

# Mechanical Properties of Atomically Thin Tungsten Dichalcogenides: WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub>

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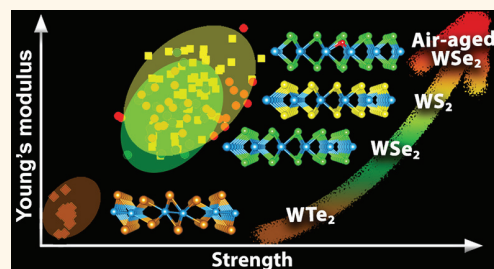
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Supporting Information

**ABSTRACT:** Two-dimensional (2D) tungsten disulfide (WS<sub>2</sub>), tungsten diselenide (WSe<sub>2</sub>), and tungsten ditelluride (WTe<sub>2</sub>) draw increasing attention due to their attractive properties deriving from the heavy tungsten and chalcogenide atoms, but their mechanical properties are still mostly unknown. Here, we determine the intrinsic and air-aged mechanical properties of mono-, bi-, and trilayer (1–3L) WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> using a complementary suite of experiments and theoretical calculations. High-quality 1L WS<sub>2</sub> has the highest Young's modulus ( $302.4 \pm 24.1$  GPa) and strength ( $47.0 \pm 8.6$  GPa) of the entire family, overpassing those of 1L WSe<sub>2</sub> ( $258.6 \pm 38.3$  and  $38.0 \pm 6.0$  GPa, respectively) and WTe<sub>2</sub> ( $149.1 \pm 9.4$  and  $6.4 \pm 3.3$  GPa, respectively). However, the elasticity and strength of WS<sub>2</sub> decrease most dramatically with increased thickness among the three materials. We interpret the phenomenon by the different tendencies for interlayer sliding in an equilibrium state and under in-plane strain and out-of-plane compression conditions in the indentation process, revealed by the finite element method and density functional theory calculations including van der Waals interactions. We also demonstrate that the mechanical properties of the high-quality 1–3L WS<sub>2</sub> and WSe<sub>2</sub> are largely stable in air for up to 20 weeks. Intriguingly, the 1–3L WSe<sub>2</sub> shows increased modulus and strength values with aging in the air. This is ascribed to oxygen doping, which reinforces the structure. The present study will facilitate the design and use of 2D tungsten dichalcogenides in applications such as strain engineering and flexible field-effect transistors.

**KEYWORDS:** two-dimensional materials, tungsten dichalcogenides, mechanical property, sliding energy, air degradation



Atomically thin transition-metal dichalcogenides (TMDs) are an important group of two-dimensional (2D) materials with bandgaps mostly ranging from 0 to 2.5 eV.<sup>1</sup> Monolayer (1L) molybdenum disulfide (MoS<sub>2</sub>) sparked intensive attention first due to the discoveries of its transition to direct bandgap<sup>2</sup> and high mobility at room temperature,<sup>3</sup> enabling high-performance flexible light-emitting, photodetecting, and electronic devices. Then the exploration extended to other 2D TMDs and their wider applications, such as in energy harvesting and storage, chemical sensing, catalysis, and mechanical reinforcement, etc.<sup>1</sup>

2D TMDs with heavier transition metals and chalcogens have many advantages. Due to the reduced effective mass, 1L tungsten disulfide (WS<sub>2</sub>) has been predicted to have the highest mobility and best performance in field-effect transistors (FETs) among 2D TMDs.<sup>4</sup> Thanks to the heavy W atoms, the valence band splitting for 1L tungsten diselenide (WSe<sub>2</sub>) is about three times larger than that for 1L MoS<sub>2</sub>, and this

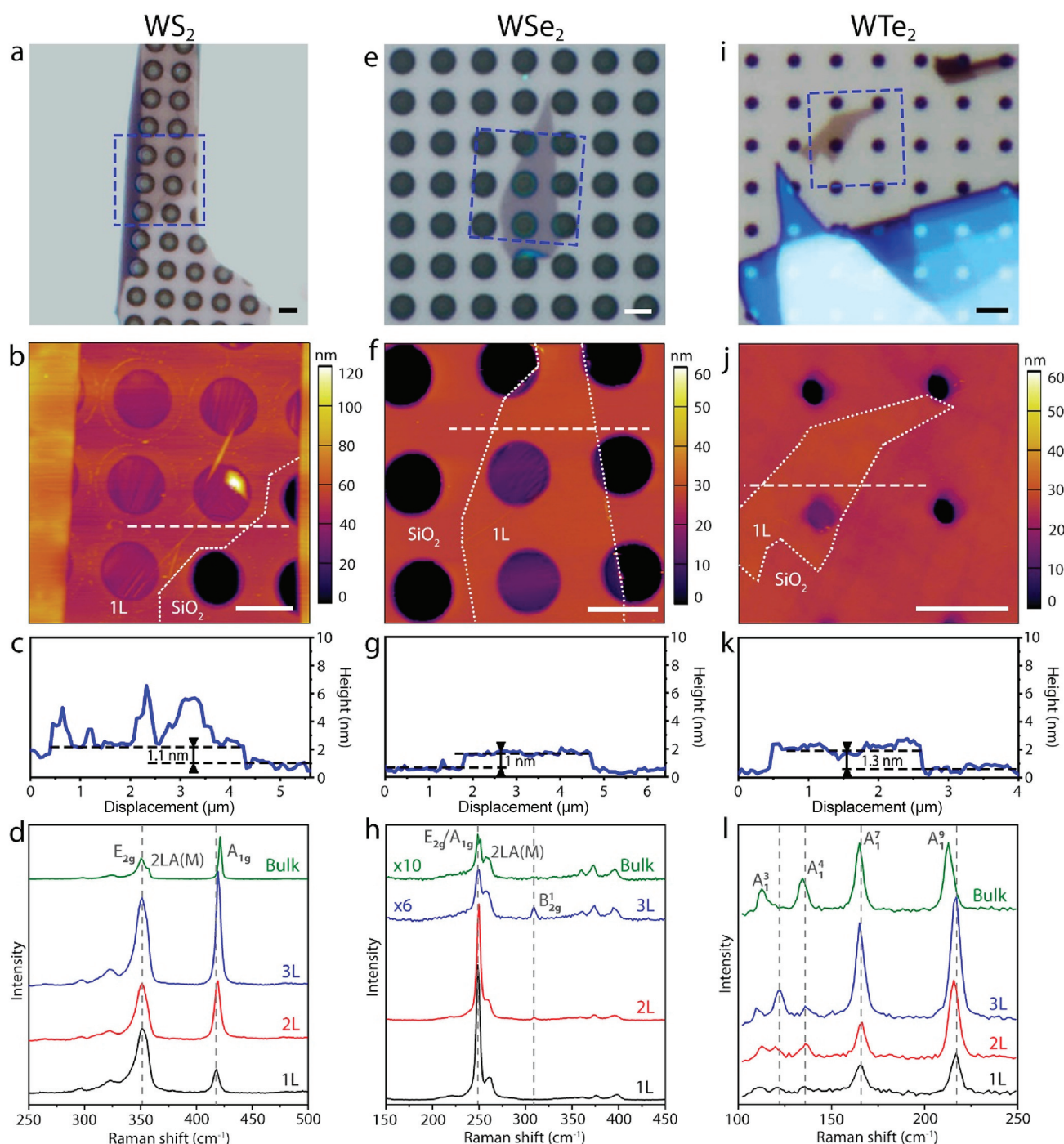
renders it more suitable for spintronic and valleytronic applications.<sup>5,6</sup> Quantum spin Hall (QSH) effects have been observed in heavy tungsten ditelluride (WTe<sub>2</sub>) monolayers because of its most energetically favored semimetallic 1T' phase,<sup>7–9</sup> unlike the other 2D TMDs in a 2H phase. In addition, huge positive magnetoresistance has been found in WTe<sub>2</sub> below 5 K, and more intriguingly, the magnetoresistance does not saturate even under magnetic fields up to 60 T.<sup>10</sup> The reduced intralayer atomic interactions between heavier transition metals and chalcogens make their chemical modification, doping, and functionalization easier to achieve.<sup>11</sup>

