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Hydrogen-assisted Post-growth Substitution of Tellurium into Molybdenum Disulfide Monolayers with Tunable Compositions

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Abstract

Herein we report the successful doping of tellurium (Te) into molybdenum disulfide (MoS₂) monolayers to form MoS₂xTe_{2(1-x)} alloy with variable compositions via a hydrogen-assisted post-growth chemical vapor deposition (CVD) process. It is confirmed that H₂ plays an indispensable role in the Te substitution into as-grown MoS₂ monolayers. Atomic-resolution transmission electron microscopy (TEM) allows us to determine the lattice sites and the concentration of introduced Te atoms. At a relatively low concentration, tellurium is only substituted in the sulfur sublattice to form

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4 monolayer $\text{MoS}_{2(1-x)}\text{Te}_{2x}$ alloy, while with increasing Te concentration (up to $\sim 27.6\%$
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6 achieved in this study), local regions with enriched tellurium, large structural
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8 distortions, and obvious sulfur deficiency are observed. Statistical analysis of the Te
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10 distribution indicates the random substitution. Density functional theory calculations
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12 are used to investigate the stability of the alloy structures and their electronic properties.
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14 Comparison with experimental results indicate that the samples are unstrained and the
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16 Te atoms are predominantly substituted in the top S sublattice. Importantly, such
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18 ultimately thin Janus structure of $\text{MoS}_{2(1-x)}\text{Te}_{2x}$ exhibits properties that are distinct from
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20 their constituents. We believe our results will inspire further exploration of the versatile
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22 properties of asymmetric 2D TMD alloys.
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29 30 **1. Introduction**

31
32 Monolayer molybdenum disulfide, a representative member of the transition metal
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34 dichalcogenide (TMD) materials family, holds promise for applications in
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36 nanoelectronics and nanophotonics, along with the existing industrial applications of
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38 its bulk counterpart as a catalyst in hydrodesulphurization. The material properties of
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40 pristine 2D TMDs, as desired for certain applications, can be further tuned e.g. by
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42 controlling the type and content of dopants or by various chemical and physical
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44 functionalization approaches [1-5]. Among them, isoelectronic doping with homo-
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46 group element, that is, substitution between transition metal, i.e., molybdenum and
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48 tungsten, or chalcogen, i.e., sulfur, selenium and tellurium, to form the alloyed TMD
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50 monolayers, has drawn broad interest, as they could provide a tunable band gap over
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52 wide range of energies and with spatial composition modulation. Remarkable progress
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4 has been made in the controlled growth of 2D TMD alloys and their device applications.

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6 For instance, Gong et al. reported[6] that optical band gap modulations of monolayer
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8 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ can be tuned between ~ 1.85 eV (in monolayer MoS_2) and ~ 1.54 eV (in
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10 monolayer MoSe_2) depending on the concentration of Se. Duan et al.[7] and Li et al.[8]
11
12 demonstrated a carrier type modulation in $\text{WS}_{2(1-x)}\text{Se}_{2x}$ and $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ nanosheets, via
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14 either the substitution of S with Se or Mo with W. So far, previous reports [6-15] have
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16 mainly focused on the S- and Se-based systems including $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, $\text{Mo}_x\text{W}_{1-x}\text{Se}_2$,
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18 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ and $\text{WS}_{2(1-x)}\text{Se}_{2x}$ etc, while alloys with Te have remained less studied.

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25 MoTe_2 itself hosts several features that are distinct from other 2D TMDs: (i) The
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27 semiconducting 2H-phase MoTe_2 monolayer has the lowest energy band gap (~ 1 eV)
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29 among 2D Mo-dichalcogenides, and thus in principle it can provide a larger range of
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31 band gap tunability via alloying with tellurium. (ii) Strong spin-orbit coupling is
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33 expected in Te-based 2D TMDs associated with the heavy Te atom, which is relevant
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35 in spin- and valleytronics devices. (iii) The energy difference between semiconducting
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37 2H phase and (semi-)metallic 1T' phase of 2D MoTe_2 is very small, < 0.1 eV per unit
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39 cell, that may favor applications in data storage and in electronics via phase engineering
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41 [16-29]. (iv) Finally, the so-called type-II Weyl semimetal behavior in octahedral bulk
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43 MoTe_2 (also known as T_d phase) has been confirmed [30- 33]. Given the versatile
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45 structural and electronic properties of 2D MoTe_2 , it is increasingly important to also
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47 investigate the Te-substituted Mo- and W-dichalcogenides.

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58 So far, a number of methods have been proposed to prepare monolayer TMD alloys
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60 including the growth of single crystals by chemical vapor transport followed by

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3 mechanical exfoliation (ME) [9-11], physical vapor deposition (PVD)[7, 12, 13], and
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5 one-step chemical vapor deposition (CVD)[6, 14, 15]. Of these, CVD is perhaps the
6
7 most widely adopted method owing to its capability to prepare high-quality 2D TMD
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9 alloys with large flake sizes and with well-controlled morphology. Compared to S and
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11 Se, Te has relatively low chemical reactivity, and it still remains an open question
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13 whether it is feasible to substitute Te into as-formed 2D TMDs like MoS₂ via CVD. In
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15 this work, we describe our efforts on preparing MoS_{2(1-x)}Te_{2y} (y<=x) monolayers via Te
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17 substitution into as-grown MoS₂ monolayer through a two-step post-growth CVD
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19 process. Raman spectra, PL and atomic-resolution ADF-STEM techniques were used
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21 to determine the lattice sites and concentration of substituted Te atoms. Our results
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23 confirm, that: (i) Hydrogen carrier gas plays an indispensable role in the substitution
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25 process. (ii) The composition of Te can be modulated by varying the reaction time and
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27 temperature during doping. (iii) The atomic structures of the final MoTe monolayers
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29 depend on the Te concentration. In particular, the heavy structural distortions observed
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31 in higher concentrations, indicated that there exists an upper limit for the composition
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33 of the substituted Te atoms through the post-growth CVD process.
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43 2. Experimental Section

