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Extended Polymorphism of Two-Dimensional Material

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Supporting Information

ABSTRACT: When controlling electronic properties of bulk materials, we usually assume that the basic crystal structure is fixed. However, in two-dimensional (2D) materials, atomic structure or polymorph is attracting growing interest as a controlling parameter to functionalize their properties. Various polymorphs can exist in transition metal dichalcogenides (TMDCs) from which 2D materials are generated, and polymorphism has drastic impacts on the electronic states. Here we report the discovery of an unprecedented polymorph of a TMDC 2D material. By mechanical exfoliation, we made thin flakes from a single crystal of 2Ha-type tantalum disulfide (TaS₂), a metallic TMDC with a charge-density-wave (CDW) phase. Microbeam X-ray diffraction measurements and electrical transport measurements indicate that thin flakes possess a polymorph different from any one known in TaS₂ bulk crystals. Moreover, the flakes with the unique polymorph displayed the dramatically enhanced CDW ordering temperature. The present results suggest the potential existence of diverse structural and electronic phases accessible only in 2D materials.

KEYWORDS: Polymorphism, two-dimensional material, charge-density-wave (CDW), electric double layer transistor (EDLT), microbeam X-ray diffraction

TMDCs have the chemical formula of MX₂, where M and X represents transition metal and chalcogen, respectively. The polymorphism comes from how the X–M–X layers are stacked,^{1,2} whose dramatic effects on electronic properties have long been investigated in bulk crystals.^{3–5} In TaS₂, the polymorphism results in diverse types of CDW phases. To date, the 1T, 2Ha, 4Hb, and 6R forms are widely known to exist stably in the TaS₂ bulk crystals (see Figure 1a).^{2,3,6,7} The 2Ha form is a purely trigonal polymorph whereas the 1T octahedral. The 4Hb and 6R forms are mixed octahedral–trigonal polymorphs. As with the 2Ha, the 2Hb and 3R consist only of trigonal prisms (see Figure 1a). However, the 3R-TaS₂ has rarely been synthesized,⁸ and there is no report of the growth of the 2Hb-TaS₂. The nature of CDWs strongly depends on the polymorph.³ 2Ha-TaS₂ shows a transition to an incommensurate CDW (ICCDW) phase from a normal metal at 76 K, and the metallic nature is enhanced after the transition. 1T-TaS₂ is a normal metal above 550 K and is cooled down to be an

insulating commensurate CDW system through undergoing CDW transitions.⁹ Recently, it was revealed that the polymorphism has highly controllable nature in 2D materials,^{10–16} which increases the possibility to find hidden polymorphs with exotic CDW states in 2D TaS₂ crystals.

We prepared devices of thin flakes exfoliated from a 2Ha-TaS₂ single crystal, whose thickness ranged from 7–35 nm. We performed the microbeam X-ray diffraction measurements in Spring-8^{17,18} on the flakes partially covered with electrodes for resistivity measurement as shown in Figure 1b. Figure 1c is the image of a device captured by fluorescent X-rays from the gold electrodes, which enables us to position the focal point of the microbeam X-ray to the channel area.

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Figure 1. Structural characterization of TaS₂ flakes exfoliated from a 2Ha-TaS₂ single crystal. (a) Crystal structures of 2Ha-, 1T-, 4Hb-, and 6R-TaS₂. The structures of the 2Hb and 3R are also shown for reference. (b) Optical microscope image of a TaS₂ thin flake device. (c) Image of the TaS₂ device captured by fluorescent X-rays from the gold electrodes. The orange circles in panels b and c represent the position at which the microbeam X-ray impinges. (d) Bragg peaks from (0 0 *l*) planes of six TaS₂ thin flake devices. The black lines are the fits to the Gaussian function. The black dashed line denotes the Bragg peak from (0 0 8) plane of the bulk 2Ha-TaS₂ single crystal. (e) The *c*-axis lattice constants (*c*'s) of the six TaS₂ thin flakes and of the bulk crystal from which the flakes were exfoliated. The green, blue, light-blue, and gray colored dashed lines represent the typical values of *c*'s for 2Ha-, 6R-, 4Hb-, and 1T-TaS₂ bulk crystals, respectively (refs 2, 19, 7, 19, 6, 20, and 2 from the top). The gray colored triangles represent the literature values of 1T-TaS₂ thin flakes (ref 9). (f) Schematic picture of the mechanical exfoliation to explore exotic phases.