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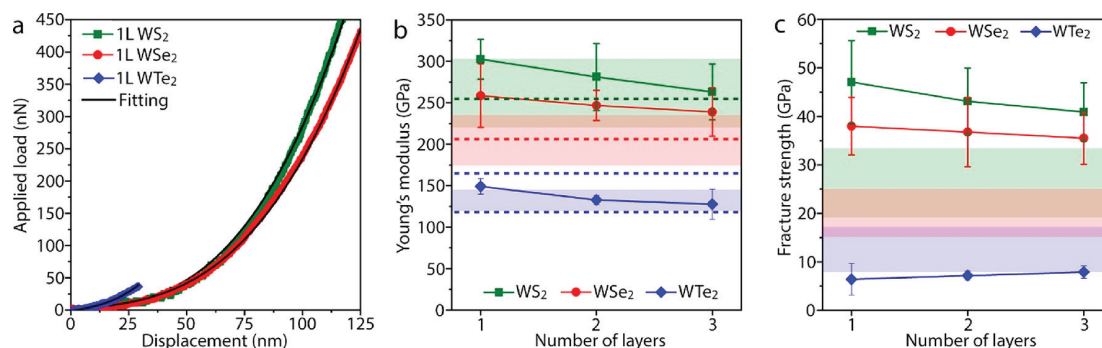


**Figure 1.** Characterizations of the atomically thin tungsten dichalcogenides. Optical microscopy images of the exfoliated 1L (a) WS<sub>2</sub>, (e) WSe<sub>2</sub>, and (i) WTe<sub>2</sub> over microwells in SiO<sub>2</sub>/Si. AFM images of the (b) WS<sub>2</sub>, (f) WSe<sub>2</sub>, and (j) WTe<sub>2</sub> corresponding to the dashed squares on their optical images; the height traces of (c) WS<sub>2</sub>, (g) WSe<sub>2</sub>, and (k) WTe<sub>2</sub> corresponding to the dashed lines in their AFM images. Raman spectra of 1–3L and bulk (d) WS<sub>2</sub>, (h) WSe<sub>2</sub>, and (l) WTe<sub>2</sub> using 514.5 nm excitation wavelength. All scale bars: 2  $\mu$ m.

Tungsten dichalcogenides also have higher electrical conductivities than molybdenum dichalcogenides.<sup>12</sup> The recent advances in the wafer-scale growth based on metal–organic chemical vapor deposition<sup>13</sup> and gold-assisted millimeter-scale mechanical exfoliation<sup>14</sup> permit high-quality 2D TMDs to be produced, facilitating their use in various applications.

Understanding the mechanical properties of 2D TMDs is essential to harness their full potential for applications, such as

in strain engineering and flexible FETs. Extensive studies have been conducted on 2D molybdenum dichalcogenides. The Young's moduli of 1L and 2L MoS<sub>2</sub> prepared by mechanical exfoliation and measured by indentation were reported to be  $180 \pm 60$  N m<sup>-1</sup> ( $270 \pm 100$  GPa) and  $260 \pm 70$  N m<sup>-1</sup> ( $200 \pm 60$  GPa), respectively; their fracture strengths were  $15 \pm 3$  N m<sup>-1</sup> ( $22 \pm 4$  GPa) and  $28 \pm 8$  N m<sup>-1</sup> ( $21 \pm 6$  GPa), respectively.<sup>15</sup> The intrinsic Young's moduli of 5–25L MoS<sub>2</sub>



**Figure 2.** Mechanical properties of 1–3L tungsten dichalcogenides. (a) Typical load–displacement curves of 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> (note WTe<sub>2</sub> was suspended over smaller microwells), along with the corresponding fittings. (b) The volumetric Young's moduli and (c) fracture strengths of 1–3L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> ( $N = 13, 23$ , and  $16$  for 1–3L WS<sub>2</sub>, respectively;  $N = 12, 7$ , and  $6$  for 1–3L WSe<sub>2</sub>, respectively;  $N = 3, 5$ , and  $11$  for 1–3L WTe<sub>2</sub>, respectively). Colored regions in (b, c) show the ranges of the theoretical values of 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> from literature,<sup>17,24–28</sup> and the dashed lines show the Young's moduli of 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> (in two directions) from our DFT calculations.

were also reported.<sup>16</sup> The elasticity of CVD-grown 1L MoS<sub>2</sub> measured by indentation was  $171 \pm 12 \text{ N m}^{-1}$  ( $264 \pm 18 \text{ GPa}$ ), and this value is comparable to that of the exfoliated sample.<sup>17</sup> However, the strength of few-layer CVD samples measured by *in situ* tensile testing was only  $\sim 1 \text{ GPa}$ ,<sup>18</sup> 1 order of magnitude smaller than that of the exfoliated MoS<sub>2</sub>. This is unlikely to be due to the different test geometry; *in situ* tensile tests provide strength values similar to those obtained using indentation.<sup>19</sup> Rather, it is likely that defect levels are playing a role. The strength of 2D materials is highly sensitive to defects; more so than the Young's modulus.<sup>20</sup> The mechanical properties of molybdenum diselenide (MoSe<sub>2</sub>) and molybdenum ditelluride (MoTe<sub>2</sub>) have been experimentally studied as well.<sup>21,22</sup>

In contrast, there have been very few studies on the mechanical properties of atomically thin tungsten dichalcogenides. The Young's modulus of CVD-grown 1L WS<sub>2</sub> measured by indentation was  $177 \pm 12 \text{ N m}^{-1}$  ( $272 \pm 18 \text{ GPa}$ ).<sup>17</sup> The Young's moduli of 5L, 6L, 12L, and 14L WSe<sub>2</sub> prepared by mechanical exfoliation using indentation and the obtained values were  $596 \pm 23 \text{ N m}^{-1}$  ( $170 \pm 7 \text{ GPa}$ ),  $690 \pm 25 \text{ N m}^{-1}$  ( $166 \pm 6 \text{ GPa}$ ),  $1411 \pm 61 \text{ N m}^{-1}$  ( $168 \pm 7 \text{ GPa}$ ), and  $1615 \pm 56 \text{ N m}^{-1}$  ( $165 \pm 6 \text{ GPa}$ ), respectively.<sup>23</sup> Nevertheless, no fracture strength was provided. The experimental elasticity and strength values of atomically thin WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> are still mostly unknown, despite a large number of theoretical predictions.<sup>24–28</sup> On the other hand, the long-term stability of 2D TMDs is vital to their applications, especially for the heavier tungsten dichalcogenides which might be more prone to oxidation than the corresponding molybdenum dichalcogenides. The aging of 2D WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> grown by CVD and molecular beam epitaxy (MBE) in ambient conditions could cause catastrophic degradation and lead to quenched luminescence and deteriorated mobility.<sup>29–32</sup> The air-aging effect on the mechanical properties of 2D TMDs, including tungsten dichalcogenides, however, has never been ascertained.