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45 CVD growth of MoS₂: We adapted a two-step synthesis of Te-doped MoS₂ monolayer
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47 alloys with varied compositions on the 300 nm SiO₂/Si substrates by CVD. The
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49 monolayer MoS₂ was synthesized first by the sulfurization of MoO₂. The MoO₂ powder
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51 (Sigma-Aldrich, 99%) and sulfur powder (Alfa Aesar, 99.5%) were used as the
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53 precursors. SiO₂/Si substrates were placed face-down to the MoO₂ powder (10 mg).
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55 The furnace was ramped to 750 °C in 35 minutes and then sulfur powder (80 mg) was
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4 The structural characterizations were carried out with a probe corrected Titan
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The structural characterizations were carried out with a probe corrected Titan ChemiSTEM (FEI Inc.). The microscope was operated at the acceleration voltage of 200 kV. The probe current was set at less than 80 pA and the convergence angle was about 22 mrad. And the collection angle is about 43.4 to 200 mrad. A GIF Quantum 965 X (Gatan Inc.) recorded electron energy loss spectra (EELS). XEDS data was recorded by a Bruker Super-X detector system.

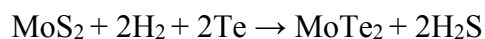
All calculations are carried out with VASP and PBE exchange-correlation functional [34-36], adopting 500 eV plane-wave cutoff. For alloy calculations we used 5x5 supercells, where random substitution of Te atoms was modeled using the special quasirandom structures. The Brillouin zone was sampled with $2 \times 2 \times 1$ k-point mesh. In ribbon calculations, the system size was 4 units along the ribbon and about 8 units normal to it (see Figure 8a for a side view). 2 k-points were used along the ribbon direction. Calculations demonstrating the Rashba effect were carried out with spin-orbit coupling, but otherwise in non-spin-polarized mode.

3. Result and Discussions

MoS₂ monolayers are grown on SiO₂/Si substrates via a CVD process, and then loaded into another CVD furnace for Te doping during which the as-grown MoS₂ samples were contained in a half-open mini-quartz tube to increase the partial pressure of Te, as shown in Figure 1a. The samples after tellurization on SiO₂/Si substrates are characterized by optical microscope (OM) as shown in Figure 1b, and that of pristine

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4 MoS₂ monolayer is also given as a reference. For comparison, images of tellurized
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6 samples with and without H₂ carrier gas are displayed in the top and bottom panels,
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8 respectively. In the absence of H₂, we find that the as-grown MoS₂ monolayer starts to
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10 sublimate (like via oxidative etching) from the apex regions (arrows in the middle
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12 bottom panel) after the tellurization reaction proceeds for 10 minutes at 600 °C. As the
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14 tellurization time further increases, the flake is completely sublimated without any
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16 detectable residues (see bottom right panel). In contrast, in the presence of H₂ during
17
18 tellurization, the products preserve their original morphology as found in the pristine
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20 monolayer MoS₂, as shown by the optical microscope images in the top panels. Figure
21
22 1c presents Raman spectra recorded on the MoS₂ after tellurization at 700 °C (green),
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24 650 °C (pink), and 600 °C (orange) for 25 minutes, in which the spectra of pristine
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26 MoS₂ is also given as a reference (purple). The well-known characteristic resonance
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28 peaks of pristine 2H MoS₂ monolayer located at 383 cm⁻¹ (known as E_{2g} mode) and
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30 403 cm⁻¹ (known as A_{1g} mode) are observed in all these samples, indicating the
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32 preservation of the 2H phase[37]. On the other hand, the appearance of a peak at 243
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34 cm⁻¹ at 600 °C, 650 °C, and 700 °C tellurization samples, corresponding to the E_{2g} mode
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36 of 2H-MoTe₂[27], not shown in 2H MoS₂ monolayer, provide evidence that the Te
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38 atoms were successfully substituted. In order to synthesize Te-doped MoS₂ monolayer
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40 alloys, hydrogen as a strong reducer is required due to the low chemical reactivity of
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42 Te, which is similar to the synthesis of Se-based TMDC materials (like MoSe₂, WSe₂)
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44 [38, 39]. And during this substitution reaction, S vacancy [40] could be produced by
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46 the introduction of hydrogen at high temperature, which can promote the substitution
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4 reaction of the S with Te atoms. We propose that the chemical reaction during the
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6 tellurization of MoS₂ is as follows:
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11 We then turn to the electron microscopy characterization of the microscopic structure
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13 and chemical composition of the tellurized MoS₂ samples. Figure 2a shows a low-
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15 magnification ADF-STEM image of a Te-doped MoS₂ (700 °C, 25 min) flake with
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17 well-preserved triangular shape. Chemical analysis via electron energy loss
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19 spectroscopy (EELS) and X-ray energy-dispersive spectrometer (XEDS) over 50
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21 samples both confirm the existence of Te atoms, with typical spectra displayed in
22
23 Figure 2b (EELS) and Figure 2c (XEDS). Note that here both the EELS and XEDS
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25 spectra were collected over a large number of samples and reflect the average chemical
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27 composition, not locally. The appearance of oxygen K-edge at 532 eV in the EELS
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29 spectra may come from the residual PMMA that were used during the sample transfer.
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40 To analyze in more detail the statistical distribution of the Te substitution sites, we
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42 carried out atomically resolved ADF-STEM characterization over large number of
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44 samples and sample areas. Shown in Figure 3a-c are three representative ADF-STEM
45
46 images of the Te-doped MoS₂ monolayers prepared under different tellurization
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48 conditions, corresponding to 600 °C, 650 °C, and 700 °C for 25 minutes. These ADF-
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50 STEM images are Z-contrast images [41], which enables straightforward identification
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52 of the Te substitution sites (marked with yellow circles), although the top and bottom
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54 chalcogen sublattices cannot be separated. Fig 4a, b (650°C for 25 minutes) show the
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4 result where the different types of sites are indicated (yellow circle represent S₂ site,
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6 green and blue, respectively S + Te site and Te₂ site). Next, we analyze the alloying
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8 degree (J) for Te (include Te₂ site and S + Te site). The value of alloying degree (J)
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10 can be given as
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$$J_{Te} = P_{observed} / P_{random} \times 100\% \quad [9] \quad (1)$$

