. As displayed in Figure S4, bulk Td WTe2 takes on a slightly increasing electrical resistance with increasing temperature, implying intrinsic metallic behavior, while the electrical resistance of the exfoliated nanosheets decreases as the temperature increases, exhibiting typical semiconductor behavior (Figure 4c). The results above clearly indicate the electronic phase transition from metal to semiconductor when the bulk WTe2 was exfoliated into ultrathin nanosheets by lithium-intercalated reaction, which is in accordance with the result of structural phase transition from Td to 2H.

Furthermore, the magnetic transport property of the 2H WTe<sub>2</sub> nanosheets was investigated by using four-probe devices in a commercial physical property measurement system, in which the sample was fabricated into a film by a layer-by-layer assembly strategy. As displayed in Figure 4d, the external magnetic field greatly increases the resistance of the 2H WTe<sub>2</sub> nanosheets, resulting in a large positive magnetoresistance effect. This magnetoresistance value can be calculated by the formula MR % = [R(H) - R(0)]/R(0), where R(H) is the resistance under a magnetic field and R(0) is the resistance without a magnetic field. Accordingly, at 10 K, the positive

magnetoresistance values were as large as 21.4% at 3 T, 26.2% at 6 T, and 29.5% at 9 T. Moreover, the nanosheets can also achieve large room-temperature positive magnetoristance (16.2%, 300 K, 9 T). To the best of our knowledge, the 2H WTe<sub>2</sub> nanosheets with large positive magnetoristance were first reported in this work, which may attract more attention about their electronic properties in the future. Besides, we performed a preliminary exploration on its photodetector performance (Figure S5), which exhibited a high photosensitivity under simulated sunlight, showing a great hold in photodetector application.

In summary, we have successfully synthesized the hexagonalphase WTe<sub>2</sub> nanosheets with semiconducting electronic properties. Detailed structural characterizations revealed the occurrence of a structural phase transition from Td to 2H when bulk WTe2 was exfoliated into an ultrathin nanosheet. Furthermore, from the analysis results of Raman spectroscopy, we suspected that the lithium-intercalated process may cause the movement of Te atoms, resulting in the structural phase transition. Besides, the corresponding electronic phase transition from metal to semiconductor was confirmed by theoretical calculations and experimental measurements. More importantly, the semiconducting 2H WTe<sub>2</sub> nanosheets were found to exhibit a large positive magnetoresistance with values of up to 29.5% (10 K) and 16.2% (300 K) at 9 T. We believe that our work will be an interesting addition to the semiconductor families with new 2D materials.

## ASSOCIATED CONTENT

## **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02049.

Experimental details and additional characterization information for the products (PDF)

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#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the NSF of China (Grants 21805165, 21971143, 21673127, 21671119, and 51572152), NSRF of Hubei Provincial Education Office of China (Grant Q20181203), 111 Project (Grant D20015), and ITOYMR in the Higher Education Institutions of Hubei Province (Grant T201904).

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