Here, we systematically investigate the intrinsic and air-aged mechanical properties of high-quality 1–3L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> by indentation. With an increased mass of chalcogenide, the elasticity and fracture strength of 1L tungsten dichalcogenides decreases, where WTe<sub>2</sub> is notably weaker than WS<sub>2</sub> and WSe<sub>2</sub>. Nevertheless, the ultimate strain is less affected by chalcogenide mass, as those of 1L WS<sub>2</sub> and WSe<sub>2</sub> are seen to be quite close. Lighter chalcogenides show more reduced

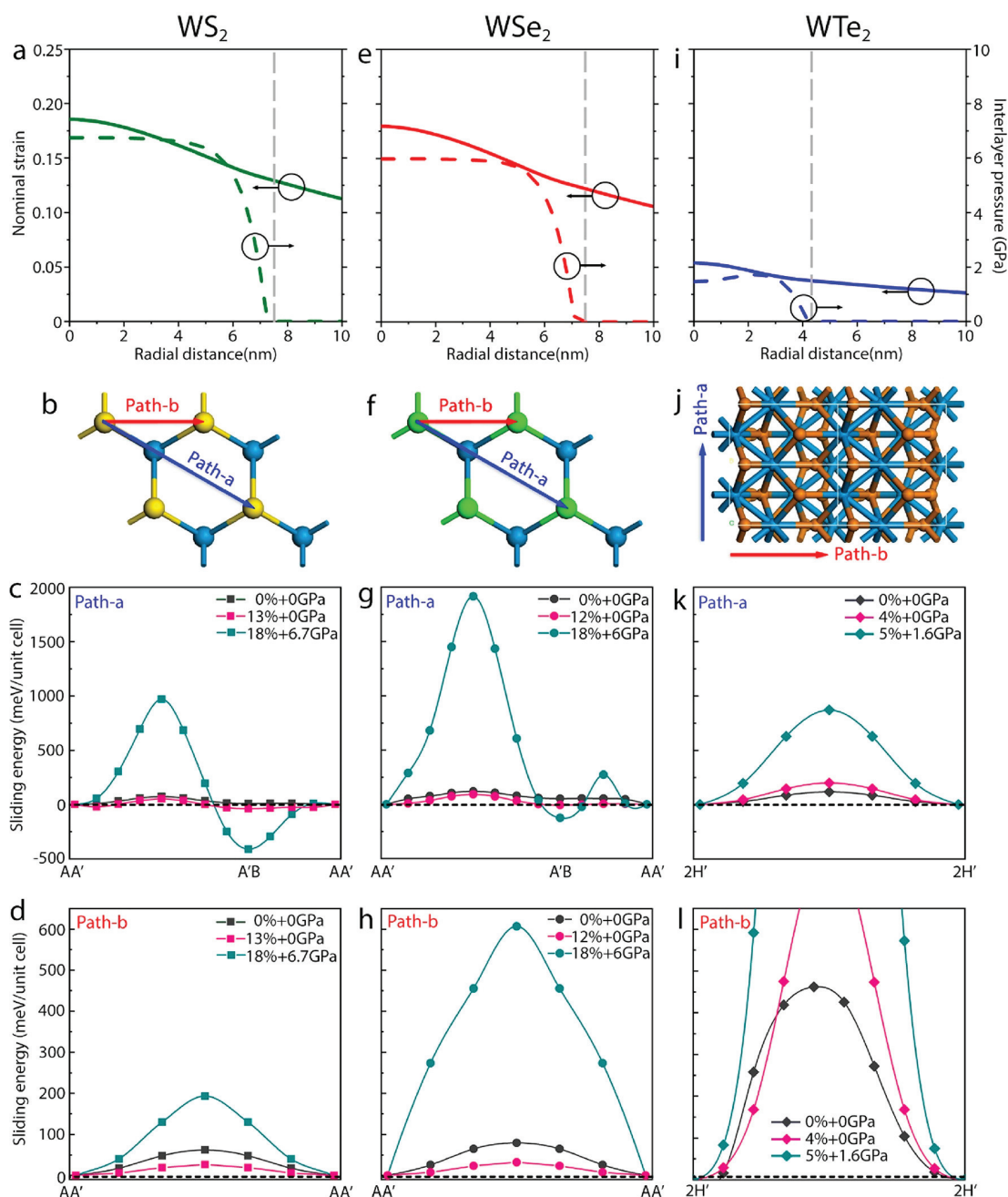
Young's modulus and strength with increased layer thickness. To better understand this phenomenon, we combine finite element method (FEM) with *ab initio* van der Waals (vdW)-corrected density functional theory (DFT) calculations to reveal the distinct sliding tendencies in WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> under strain. Although atomically thin WTe<sub>2</sub> is not stable in air, the mechanical properties of 1–3L WS<sub>2</sub> and WSe<sub>2</sub> are not dramatically influenced by exposure to air for up to 20 weeks. The Young's modulus and fracture strength of 2D WSe<sub>2</sub> increase after air aging, and the underlying mechanism is theoretically explored.

## RESULTS AND DISCUSSION

**Sample Preparation and Characterization.** All atomically thin tungsten dichalcogenides were mechanically exfoliated on silicon wafers covered by silicon oxide (SiO<sub>2</sub>/Si) with pre-etched circular microwells of  $0.7\text{--}1.8 \mu\text{m}$  in diameter (see *Methods*). The smaller microwells were used for WTe<sub>2</sub> due to its much lower exfoliation yield over the larger microwells. Optical microscopy was employed to locate 1–3L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> suitable for mechanical tests, as illustrated in Figure 1a,e,i. The corresponding atomic force microscopy (AFM) images (and height profiles) are displayed in Figure 1b(c),f(g),j(k), respectively. The measured thicknesses were in the range of  $1.0\text{--}1.3 \text{ nm}$  for the monolayers.

The Raman spectra of the WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> for different thicknesses are shown in Figure 1d,h,l. For WS<sub>2</sub>, the increased intensity ratio between the E<sub>2g</sub> peak (in-plane vibrational mode) and A<sub>1g</sub> peak (out-of-plane vibrational mode) manifested its atomic thickness due to the changed Coulomb interlayer coupling (Figure 1d).<sup>33</sup> Furthermore, the intensity of the 2LA(M) peak increased with thickness reduction and maximized at the monolayer thickness. The A<sub>1g</sub> peak also experienced redshifts with reduced thickness. For WSe<sub>2</sub>, the dramatically increased intensity of the E<sub>2g</sub>/A<sub>1g</sub> peak verified their atomic thickness (Figure 1h). In addition, 2–3L WSe<sub>2</sub> showed B<sub>2g</sub> peaks corresponding to a combination of the rigid interlayer shear and E<sub>2g</sub> modes, which was not present in 1L or bulk WSe<sub>2</sub> (Figure 1h).<sup>34</sup> Distinct from the hexagonal structures of WS<sub>2</sub> and WSe<sub>2</sub>, WTe<sub>2</sub> has a distorted orthorhombic phase due to its tilted out-of-plane vibrations caused by metal–metal interaction.<sup>35</sup> WTe<sub>2</sub> mainly showed four Raman peaks A<sub>1</sub><sup>7</sup> (in-plane vibrational mode) and A<sub>1</sub><sup>4</sup>, A<sub>3</sub><sup>4</sup>,





**Figure 3.** Sliding energies of 2L tungsten dichalcogenides under different in-plane strain and out-of-plane compression conditions. FEM-deduced in-plane strain (solid lines) and out-of-plane pressure (dashed lines) distributions in 2L (a)  $\text{WS}_2$ , (e)  $\text{WSe}_2$ , and (i)  $\text{WTe}_2$  along a radial distance of 10 nm from the indentation center under fracture loads from an indenter of 10.6 nm in radius. Diagrams showing the path-a and path-b sliding directions in 2L (b)  $\text{WS}_2$ , (f)  $\text{WSe}_2$ , and (j)  $\text{WTe}_2$ . The sliding energies in path-a in 2L (c)  $\text{WS}_2$ , (g)  $\text{WSe}_2$ , and (k)  $\text{WTe}_2$  and in path-b in 2L (d)  $\text{WS}_2$ , (h)  $\text{WSe}_2$ , and (l)  $\text{WTe}_2$  under different in-plane strain and out-of-plane compression conditions, including equilibrium states far away from the indentation center (0% strain + 0 GPa interlayer pressure), large in-plane strain but no out-of-plane compression adjacent to the contact area (*i.e.*, 13% strain + 0 GPa pressure for  $\text{WS}_2$ , 12% strain + 0 GPa pressure for  $\text{WSe}_2$ , and 4% strain + 0 GPa pressure for  $\text{WTe}_2$ ), and maximum strain and pressure directly under the contact area (*i.e.*, 18% strain + 6.7 GPa pressure for  $\text{WS}_2$ , 18% strain + 6.0 GPa pressure for  $\text{WSe}_2$ , and 5% strain + 1.6 GPa pressure for  $\text{WTe}_2$ ).