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17 Where P_{observed} is the ratio of the averaged S coordination number to the total
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19 coordination number and P_{random} is the atomic ratio of S in the examined layer. J_{Te} close
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21 to 100% means that the Te and S atoms are distributed randomly around the Te sites.
22
23 J_{Te}<100% means a homophilic configuration, while J_{Te}>100% implies a heteroatom-
24
25 rich configuration. J_{S₂} can also be obtained from the same ADF image. As shown in
26
27 Figure 4c, the average of J_{Te} is 100.6% and J_{S₂} is 98.4%, indicating that the Te
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29 distribution is very close to random substitution. Note: A recent study by Fang et al.
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31 [42] reported a phase separation in the MoS_{2(1-x)}Te_{2x} which may be caused due to the
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33 lower tellurization temperature (500 °C) used there.
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43 Figure 4d shows the relationship between the growth temperature and the
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45 corresponding substituted Te atom proportion. After statistical analysis of dozens of
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47 atomically resolved STEM images in different growth temperatures, it was found that
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49 the Te ratio N_{Te} / (N_{Te} + N_S), where the N_{Te} is the number of Te atoms, and N_S is the
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51 number of S atoms increases steadily with the growth temperature, yielding 3.3%, 6.6%,
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53 and 27.3% for samples grown at 600 °C, 650 °C, and 700 °C, respectively, for 25 min.
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58 The post-growth process adopted here, with MoS₂ sheet placed on substrate and only
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4 the top side exposed to the tellurization, could naturally lead to Te asymmetry in the
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7 two sides of the sheet. From the STEM images, we cannot distinguish which S atom
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9 was replaced by Te atom. Based on an assumption of random substitution, we evaluated
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11 statistical estimates of the site proportions (see SI) and compared them to the
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13 experimental proportions in Figure 4d, which indicated that the samples could show at
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15 least partial Te asymmetry.
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22 Having assessed the composition and possible composition asymmetry, we analyze the
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24 stability of these structures with the help of density functional theory calculations. We
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26 generated models with randomly substituted Te, both in the symmetric and asymmetric
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28 configurations. We define the mixing enthalpy (at 0 K)
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$$E_{mix} = E_{MoS_{2x}Te_{2(1-x)}} - [x * E_{MoS_2} + (1-x) * E_{MoTe_2}] \quad (2)$$