As presented in Figure 1d, clear shifts of Bragg peak angle were detected in the measured six thin flakes. Figure 1e is a summary of the *c*-axis lattice constants for the flakes and literature,^{2,6,7,19,20} suggesting that the diversity of the lattice constant is not simply driven by decreasing thickness. We can categorize the thin flakes into three groups in terms of *c*-axis parameter. The first group [sample No. 1 (thickness, *t* = 18 nm) and 2 (*t* = 7 nm)] is a bulk-like group where the 2Ha structure type^{2,19} is assigned. The second group [sample No. 3 (*t* = 29 nm), 4 (*t* = 26 nm), and 5 (*t* = 36 nm)] has the *c*-axis parameter close to that of the 6R.⁷ The last third group [sample No. 6 (*t* = 18 nm)] possesses the shortest lattice constant. Such diversity in lattice constant implies that we may have generated thin flakes with different polymorphs by exfoliating a bulk crystal, as depicted in Figure 1f. To verify this scenario, we carried out temperature dependent resistivity measurements on many thin flakes including the samples measured by the microbeam X-ray.

We first measured the transport properties of the bulk single crystal, whose data are represented by the gray colored lines in Figure 2a and b. An anomaly in resistivity appeared at 76 K, and Hall coefficient (*R*_H) started to decrease below the temperature, which indicated the occurrence of a normal–ICCDW transition.²¹ The CDW transition was observed in many thin flakes such as sample No. 2 that displayed the kink in resistivity at 70 K. On the other hand, in sample No. 1, the ICCDW phase was absent, and a superconductivity (SC) transition occurred at 3.6 K. The SC was observed in several flakes as shown in Figure 2c, which was also reported previously.^{22,23} These results are summarized in the electronic phase diagram in Figure 2d. The ICCDW phase is suppressed and the SC

phase is enhanced as *R*_H at 300 K is increased, where the increase in the positive *R*_H corresponds to the electron doping. This picture of CDW/SC competition as a function of the initial carrier density makes a good accordance with a previous report on chemically doped 2Ha-TaS₂ system.²⁴ Therefore, these flakes are assigned as 2Ha-TaS₂. The electron doping occurred unintentionally probably during the device fabrication process.

Figure 3a shows the temperature (*T*) dependent normalized resistivity [$\rho(T)/\rho(300\text{ K})$] of the three thin flakes in the second group consisting of samples Nos. 3, 4, and 5. Each sample shows a clear CDW transition with a hysteresis in resistivity around 300 K, which is a characteristic of the 6R⁷ and 4Hb.⁶ Given the experimental values of lattice constants close to that of the 6R⁷ (see Figure 1d), it is reasonable to conclude that these thin flakes are of the 6R-TaS₂. Here we found that by mechanical exfoliation, we can obtain thin flakes with a polymorph, which is different from that of the bulk crystal. However, we cannot determine the possible scenario how the 6R-type flakes were generated from the 2Ha-type bulk crystal: whether they a priori existed as a minor phase in the bulk single crystal or they are the results of cleavage-induced change in crystal structure. It should be noted that the X-ray diffraction measurement on the original bulk crystal indicates the absence of minor phases. The volume ratio of the 6R to the 2Ha is less than 10^{−3} in the bulk crystal (see Figure S1 in the Supporting Information).

We can also find a feature in the 6R-type thin flakes. As shown in Figure 3b, the *c*-axis lattice constants of thin flakes are longer than that of 6R-type bulk crystal. Such thinning-induced swelling was theoretically predicted in NbSe₂²⁵ and exper-

Figure 2. TaS₂ thin flakes with 2Ha-type characteristics. (a) Temperature (T) dependence of normalized resistivity [$\rho(T)/\rho(300\text{ K})$] for the bulk single crystal (the gray colored line) and the thin flakes (others) with 2Ha-type characteristics. $\rho(T)/\rho(300\text{ K})$ for the flakes are shifted upward by 0.2 for clarity. The black arrows represent the normal–ICCDW phase transitions. (b) T dependence of Hall coefficient R_H . (c) $\rho(T)/\rho(4\text{ K})$ versus T curves for superconducting thin flakes. (d) Electronic phase diagram for the 2Ha-type thin flakes. The horizontal axis is the value of the R_H at 300 K.