$A_1^9$  (out-of-plane vibrational modes) (Figure 11). The intensities of the  $A_1^7$  and  $A_1^9$  peaks attenuated with thickness reduction to monolayer, and the  $A_1^4$  and  $A_1^3$  peaks almost disappeared due to the structural transition from non-centrosymmetric (distorted orthorhombic) to centrosymmetric phase.<sup>36</sup> While the  $A_1^7$  peak was almost constant in its position, the  $A_1^3$  and  $A_1^9$  peaks blueshifted with thickness

reduction. To avoid potential damage by laser, all samples measured by Raman were not used in mechanical tests.

**Mechanical Properties.** The mechanical behaviors of 1–3L  $\text{WS}_2$ ,  $\text{WSe}_2$ , and  $\text{WTe}_2$  were measured by AFM-based nanoindentation (see Methods).<sup>37,38</sup> The load–displacement relations were obtained from the deflection of the central part of the suspended atomically thin sheets under an applied load

using cantilevers with diamond tips. The curves were analyzed based on the well-established force ( $f$ )–displacement ( $\delta$ ) relationship introduced by Lee *et al.*<sup>37</sup> and later extended by Lin *et al.*<sup>39</sup> The relation was employed to determine the starting (zero) coordinates of indentation and the linear and cubic regions of the indentation curve:

$$f = f_0 + k_1(\delta - \delta_0) + k_2(\delta - \delta_0)^3 \quad (1)$$

where  $f_0$  and  $\delta_0$  are the zero-point coordinates,  $k_1 = \sigma_0^{2D}/\pi$ ,  $k_2 = E^{2D}(q^3/a^2)$ , where  $\sigma_0^{2D}$  and  $E^{2D}$  are the effective pretension and effective Young's modulus of a 2D material, respectively,  $a$  is the radius of the suspended sheet, and  $q = 1/(1.049 - 0.15\nu - 0.16\nu^2)$  is a dimensionless coefficient related to Poisson's ratio ( $\nu$ ). The Poisson ratios of 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> are 0.22, 0.19, and 0.18, respectively.<sup>24,26</sup> In order to convert the 2D mechanical values to volumetric values, the effective thicknesses of 0.62, 0.65, and 0.71 nm for 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub>, respectively, were adopted.<sup>27</sup> The typical load–displacement curves and corresponding fittings of the three monolayers are compared in Figure 2a.

The volumetric Young's moduli of the 1–3L tungsten dichalcogenides are shown in Figure 2b, and the values with standard deviations for 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> were 302.4 ± 24.1 GPa (187.5 ± 14.9 N m<sup>−1</sup>), 258.6 ± 38.3 GPa (168.1 ± 24.9 N m<sup>−1</sup>), and 149.1 ± 9.4 GPa (105.9 ± 6.6 N m<sup>−1</sup>), respectively. These values were comparable to the previous theoretical predictions,<sup>17,24–28</sup> illustrated by the colored regions in Figure 2b. We also used DFT to calculate the elastic constants of the three monolayers, and the results were in line with the previous reports (dashed lines in Figure 2b). With the increased number of layers from 1L to 3L, WS<sub>2</sub> showed more decreased Young's moduli. This conclusion was confirmed by *t*-tests (see Supporting Information, Note 1). The Young's moduli of 3L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> were 263.1 ± 33.7 GPa (489.4 ± 62.7 N m<sup>−1</sup>), 238.9 ± 29.4 GPa (465.9 ± 57.3 N m<sup>−1</sup>), and 127.7 ± 18.1 GPa (272.0 ± 38.0 N m<sup>−1</sup>), respectively. According to our DFT calculations, 1T' WTe<sub>2</sub> should be the most stable phase (Supporting Information, Table S2), consistent with the Raman results. To better show the effect of chalcogens on the mechanical properties, we also calculated and included the elastic constants of 1T-WS<sub>2</sub>, 1T-WSe<sub>2</sub>, and 2H-WTe<sub>2</sub> in Supporting Information, Table S3.

The fracture strength was calculated by FEM based on the load–displacement curves from the experiment (see Methods). The fracture strength values of the 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> were 47.0 ± 8.6 GPa (29.2 ± 5.3 N m<sup>−1</sup>), 38.0 ± 6.0 GPa (24.7 ± 3.9 N m<sup>−1</sup>), and 6.4 ± 3.3 GPa (4.5 ± 2.3 N m<sup>−1</sup>), respectively (Figure 2c). The strength values of the 1L WS<sub>2</sub> and WSe<sub>2</sub> were larger than the theoretical predictions, but that of 1L WTe<sub>2</sub> was smaller (colored regions in Figure 2c). Note that although no covalent bond formed between the indentation tip and samples even under fracture loads (see Supporting Information, Note 4), these strength values should be overestimated due to the frictionless models used in FEM simulations.<sup>40</sup> Similar to the trend observed in Young's modulus, the strength of WS<sub>2</sub> dropped more with increased thickness, which was confirmed by *t*-tests (see Supporting Information, Note 1). The fracture strength values of 3L WS<sub>2</sub> and WSe<sub>2</sub> were 40.9 ± 6.0 GPa (76.1 ± 11.2 N m<sup>−1</sup>) and 35.5 ± 5.4 GPa (69.2 ± 10.5 N m<sup>−1</sup>), respectively. In contrast, the strength of WTe<sub>2</sub> with additional layers showed the opposite trend. It has been reported that the stability of WTe<sub>2</sub> decreases