32
33 where the energies on the right side refer to DFT total energies. Mixing free energy is
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35 then obtained by adding the entropy of mixing and here evaluated at 650 C. The results
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37 in Figure 5 show that there are no limits for mixing ($E_{mix} < 0$) when Te is substituted
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39 symmetrically on both sides and without strain. When Te is substituted on only the top
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41 sublattice, we obtain a limit of 33 % (or 66% of the top sublattice sites), above which
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43 segregation is expected. Since the lattice constant could be close to that of MoS₂ during
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45 the tellurization, we repeated the calculations with the lattice constant fixed to that of
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47 MoS₂. The obtained limits for mixing in the symmetric and asymmetric case are 28 %
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49 and 19 %, respectively. The limits in the unstrained asymmetric and strained symmetric
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51 cases both agree well with the experiment, suggesting that the composition is limited
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4 either by the strain or by the asymmetry, but it is difficult to draw conclusions on the
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6 amount of asymmetry from these results.
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11 In the relatively gentle growth conditions (600 °C, 650 °C), the structure retains the
12 hexagonal lattice and shows no significant difference from the MoS_xSe_y alloys [6]. On
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14 the other hand, as Te proportion increases (sample grown at 700 °C, corresponding to
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16 Te ratio of 27.3%), it seems that the Te atoms tend to aggregate (Figure 6a), which is
17
18 different from the MoS_xSe_y alloy case. We notice local structural modulations, where
19
20 the aggregated Te atoms tend to form triangular regions, as outlined by purple triangle
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22 in Figure 6a. In few cases, the Te atoms are located in between the neighboring Mo
23
24 atoms, forming an atomic chain, as highlighted by yellow lines. Figure 6b, c show the
25
26 distortion structure in Te-doped MoS_2 monolayer alloys grown at 700 °C. Triangles
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28 with excess or deficiency of Te are shown in Figure 6b, c and marked in purple. The
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30 triangles are surrounded by the chain-like structures that could originate from
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32 displacement of Te atoms due to buildup of strain during the growth. The schematic of
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34 outward displacement of Te atoms is shown in Figure 6b, in which purple arrows (and
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36 orange ones in ADF-image) illustrate the shift direction of Te atoms. The gathered Te
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38 atoms shift away from the origin X_2 sites radially, leading to a triangle in which center
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40 Te atom still located in the X_2 site. At the edge of such distortion triangles, the Te atoms
41
42 are located right between two nearby Mo atoms, with Mo-Te-Mo angle (projected angle)
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44 at 180°, forming atomic chains. Around the Te-deficient regions, shown as a triangle
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46 with dimmer contrast in Figure 6c, the Te atoms move towards the undoped regions.
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4 Considering the atomic chains in more detail, Figure 6d, e show the X_2 sites across the
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6 triangle and along the atom chain. It is found that the intensity at X_2 sites along the
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8 atomic chain are relatively lower than in the undistorted parts, indicating the
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10 disappearance of S atoms, with the possible structure shown in Figure 6d, e. The S
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12 vacancies could be generated to release the strain induced by the Te substitution. Linear
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14 arrangements are known to be the lowest energy configuration for vacancies in MoS_2
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16 [43, 44]. Here, the vacancies appear to similarly agglomerate to lines, finally leading to
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18 the observed local reconstruction of the alloy structure. As previously reported for
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20 MoS_2 and MoSe_2 [44-47], electron beam irradiation creates S vacancies in the lattice,
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22 and provides the energy for the vacancies to overcome the migration energy barrier. In
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24 our observation, high growth temperature instead of electron beam likely offers the
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26 energy for migration, and could also explain the increased vacancy concentration. In
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28 addition, the vacancies could be created by the strain buildup. The calculated vacancy
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30 formation energies as a function of alloy concentrations are shown in Figure 5b. In the
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32 case of unstrained lattice, the formation energies are close to those in pristine MoS_2 ,
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34 but under strain the formation energy decreases strongly, which would then give rise to
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36 increased vacancy concentration. Overall, the case of Te substitution appears to differ
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38 markedly from that with Se. The Se concentration can be continuously tuned in the
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40 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloys without disturbing the 2H phase lattice, while there
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42 appears to be intrinsic limits in the case of Te. Moreover, when close to this limit, the
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44 local structure becomes distorted due to either the 10% lattice mismatch (3.161 Å and
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46 3.518 Å for MoS_2 and MoTe_2 , respectively) or the 16.7% difference in the ionic radii
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4 of ($R_S=1.84 \text{ \AA}$ and $R_{Te}=2.21 \text{ \AA}$ for S^{2-} and Te^{2-}). This is consistent with the experimental
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6 results as shown in Fig. S6 where the lattice constant of the doped MoS_2 monolayer
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8 becomes larger as the Te concentration increases.
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14 Finally, we discuss the electronic structure and optical properties of our samples. The
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16 photoluminescence spectra of the samples are shown in Figure 7a. The peak position,
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18 assigned to A exciton, shifts to lower energies and the intensity decreases rapidly as the
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20 Te concentration increases. The peak positions as a function of the composition are
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22 collected in Figure 7b, where we compare them to the calculated band gap values
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24 (shifted to match the MoS_2 value at the endpoint). The agreement is clearly better with
25
26 respect to the calculations with unstrained lattice, whereas the degree of asymmetry
27
28 does not seem to play a large role. In addition, we plotted effective band structures of
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30 all the alloy configurations (Figure S2), which indicate that the band gap changes from
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32 direct (K-K) to indirect (Γ -K) at around 10% Te in the asymmetric and unstrained case.
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34 In the symmetric case, the gaps remains direct for the unstrained systems, but again
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36 changes to indirect (K-T) at around 10% Te. It is worth noting, that the band structures
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38 are only weakly distorted in comparison to the pristine ones, i.e., they do not show
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40 pronounced defect states localized on the Te atoms, and thus it seems unlikely that the
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42 intensity change could be assigned to strong increase in non-radiative recombination
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44 rate.
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4 Taken alone, the calculated mixing limits, the vacancy concentration, and the PL
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6 intensity variation could all be assigned to either symmetric (and strained) or
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8 asymmetric (and unstrained) configurations, whereas the statistical analysis gives weak
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10 indication that Te is preferentially substituted in the top of the sheet. On the other hand,
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12 PL peak positions strongly points to unstrained samples, which, when coupled with the
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14 mixing limits, suggest asymmetric distribution (there should be no concentration limits
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16 in the unstrained symmetric case, in contradiction with the experiments). Thus, we
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18 tentatively assign our samples to be the asymmetric-type Janus structures[48] of
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20 $\text{MoS}_{2(1-x)}\text{Te}_{2x}$. Asymmetric Te distribution is expected to induce bending strain in the
21
22 sheet. The radius of curvature is evaluated using a ribbon geometry as shown on top of
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24 Figure 8a, and seen to be fairly small at larger Te concentrations. The associated energy
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26 cost for keeping the layer flat instead of bending can be quantified from the energy
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28 difference between the symmetric and asymmetric systems and scaled to the area of the
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30 sheet, and is shown in Figure 8b. The bending energy is found to be relatively small at
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32 less than $16 \text{ meV}/\text{\AA}^2$. This can be compared to the binding energy of MoS_2 sheet to
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34 SiO_2 , which was calculated to be about $13\text{-}15 \text{ meV}/\text{\AA}^2$ in Ref. [49] or to typical binding
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36 energies in layered systems of about $20 \text{ meV}/\text{\AA}^2$ [50]. We conclude that the interaction
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38 with the substrate is sufficiently strong to prevent the system from bending for all but
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40 the highest concentrations (or concentration imbalance).
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56 The asymmetry can also lead to interesting properties since it breaks the mirror
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58 symmetry and essentially leads to internal electric field perpendicular to the sheet. This
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4 for instance generates Rashba splitting of the VBM states at the Γ -point [51, 52]. The
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6 effective band structure for the case of 32% asymmetric Te concentration is shown in
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8 Figure 7c. The inset shows zoom-in to the VBM around Γ -point, where the states are
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10 colored by the spin-component perpendicular to the k-point and in-plane. The (normally
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12 spin-degenerate) VBM states exhibit Rashba-type splitting, that is linear in k and with
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14 the spin orientation perpendicular to k. At the VBM, located in $k=0.02 \ 2\pi/a$, the splitting
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16 is about 10 meV.
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25 **4. Conclusion**