Figure 3. TaS₂ thin flakes with 6R-type characteristics. (a) Temperature (T) dependence of normalized resistivity [$\rho(T)/\rho(300\text{ K})$] for the thin flakes with 6R-type characteristics. $\rho(T)/\rho(300\text{ K})$ are shifted upward by 0.2 for clarity. (b) Relationship between the CDW transition temperature (T_{CDW}) and the c -axis parameter (c).

imentally observed in 1T-TaS₂,⁹ which seems to be the characteristic of 2D material. Figure 3b also exhibits that the CDW transition temperature decreases as the c -axis parameter expands. This systematic behavior may reflect the three-dimensionality of the CDW because the interlayer interaction is reduced as the c -axis lattice constant is elongated.

We then clarified the properties of the third group including sample No. 6. The microbeam X-ray diffraction measurement revealed that the flake has a short c -axis lattice constant, which is close to those of 1T-type bulk crystals^{2,20} and thin flakes.⁹ However, the sample No. 6 is not a 1T-type flake in terms of

electronic transport properties. Although the 1T-type flakes become insulating upon cooling,⁹ the sample No. 6 is always metallic as represented by the light-blue colored line in Figure 4a.

In the normalized ρ – T curve of the sample No. 6 shown in Figure 4a, we can find an anomaly in the resistivity at 210 K and that the metallicity is enhanced below the temperature. Such behavior strikingly resembles that of 2Ha-TaS₂ showing the normal–ICCDW transition at 76 K. Therefore, the resistance anomaly at 210 K in sample No. 6 is likely attributed to the normal–ICCDW transition. As shown in Figure 4a, several flakes also exhibited the normal–ICCDW transition temperatures (T_{ICCDW} 's) of $T_{\text{ICCDW}} = 130$ – 190 K , which are significantly higher than that of the 2Ha-TaS₂. Figure 4b is the R_H versus T curves for the flakes with the high T_{ICCDW} 's. All the flakes show an increase in R_H below T_{ICCDW} , which is the clearest in the flake whose data are colored with red. The increase in R_H below T_{ICCDW} indicates the reduction in the carrier concentration caused by the opening of CDW gap.

What is the polymorph of the third group other than 2Ha or 1T? Figure 1e shows that the c -axis parameter of sample No. 6 is slightly shorter than that of the bulk 4Hb-TaS₂ so that the flake may be a strained 4Hb-type film. However, T_{ICCDW} of the 4Hb-TaS₂ is around 20 K,⁶ and it decreases with reducing lattice constants via pressurization.²⁶ Such a low T_{ICCDW} of 4Hb-TaS₂ crystals is distinct from the high T_{ICCDW} of the flakes including sample No. 6. Therefore, we can exclude the possibility that the flakes are 4Hb-TaS₂.

As in the case of the emergent 6R-type flakes, we possibly isolated or induced the TaS₂ flakes with an unprecedented polymorph, which exhibits a high normal–ICCDW transition temperature. Here we temporally name the unique polymorph as the 2H' because its normal–ICCDW transition resembles that of 2H-TaS₂ in the kink of ρ – T curve. The differences in T_{ICCDW} among samples probably come from the unintentional carrier doping as observed in 2Ha-type thin flakes. However, we could not observe a systematic relation between T_{ICCDW} and R_H , which may be attributed to the sample-dependent amount of disorders that affects the carrier mobility and R_H . To uncover the electronic diagram of the 2H'-TaS₂, we made an electric double layer transistor (EDLT) structure^{27,28} with the 2H'-TaS₂ flake as the channel material by using an ionic liquid (*N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium bis-trifluoromethylsulfonyl-imide, DEME-TFSI) as the gate dielectric. We applied gate voltage (V_G) at 210 K and cooled down the sample. The application of positive and negative V_G corresponds to electron and hole doping, respectively.

Figure 4c is the temperature dependence of the four-terminal resistance (R) in the EDLT for a 20 nm-thick 2H'-TaS₂ flake, where the T_{ICCDW} was systematically decreased by increasing V_G . At the lowest temperature, the residual resistance (R_0) was increased with reducing the ICCDW ordering temperature. The resistivity is expressed as $\rho = \rho_{\text{ph}} + \rho_{\text{imp}} + \rho_{\text{CDW}}$, where ρ_{ph} , ρ_{imp} , and ρ_{CDW} are the resistivity values due to the scattering by phonons, impurities, and CDW fluctuations, respectively.²¹ Because the contribution of phonons is negligible at low temperatures and the amount of impurity is constant upon electrostatic carrier doping, the increase in R_0 indicates the enhancement of the CDW fluctuations by suppressing the CDW ordering temperature. Figure 4d shows the R_H versus T curves for the EDLT, where the decrease of R_H at the lowest temperature by increasing V_G suggests that the hole-like Fermi surface is less destroyed as the CDW ordering is suppressed.