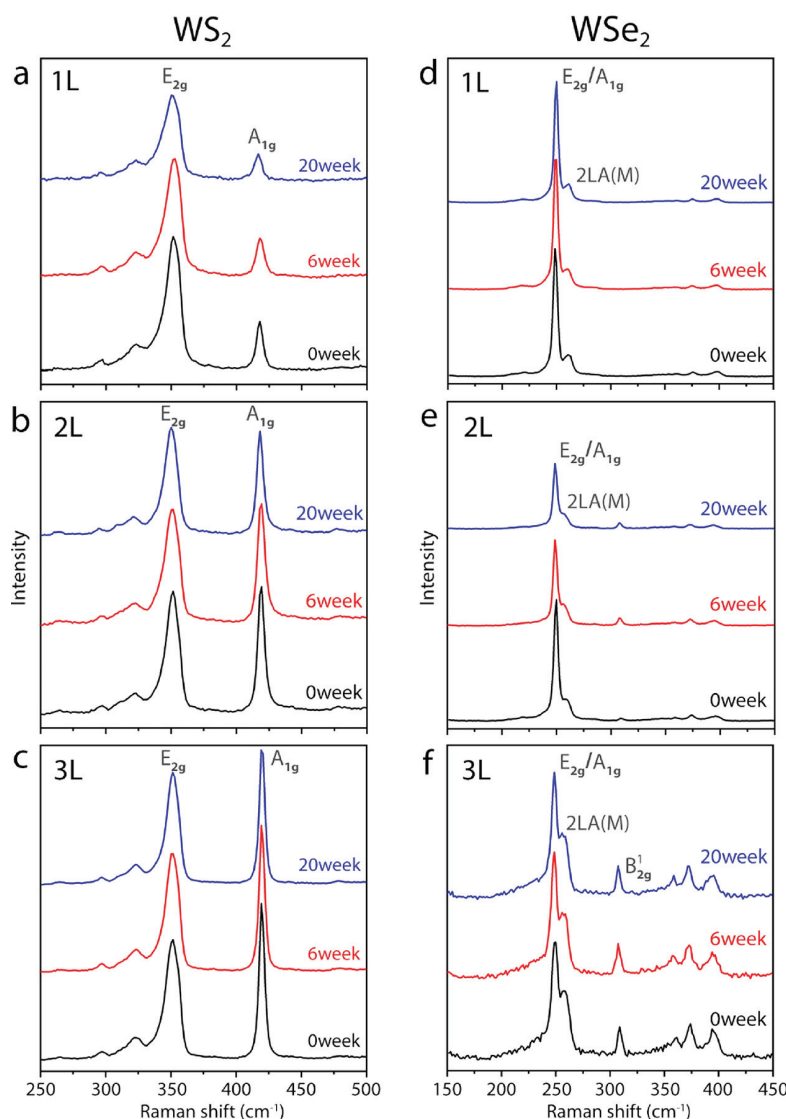
with thickness reduction, and 1L WTe<sub>2</sub> degrades in the air in just a few minutes.<sup>30</sup> The opposite trend observed in WTe<sub>2</sub> was most likely due to its degradation, though its AFM indentations were conducted under constant nitrogen gas flow at 1 L/min. The gas flow did not affect the AFM results according to our comparison tests.

We also calculated the strain distribution using FEM and defined the ultimate strain as the average strain in the material in contact with the indenter at fracture. The strain at the center of the material in contact with the indenter was highly localized and considerably higher than that in the rest of the suspended material that almost followed the linear elastic behavior.<sup>38</sup> The ultimate strains for 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> were 19.8 ± 4.3%, 19.7 ± 4.3%, and 4.4 ± 2.7%, respectively. The thickness increases in WS<sub>2</sub> and WSe<sub>2</sub> only slightly increased these values, but the ultimate strain for 3L WTe<sub>2</sub>, that is, 6.8 ± 0.9%, was much larger than that for 1L WTe<sub>2</sub>, which could be due to more degradation of 1L WTe<sub>2</sub> in the air. The ultimate strain values of atomically thin WS<sub>2</sub> and WSe<sub>2</sub> were comparable to that of 1L graphene but a lot larger than that of 1L BN.<sup>37,38</sup> It suggests the possibility of strain engineering in atomically thin WS<sub>2</sub> and WSe<sub>2</sub> to large extents without fracture.

**Interlayer Interactions.** The elasticity and strength of WS<sub>2</sub> showed more decreases with increased thickness than WSe<sub>2</sub> and WTe<sub>2</sub>. The different interlayer interactions in the three materials could be the key to understand the phenomenon. To examine this effect, *ab initio* vdW-corrected DFT calculations on sliding energies under different levels of in-plane strain and out-of-plane compression were performed (see Methods). The strain and compression levels were selected by applying conditions encountered at three radial distances from the indentation center of the suspended 2L sheets under maximum loads.

According to the FEM simulations, the 2L sheets displayed negligible strain at the edge of the microwells. That is, far away from the indentation center, the materials were in relaxed equilibrium states, and almost no strain and compression were present. Figure 3a,e,i shows the FEM deduced in-plane nominal strain (solid lines) and out-of-plane hydraulic pressure (dashed lines) distributions close to the indentation center of the three 2L tungsten dichalcogenides at the moment of fracture for a 10.6 nm indenter tip. Close to the contact between the tip and sheet at radial distances of 7.5 nm for WS<sub>2</sub>, 7.5 nm for WSe<sub>2</sub>, and 4.2 nm for WTe<sub>2</sub> (see the vertical dashed lines in Figure 3a,e,i), large in-plane strains were applied without out-of-plane compression. Directly under the contact area (*i.e.*, radial distances of 0–6 nm for WS<sub>2</sub>, 0–6 nm for WSe<sub>2</sub>, and 0–3 nm for WTe<sub>2</sub> in Figure 3a,e,i), the maximum in-plane strain and out-of-plane pressure were reached. The detailed strain and pressure values used in the DFT calculations on the sliding energies of 2L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> are shown in Figure 3c,d,g,h,k,l. The sliding energies of WS<sub>2</sub> and WSe<sub>2</sub> were calculated based on AA' stackings. The sliding energies of WTe<sub>2</sub> were calculated based on 1T' structural configuration in the 2H' stacking order. These stacking sequences are the most energetically favored. Two sliding pathways were considered in each material, that is, path-a and path-b (Figure 3b,f,j).

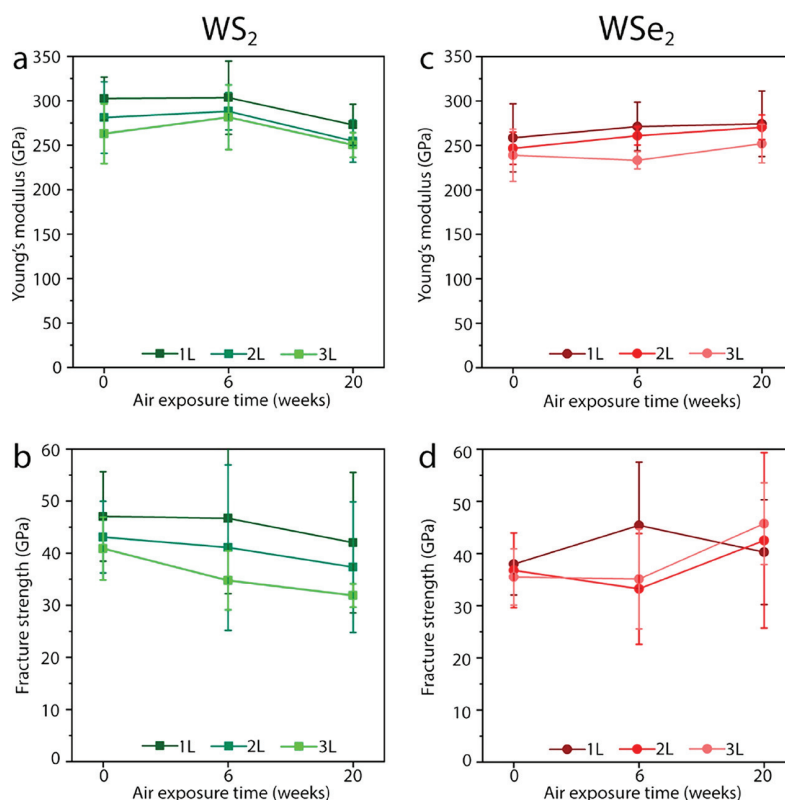
Figure 3c,d,g,h,k,l reveals how the in-plane strain and out-of-plane compression changed the sliding energies and tendencies in 2L tungsten dichalcogenides. In the relaxed unstrained and unstressed states (*i.e.*, 0% strain + 0 GPa compression), WSe<sub>2</sub> displayed slightly larger sliding energies



**Figure 4.** Raman characterization of air-aged WS<sub>2</sub> and WSe<sub>2</sub>. Raman spectra of 1–3L (a–c) WS<sub>2</sub> and (d–f) WSe<sub>2</sub> after exposed to air for 6 and 20 weeks.