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27 In summary, we have shown that $\text{MoS}_{2(1-x)}\text{Te}_{2x}$ monolayers can be synthesized by the
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29 tellurization of MoS_2 via tuning CVD parameters. The type and distribution of Te atoms
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31 have been analyzed based on ADF images. A large area of local distortion and single
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33 atom chain was observed at a higher deposition temperature. Due to the introducing of
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35 metallic Te element, $\text{MoS}_{2(1-x)}\text{Te}_{2x}$ alloys can have larger-range tunable band-gap
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37 ($\sim 0.7\text{eV}$) than $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloys ($\sim 0.3\text{eV}$) [53], which broadens its application in
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39 nanoelectronics and nanophotonics. Comparison of experimental results and first
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41 principles calculations led us to conclude that the Te substitution preferentially takes
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43 place in the top chalcogen sublattice. The asymmetric distribution leads to unusual
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45 physical properties, such as the change from direct to indirect gap and Rashba-type
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47 splitting of the VBM. Recently, it has also been reported that the superconductivity in
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49 MoTe_2 single crystal can be greatly enhanced by the partial S substitution [29]. This
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work gives insight for CVD growth of Te-doped 2D TMD alloys with controlled composition and could empower the further study on its electronics and optoelectronics.

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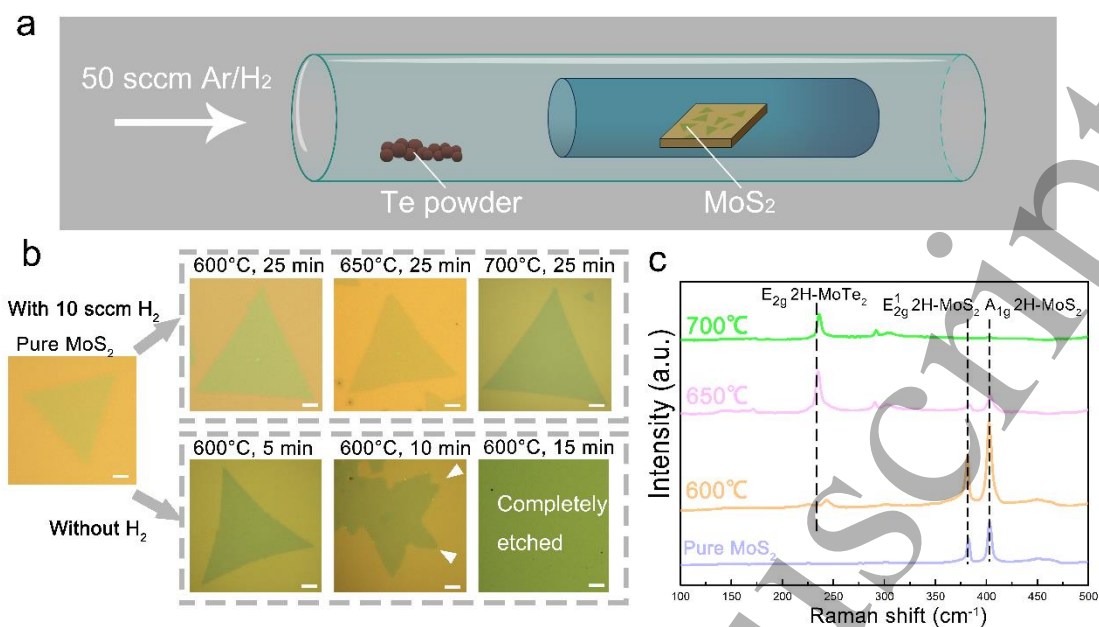


Figure 1. (a) Schematic setup for the post-growth doping. (b) Typical optical images of monolayer MoS₂ before (left) and after doping with tellurium under different conditions: with 10 sccm H₂ (top right row), without H₂ (right bottom row). Detailed conditions (temperature and reaction time) are listed above each display. Scale bar = 5 μm in all displays. (c) Raman spectra of Te-doped MoS₂ monolayer alloys grown at same doping time (25 min) and different doping temperature.