Figure 4. 2H'-TaS₂ thin flakes with the enhanced CDW ordering temperature. (a, b) Temperature (T) dependence of (a) normalized resistivity [$\rho(T)/\rho(300\text{ K})$] and (b) Hall coefficient (R_H) for the thin flakes with an unprecedented polymorph (2H'-TaS₂). $\rho(T)/\rho(300\text{ K})$ are shifted upward by 0.2 for clarity. The black arrows represent the normal-ICCDW phase transitions. (c, d) T dependence of (c) 4-terminal resistance (R) and (d) R_H for a 20 nm-thick 2H'-TaS₂ EDLT. (e) R - T curves for a 30 nm-thick 2H'-TaS₂ EDLT. (f) Electronic phase diagram for 2H'-TaS₂ revealed by ionic liquid gating.

We observed a gate-tuned normal-ICCDW transition also in a 30 nm-thick 2H'-TaS₂ flake as presented in Figure 4e, where the electron and hole doping resulted in the decrease and increase in T_{ICCDW} , respectively. The overall behavior of the 2H'-TaS₂ is summarized in the electronic phase diagram presented in Figure 4f. By using V_G as a tuning parameter, Fermi surface is modified, and the normal-ICCDW transition in 2H'-TaS₂ is driven up or down in temperature. Figure 4f indicates that the Fermi surface topology indeed plays a significant role in the stabilization of the ICCDW phase and that the 2H'-TaS₂ flakes are doped with electrons.

Finally, we discuss the possible structure of the 2H'. It should be noted that TaS₂ bulk crystals with octahedrons always show first-order phase transitions that accompany steep increases in resistivity, whereas such transitions were absent in the 2H'-TaS₂ flakes. Therefore, the 2H' is likely to be composed of solely the trigonal prisms such as the 2Hb and 3R (see Figure 1a). The trigonal prism-based polymorphism is well investigated in the selenium analog of TaS₂, Ta_{1+x}Se₂ bulk crystals.²⁹ Without doping, the c -axis lattice constants of 2Hb/3R-TaSe₂ are slightly longer than that of 2Ha-TaSe₂. However, with increasing the amount of excess Ta and consequently doping electrons, the lattice parameter slowly increases in 2Ha-TaSe₂, whereas it rapidly decreases in 2Hb/3R-TaSe₂. Because the 2H'-TaS₂ flakes were revealed to be doped with electrons and have the short c -axis lattice parameter, the 2H' can be either 2Hb or 3R. The d band at Fermi energy of TaS₂ consists mainly of dz^2 orbital so that the interlayer coupling in the 2Hb/3R can be smaller than that in the 2Ha. The resultant increase in the 2D character of Fermi surface leads to the better nesting condition and the enhancement of the ICCDW ordering.

In conclusion, we demonstrate that the mechanical exfoliation of a layered bulk crystal can yield thin flakes with an unexpected polymorph. By cleaving a 2Ha-TaS₂ bulk single

crystal, we obtained thin flakes with not only 2Ha, but also 6R and an unprecedented polymorph (2H'). The 2H' is either the 2Hb or 3R, both of which have never been stably existed as TaS₂ bulk crystals. The discovery of the 2H'-TaS₂ thin flakes with highly enhanced CDW ordering temperatures indicates the potential existence of diverse metastable polymorphs with exotic electronic phases that are accessible only in the 2D materials. The revealed extended polymorphism increases the potential opportunities to functionalize 2D materials by using the atomic structure as an emergent degree of freedom.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b02374.

X-ray diffraction patterns from 2Ha-TaS₂ bulk single crystal (PDF)

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Author Contributions

M.Y. and J.T.Y. fabricated the devices and measured the transport properties. M.Y. analyzed the data. M.Y., J.T.Y., Y.J.Z., Y.L., and S.K. carried out the microbeam X-ray measurements on thin flake devices. T.N. and N.K. provided the single crystal. M.N. conducted the X-ray diffraction measurement on the bulk

single crystal. M.Y., J.T.Y., A.F., and Y.I. planned and supervised the study. M.Y. and Y.I. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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