(per unit cell) than WS<sub>2</sub> in both path-a and path-b directions. Note that sliding energy is area related, and a small change in sliding energy per unit cell can be translated to a significant overall energy barrier in a large area. In the path-a direction, the maximum sliding energies of WS<sub>2</sub> and WSe<sub>2</sub>, namely 72.0 and 118.6 meV/unit cell, respectively, were present when sliding from AA' (left) to A'B stackings (sliding from left to right in Figure 3c,g). However, the sliding energies from AA' (right) to A'B were as low as ~11.0 and 52.6 meV/unit cell for WS<sub>2</sub> and WSe<sub>2</sub>, respectively (sliding from right to left in Figure 3c,g). In the path-b direction, the maximum sliding energies were 61.9 and 79.5 meV/unit cell for WS<sub>2</sub> and WSe<sub>2</sub>, respectively (Figure 3d,h). Closer to the indentation center (*i.e.*, 7.5 nm radial distance), the 2L WS<sub>2</sub> and WSe<sub>2</sub> were under 13% and 12% nominal strain, respectively, and no out-of-plane compression was present (*i.e.*, 13% strain + 0 GPa compression for WS<sub>2</sub> and 12% strain + 0 GPa compression for WSe<sub>2</sub>). The maximum sliding energies of WS<sub>2</sub> and WSe<sub>2</sub> decreased in both directions: 51.4 (WS<sub>2</sub>) and 91.5 (WSe<sub>2</sub>) meV/unit cell in path-a (Figure 3c,g) and 26.5 (WS<sub>2</sub>) and 32.1 (WSe<sub>2</sub>) meV/unit

cell in path-b (Figure 3d,h), respectively. That is, the maximum sliding energies in WS<sub>2</sub> and WSe<sub>2</sub> reduced by ~25% and ~58% in path-a and path-b, respectively. Interestingly, the path-a results indicated that the AA' stacking in WS<sub>2</sub> under 13% strain was no longer stable, as the A'B stacking had the minimum sliding energy of -38.6 meV/unit cell (Figure 3c). It means that the 2L WS<sub>2</sub> should spontaneously slide from AA' (right) to A'B stacking. In comparison, the AA' stacking was still the most energetically favored position in WSe<sub>2</sub>, though the sliding energy barrier from AA' (right) to A'B became very small, that is, 3.8 meV/unit cell (sliding from right to left in Figure 3g). Directly under the indenter, the in-plane strain further increased, and additional out-of-plane compression was applied (*i.e.*, 18% strain + 6.7 GPa compression for WS<sub>2</sub> and 18% strain + 6.0 GPa compression for WSe<sub>2</sub>). In both path-a and path-b sliding directions, the maximum strain and large compression made the maximum sliding energies extremely large, that is, no less than 200 meV/unit cell in WS<sub>2</sub> and up to 1917 meV/unit cell in WSe<sub>2</sub> (Figure 3c,d,g,h). Nevertheless, the sliding energy minimum of A'B stacking in WS<sub>2</sub> further



**Figure 5.** Air-aged mechanical properties. (a, c) Young's moduli and (b, d) fracture strengths of 1–3L WS<sub>2</sub> and WSe<sub>2</sub> after air exposure for 6 and 20 weeks ( $N = 6, 5$ , and  $4$  for 1–3L WS<sub>2</sub> after 6 weeks, respectively;  $N = 4, 4$ , and  $5$  for 1–3L WSe<sub>2</sub> after 6 weeks, respectively;  $N = 4, 9$ , and  $5$  for 1–3L WS<sub>2</sub> after 20 weeks, respectively;  $N = 7, 7$ , and  $5$  for 1–3L WSe<sub>2</sub> after 20 weeks, respectively).

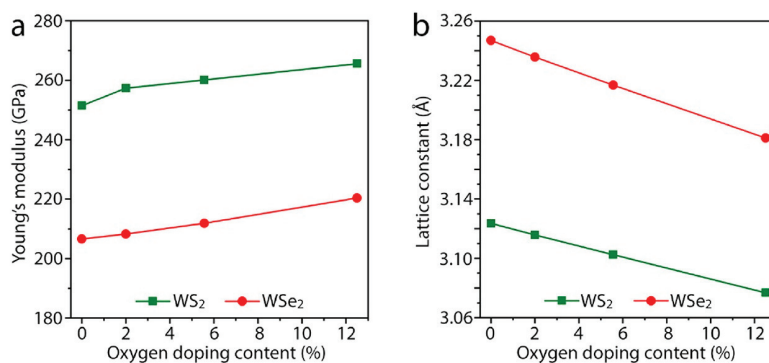
reduced to  $-411.5$  meV/unit cell (Figure 3d). So spontaneous sliding in WS<sub>2</sub> should also occur directly under the indenter. As the sliding leads to strain concentration on the bottom layer and decreases the mechanical properties,<sup>38</sup> the much higher sliding tendencies in WS<sub>2</sub> under the three sets of conditions can explain its larger drop in Young's modulus and fracture strength with increased layer number in comparison to WSe<sub>2</sub> (Figure 2b,c). The different electronegativity and electronic interactions of S and Se should be the cause for the different sliding tendencies. It should be emphasized that the above-discussed sliding energies are potentially larger than the realistic energy barriers during indentation due to non-uniform stacking changes under indenter.

WTe<sub>2</sub> has a different structure to that of WS<sub>2</sub> and WSe<sub>2</sub>, and its sliding energy under strain and compression showed a dissimilar trend as well. In the equilibrium state (*i.e.*, 0% strain + 0 GPa compression), the path-a had a much lower sliding energy than that of path-b in WTe<sub>2</sub>: 116.6 vs 461.8 meV/unit cell (Figure 3k,l). With the addition of in-plane strain and out-of-plane compression, the sliding energies in WTe<sub>2</sub> showed monotonic increases. At a 4.2 nm radial distance from the indentation center, the in-plane strain was 4% but without out-of-plane compression (*i.e.*, 4% strain + 0 GPa compression). The sliding energy increased to 199.0 meV/unit cell (Figure 3k). Upon the addition of out-of-plane compression in the contact area (*i.e.*, 5% strain + 1.6 GPa compression), the sliding energy jumped to 870.5 meV/unit cell, about 7.5 times that of the equilibrium state (Figure 3k). In path-b, the sliding energy barrier reached 4000 meV/unit cell under the same strain/compression condition. This suggests that the interlayer

interactions in WTe<sub>2</sub> were much stronger than those in WS<sub>2</sub> and WSe<sub>2</sub>, possibly due to the strong directional interlayer coupling in addition to the vdW interaction, arising from electronic hybridization of the lone electron pairs and overlap between electronic densities centered at each WTe<sub>2</sub> layer.<sup>36</sup> For comparison purposes, we also ran similar DFT calculations on the sliding energies of 2H-WTe<sub>2</sub> (Supporting Information, Figure S3).