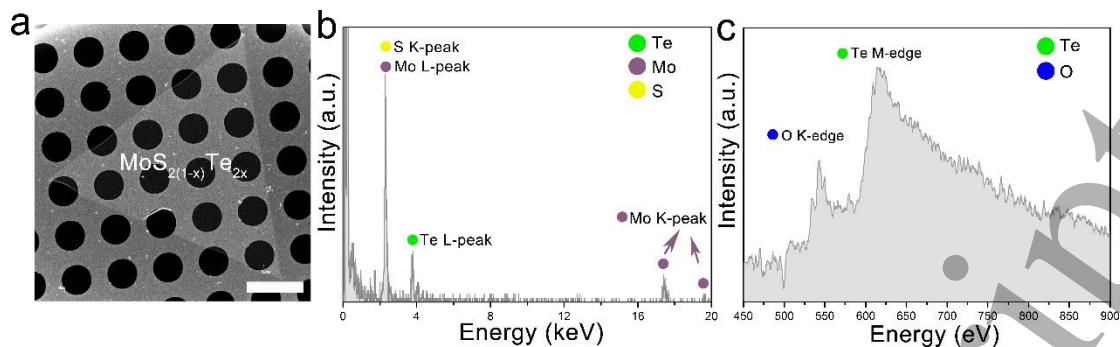


Figure 2. (a) Low-magnification ADF-STEM image of single crystal Te-doped MoS₂ monolayer alloys. Scale bar: 5 μm. (b) EELS spectra substantiates the existence of Te element. (c) XEDS spectra again confirms the presence of Te element. The EELS curve was smoothed by the origin software for a better display.

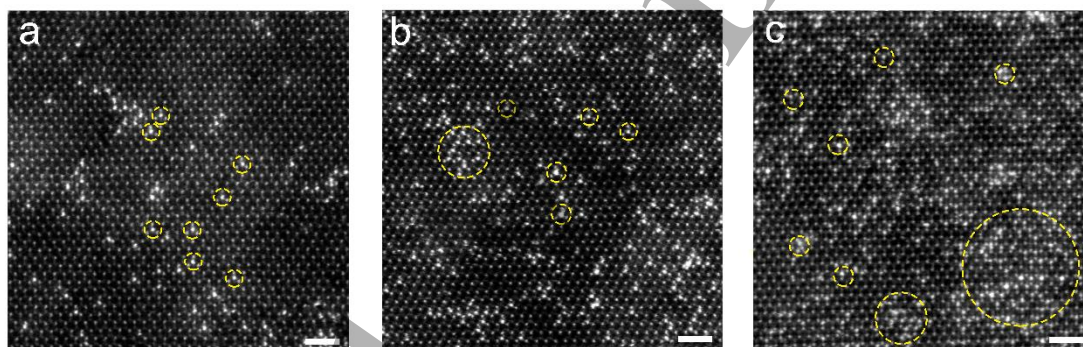


Figure 3. (a-c) Atomically resolved ADF-STEM images and b-axis atomic structure of Te-doped MoS₂ monolayers at different growth temperature. A number of bright sites corresponding to the local Te sites can be distinguished from the Z-contrast images (mark with yellow circles). (a) 600 °C, 25 min; (b) 650 °C, 25 min; (c) 700 °C, 25 min. Scale bar: 1 nm.