**Air-Aged Mechanical Properties.** Prior works showed that atomically thin tungsten dichalcogenides could be unstable under ambient conditions.<sup>29–32</sup> We found that the 1–3L WTe<sub>2</sub> disappeared after exposure to air for several days. In contrast, the mechanically exfoliated 1–3L WS<sub>2</sub> and WSe<sub>2</sub> showed almost no morphological change or crack even after 40 weeks under the same condition (Supporting Information, Figure S4). To eliminate the possibility of the WS<sub>2</sub> and WSe<sub>2</sub> turning to WO<sub>2</sub>/WO<sub>3</sub> that was observed in some studies,<sup>31,41–43</sup> we measured their thickness after air aging by AFM. The thickness of 2D WO<sub>3</sub> obtained from oxidation of 1L tungsten dichalcogenides should be 2.2–2.3 nm.<sup>41,43</sup> After 40 weeks in ambient conditions, the thickness of our 1L WS<sub>2</sub> and WSe<sub>2</sub> increased to  $\sim 1.5$ – $1.6$  nm, suggesting that these atomically thin WS<sub>2</sub> and WSe<sub>2</sub> should mostly retain their chemical composition after the long-term air exposure, and the slightly increased thickness should be due to physisorption of airborne organic molecules on their surfaces.<sup>31</sup> We also used Raman spectroscopy to probe the 1–3L WS<sub>2</sub> and WSe<sub>2</sub> aged in the air for up to 20 weeks (Figure 4). The 1L WS<sub>2</sub> showed gradually decreased  $E_{2g}$  and  $A_{1g}$  peaks with air exposure time (Figure 4a), indicating a certain degree of oxidation.<sup>43,44</sup> In





**Figure 6.** Effects of oxygen doping. DFT calculated (a) Young's moduli and (b) averaged lattice parameters of 1L WS<sub>2</sub> and WSe<sub>2</sub> with different contents of oxygen doping.

contrast, those of 2–3L WS<sub>2</sub> only decreased  $\sim 10\%$  after 20 weeks, and the relative intensity of the A<sub>1g</sub> peak very slightly declined (Figure 4b,c). The E<sub>2g</sub>/A<sub>1g</sub> peak intensities of the 1L and 3L WSe<sub>2</sub> were stable over the 20 weeks (Figure 4d,f), but that of the 2L dropped with time, and the relative intensity between the E<sub>2g</sub>/A<sub>1g</sub> and 2LA(M) peaks also reduced for 2L (Figure 4e). In all aged samples, no new Raman peak at  $\sim 800\text{--}830\text{ cm}^{-1}$  corresponding to WO<sub>3</sub> was detected.<sup>41</sup> These results reconfirmed that most of the mechanically exfoliated atomically thin WS<sub>2</sub> and WSe<sub>2</sub> were much more stable in the air than the CVD- and MBE-grown samples.<sup>29,31,32</sup> The higher level of oxidation in the 1L WS<sub>2</sub> and 2L WSe<sub>2</sub> could be due to (1) laser caused oxidation during repeated Raman measurements and (2) potentially more defects that facilitated oxidation.

It is interesting and valuable to test the air-aging effect on the mechanical properties of 2D TMDs, which has never been studied before. Figure 5 summarizes the Young's moduli and fracture strengths of the 1–3L WS<sub>2</sub> and WSe<sub>2</sub> after exposure to air for 6 and 20 weeks. Overall, both materials showed no catastrophic mechanical failure, especially that the Young's moduli and fracture strengths were mostly stable within 6 weeks of air exposure, though the standard deviations of strength became much larger. This was consistent with the mostly stable Raman spectra of the aged 1–3L WS<sub>2</sub> and WSe<sub>2</sub>. After 20 weeks, the mean Young's moduli and strengths of 1–3L WS<sub>2</sub> decreased, and those of the air-aged 1–3L WSe<sub>2</sub> remained stable or even increased in some cases, though statistically there was no significant difference in their means, due to the relatively small number of measurements and the large standard deviations (Supporting Information, Table S4).

Mechanically exfoliated and CVD-grown 2D TMDs tend to have different air-aging effects on their structures. It has been reported that air aging introduces a large number of vacancies and macroscopic cracks or etching pits to CVD-grown 2D TMDs.<sup>29,32</sup> In contrast, spontaneous oxygen substitution or doping in defect-free basal plane of mechanically exfoliated MoS<sub>2</sub> was observed under ambient conditions, and vacancy-type defects were negligible.<sup>45</sup> The difference should be due to the pre-existence of grain boundaries, various vacancies, as well as large amounts of defects in the CVD-grown samples. The vacancies let alone macroscopic cracks or pits have a catastrophic effect on the mechanical properties of air-aged CVD-grown 2D TMDs,<sup>20</sup> but it is not clear how the oxygen substitutional defects in 2D WS<sub>2</sub> and WSe<sub>2</sub> without the presence of vacancies could affect their mechanical properties. To test the influence of oxygen doping on the structural and

elastic properties of WS<sub>2</sub> and WSe<sub>2</sub> nanosheets, first-principles calculations were performed based on *ab initio* DFT (Supporting Information, Figure S5). Figure 6 shows the DFT calculated Young's moduli of 1L WS<sub>2</sub> and WSe<sub>2</sub> at 2.0%, 5.6%, and 12.5% concentrations of oxygen doping (see Supporting Information, Figure S5). Note that the oxygen doping did not change the H-phase of WS<sub>2</sub> and WSe<sub>2</sub> (Supporting Information, Figure S6 and Table S5). With increased oxygen doping, the elasticity of both materials enhanced, and the averaged lattice parameter *a* decreased, suggesting improved strength as well. Therefore, the mechanical properties of the air-aged atomically thin WS<sub>2</sub> and WSe<sub>2</sub> should be determined by the combined effects of oxygen doping and vacancy: The former reinforces, and the latter deteriorates their mechanical properties. The different trends of the long-term air-aged mechanical properties of WS<sub>2</sub> and WSe<sub>2</sub> could be due to their different ratios of oxygen doping and vacancy, possibly related to the different density and type of defects in the bulk crystals used for exfoliation.

## CONCLUSIONS

We used the indentation technique to study the mechanical properties of high-quality atomically thin tungsten dichalcogenides produced by mechanical exfoliation. The Young's moduli of 1L WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub> were  $302.4 \pm 24.1\text{ GPa}$  ( $187.5 \pm 14.9\text{ N m}^{-1}$ ),  $258.6 \pm 38.3\text{ GPa}$  ( $168.1 \pm 24.9\text{ N m}^{-1}$ ), and  $149.1 \pm 9.4\text{ GPa}$  ( $105.9 \pm 6.6\text{ N m}^{-1}$ ), respectively, and their fracture strengths were  $47.0 \pm 8.6\text{ GPa}$  ( $29.2 \pm 5.3\text{ N m}^{-1}$ ),  $38.0 \pm 6.0\text{ GPa}$  ( $24.7 \pm 3.9\text{ N m}^{-1}$ ), and  $6.4 \pm 3.3\text{ GPa}$  ( $4.5 \pm 2.3\text{ N m}^{-1}$ ), respectively. The mechanical values of WS<sub>2</sub> reduced most dramatically with increased thickness among the three materials. To understand this phenomenon, we used FEM and DFT calculations to reveal the effects of in-plane strain and out-of-plane compression on the sliding energies in these materials. It was found that WS<sub>2</sub> had the lowest sliding energies no matter in an equilibrium state or under strain and compression, and it could spontaneously slide from AA' to A'B stacking during indentation. Interlayer sliding could lead to concentrated stress on the bottom layers, resulting in reduced mechanical properties. We also investigated the long-term air-aging effect on the mechanical properties of 1–3L WS<sub>2</sub> and WSe<sub>2</sub>. According to our AFM and Raman characterizations, most of the 1–3L WS<sub>2</sub> and WSe<sub>2</sub> were stable up to 20 weeks after exposure to air. Their mechanical properties could be enhanced due to the oxygen doping by air aging. Our findings



imply the possibility of intentional property modification of 2D TMDs via aging in a controlled atmosphere.<sup>46</sup>

## METHODS

**Materials Fabrication and Characterization.** The atomically thin tungsten dichalcogenides were mechanically exfoliated from the corresponding bulk crystals by Scotch tape on 90 nm SiO<sub>2</sub>/Si with prefabricated circular microwells of 350, 800, and 900 nm in radius and 1–2  $\mu\text{m}$  in depth in a glovebox filled with argon gas. The Raman spectra were recorded using a 514.5 nm laser (a maximum power of 50 mW) and 100 $\times$  objective lens (numerical aperture 0.90) on a Renishaw inVia system. For WS<sub>2</sub> and WSe<sub>2</sub>, the laser power was set to 1%, with an absolute energy of  $\sim 0.1$  mW, and for WTe<sub>2</sub>, the laser power was set to 0.5%, with an absolute power of  $\sim 0.05$  mW to minimize potential damage. These absolute powers were measured by a Newport 1916-C optical power meter after the laser passed through all the optics and hit the samples. All Raman spectra were calibrated using a silicon peak at 520.5 cm<sup>-1</sup>. All samples measured by Raman were not used for mechanical tests to prevent the potential effect of laser-induced degradation. The mechanical properties of WS<sub>2</sub> and WSe<sub>2</sub> were measured using a Cypher AFM in air, and those of WTe<sub>2</sub> were measured in the same instrument with a constant flow of nitrogen gas at 1 L/min to reduce degradation. Cantilevers with diamond tips were chosen for indentation to minimize tip deformation-caused errors. The mechanical responses of the cantilevers were calibrated using the combined Sader and thermal noise method. The loading and unloading speeds in the indentations were 0.5  $\mu\text{m s}^{-1}$ . The loading–unloading curves with large hysteresis were excluded. Transmission electron microscopy (TEM) was employed to measure the tip apex radii, and the obtained tip radii were reconfirmed by indenting high-quality boron nitride<sup>38</sup> and graphene<sup>37</sup> with known mechanical properties. The tip radii were determined to be 3.3 nm (model DEP30: spring constant ( $k$ ) = 22.8 N/m; length ( $l$ ) = 240  $\mu\text{m}$ ; width ( $w$ ) = 35  $\mu\text{m}$ ; resonance frequency ( $f$ ) = 188.3 kHz), 10.6 nm (D300:  $k$  = 27.5 N/m;  $l$  = 124  $\mu\text{m}$ ;  $w$  = 37  $\mu\text{m}$ ;  $f$  = 289.6 kHz), 20.7 nm (D300:  $k$  = 57.0 N/m;  $l$  = 134  $\mu\text{m}$ ;  $w$  = 42  $\mu\text{m}$ ;  $f$  = 336.5 kHz), and 28.5 nm (NC-LC:  $k$  = 104.2 N/m;  $l$  = 138  $\mu\text{m}$ ;  $w$  = 40  $\mu\text{m}$ ;  $f$  = 442.3 kHz). The different tips showed statistically similar values of strength and stiffness. During air aging, the samples were mostly kept in the dark at 20  $^{\circ}\text{C}$  in a room with an air conditioner without humidity control.

**Finite Element Analysis.** The analysis was conducted using the commercial nonlinear finite element code ABAQUS (version 6.14). The monocrystal diamond tips of AFM indenters were modeled as rigid spheres. The tested nanosheets were modeled as axisymmetric circular shells with a radius of 350, 800, and 900 nm. The initial thicknesses of nanosheets were assigned to  $0.62 \times N$ ,  $0.65 \times N$ , and  $0.71 \times N$  nm for WS<sub>2</sub>, WSe<sub>2</sub>, and WTe<sub>2</sub>, respectively, where  $N$  is the number of layers. Two-node linear axisymmetric shell elements (SAX1) were used with mesh densities varying linearly from 0.1 nm (center) to 5.0 nm (outermost). Frictionless contact was assumed in the modeling of the indenter tip–nanosheet interactions. Displacement-controlled loading was applied to the indenter with a linear ramping profile. The tungsten dichalcogenides were assumed to be nonlinear elastic, and the constitutive relation is expressed as

$$\sigma = E\varepsilon + D\varepsilon^2 \quad (2)$$

where  $D$  is the third-order elastic constant, and  $\varepsilon$  is an applied strain. Detailed implementations of nonlinear elastic constitutive model in ABAQUS were described in prior work.<sup>38</sup> The Young's modulus and  $D$  values of atomically thin tungsten dichalcogenides were obtained from the experimental results. The fracture (curve termination) points in the simulated load–displacement curves were chosen based on the fracture loads from the corresponding experimental curves. Subsequently, the fracture strength and ultimate strain values were obtained as a volume average of the stress and strain values of the elements that were directly underneath the indenter at the corresponding loading steps. The surface-to-surface contact model

was chosen to determine the interlayer pressure by modeling the contact pressure between the indenter and nanosheets.

**DFT Calculations.** First-principles calculations were performed based on *ab initio* DFT using VASP 5.4.4 code.<sup>47,48</sup> The local density approximation was used to calculate the elastic properties of WX<sub>2</sub> ( $X = \text{O}, \text{S}, \text{Se}, \text{and Te}$ ) monolayers, and PAW–PBE along with optB88-vdW method was used to calculate the sliding energy for bilayer WX<sub>2</sub> ( $X = \text{S}, \text{Se}, \text{and Te}$ ).<sup>49–51</sup> A well-converged plane-wave cutoff of 550 eV was employed. The atomic coordinates were allowed to relax until the forces on the ions were  $< 1 \times 10^{-2}$  eV  $\text{\AA}^{-1}$ , and the electronic convergence was set to be  $1 \times 10^{-6}$  eV. The reduced Brillouin zone was sampled with a  $\Gamma$ -centered  $18 \times 18 \times 1$   $k$ -mesh for monolayer/bilayer systems.<sup>52</sup> A 15  $\text{\AA}$  vacuum space was used in all calculations to avoid any interactions between the supercells in the nonperiodic direction. To calculate elastic constants, we chose 11 compression-tensile structures ranging from  $-5\%$  to  $5\%$  with an interval of  $1\%$  compared with the optimized lattice. The doped WS<sub>2</sub> and WSe<sub>2</sub> monolayers were constructed using a  $2 \times 2$  supercell ( $12.5\%$ ),  $3 \times 3$  supercell ( $5.6\%$ ), and  $5 \times 5$  supercell ( $2\%$ ) with 1 S atom substituted by 1 O atom. The average lattice parameters for oxygen-doped WS<sub>2</sub> and WSe<sub>2</sub> monolayers were summarized based on the optimized doped systems. To calculate the sliding energy, we chose several intermediate structures along sliding directions (12 and 6 images for WS<sub>2</sub> and WSe<sub>2</sub> for path-a and path-b, respectively; 6 and 10 images for WTe<sub>2</sub> for path-a and path-b, respectively). Biaxial strain and hydraulic pressure were used in the calculations.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.0c07430>.

The  $t$ -test statistics; DFT calculations on the most stable phase of WTe<sub>2</sub>, elastic constants and sliding energies of 2H-WTe<sub>2</sub>, interaction between diamond tip and WS<sub>2</sub> (WSe<sub>2</sub>), and air-aged WS<sub>2</sub> and WSe<sub>2</sub> and their stable phases; optical microscopy images of the aged WS<sub>2</sub> and WSe<sub>2</sub> (PDF)

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## Author Contributions

• A.F., M.H., and H.L. contributed equally. L.H.L. conceived and directed this research. A.F. did all mechanical tests and data analysis. M.H. and K.S.N. provided the atomically thin samples. H.L. and X.W. did the DFT calculations. W.G. did Raman spectra. R.Z. and D.Q. carried out FEM calculations. M.R.B., E.J.G.S., J.C., and T.T. provided suggestions and further analysis during discussions. L.H.L. and A.F. cowrote the manuscript. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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