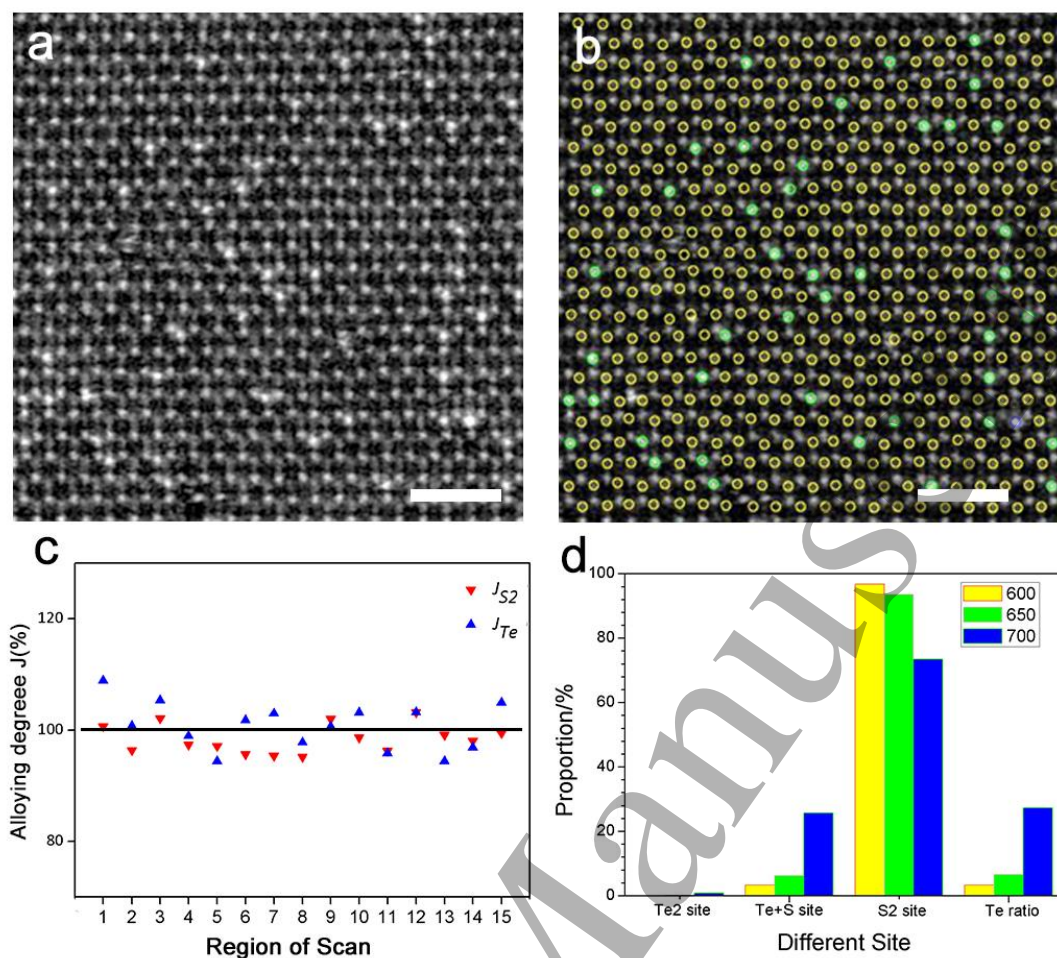


Figure 4. (a) Atomic-resolved ADF-STEM image of MoS₂(1-x)Te_{2x} monolayer, and (b) the distribution of chalcogen atoms in MoS₂(1-x)Te_{2x} monolayer (yellow circle represent S2 site, green and blue, respectively S + Te site and Te2 site). The Te substitution was conducted at 650 °C. Scale bar: 1 nm (c) The analyzed alloying degree in MoS₂(1-x)Te_{2x} monolayers from different samples which were tellurized at different temperatures (600, 650 and 700). (d) Summary of the growth conditions and Te proportion for all synthesized Te doped monolayer alloys.

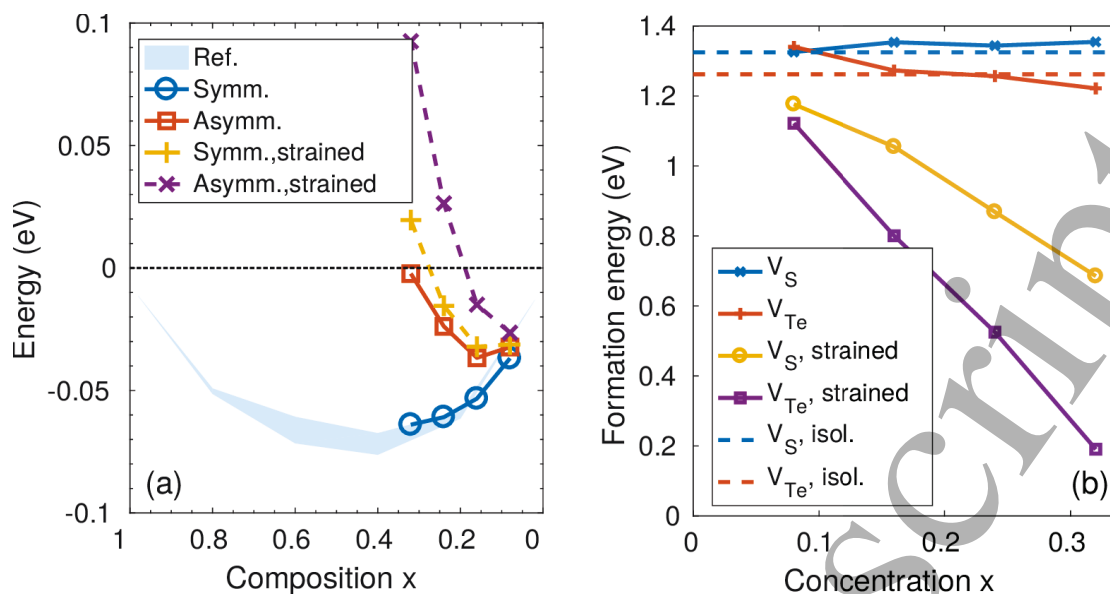


Figure 5. (a) Mixing free energy (at 650 C) as a function of the alloy concentration x , with Te substituted either symmetrically in both top and bottom sublattices or asymmetrically only in the top sublattice. Also shown are the results from strained lattice, with lattice constant fixed to that of MoS₂. The computational reference data is from Ref. 48. (b) Vacancy formation energies as a function of alloy concentrations. Both unstrained lattice and that strained to MoS₂ lattice constant are considered.

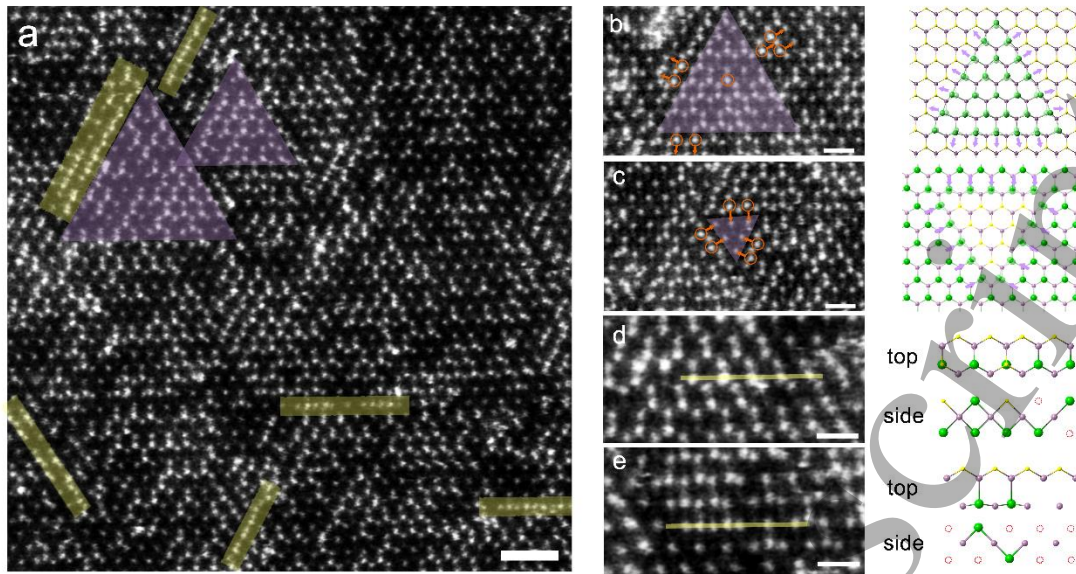


Figure 6. (a) Atomic resolved STEM-ADF images of Te-doped MoS₂ monolayer alloys grown at 700 °C for 25 min. The purple triangle indicate the local structure modulation. Te atom stands in the middle of two Mo atoms, forming an atomic chain, which was highlighted by yellow lines. Scale bar: 1 nm. (b, c) STEM-ADF images and schematic of local structure distortion. Purple: Mo; yellow: S; green: Te. Orange arrows illustrated the shift direction of Te atoms. (d, e) STEM-ADF images and schematic of possible structure of atomic chain. Scale bar: 0.5 nm

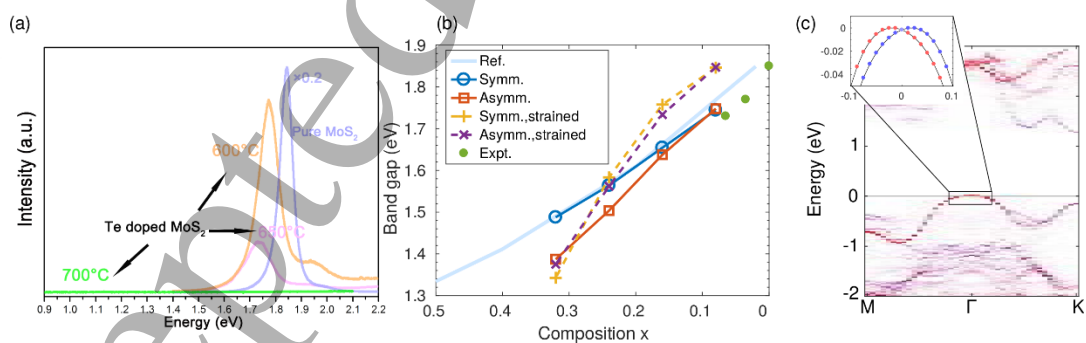


Figure 7. (a) Measured photoluminescence spectra from the three samples grown at different temperatures and compared to pristine MoS₂. (b) Comparison of experimental band gaps to the calculated band gap variations with different Te distributions and with or without strain. (c) Effective band structure of the asymmetric unstrained system with

32% Te. The states are colored by their projection to S atoms (red) and Te atoms (blue).

Inset: Zoom-in to the valence band maximum around Γ -point showing Rashba effect.

Here the states are colored according to the spin-projection in y-direction, when k-points are in x-direction.

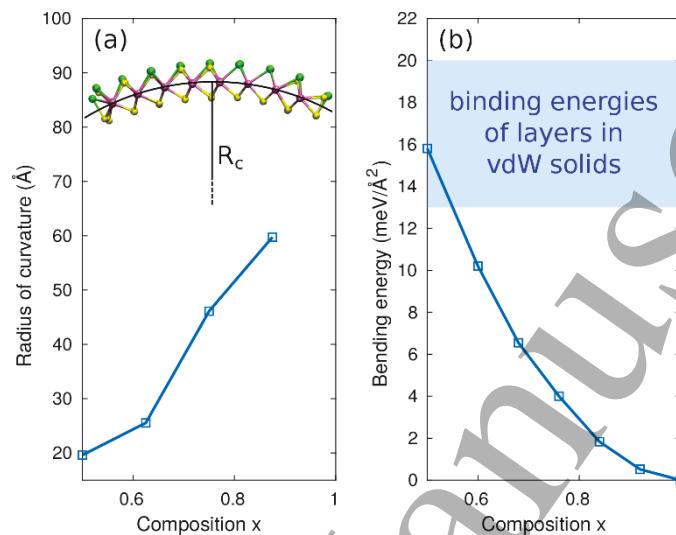


Figure 8. (a) Radius of curvature induced to the system by the asymmetric Te distribution as a function of composition. (b) Bending energy per area of sheet compared to typical vdW binding energies. Red line: energy cost estimated from the ribbon calculations.