

# 2D Transition Metal Dichalcogenide with Increased Entropy for Piezoelectric Electronics

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Piezoelectricity in 2D transition metal dichalcogenides (TMDs) has attracted considerable interest because of their excellent flexibility and high piezoelectric coefficient compared to conventional piezoelectric bulk materials. However, the ability to regulate the piezoelectric properties is limited because the entropy is constant for certain binary TMDs other than multielement ones. Herein, in order to increase the entropy, a ternary TMDs alloy,  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ , with different W concentrations, is synthesized. The W concentration in the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloy can be controlled precisely in the low-supersaturation synthesis and the entropy can be tuned accordingly. The  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy ( $x = 0.54$ ) has the highest configurational entropy and best piezoelectric properties, such as a piezoelectric coefficient of  $4.22 \text{ pm V}^{-1}$  and a piezoelectric output current of 150 pA at 0.24% strain. More importantly, it can be combined into a larger package to increase the output current to 600 pA to cater to self-powered applications. Combining with excellent mechanical durability, a mechanical sensor based on the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy is demonstrated for real-time health monitoring.

in-plane direction.<sup>[1–4]</sup> When an external force is applied, the strain-induced lattice distortion gives rise to piezoelectric polarization in the materials.<sup>[5–7]</sup> Owing to the high crystallinity and ability to endure large strain, 2D-TMDs are promising candidates in applications such as sensing<sup>[8,9]</sup> and energy conversion.<sup>[10,11]</sup> Although the piezoelectric response of binary 2D-TMDs such as  $\text{MoS}_2$ ,  $\text{WS}_2$ , and  $\text{MoSe}_2$  has been improved, the ability to regulate the piezoelectric properties is still limited because piezoelectric polarization depends on the structural asymmetry.<sup>[8,12–15]</sup> For example, the piezoelectric coefficient of the sandwiched  $\text{MoS}_2$  is limited to  $2.9 \times 10^{-10} \text{ C m}^{-1}$  because the sandwiched structure with respect to the central metal atomic plane has a lower degree of structural asymmetry.<sup>[2,5]</sup>

Recently, entropy engineering has been proposed as a novel strategy to optimize the piezoelectric<sup>[16]</sup> and thermoelectric<sup>[17]</sup> properties of materials. By increasing element species, the distortion-driven entropy, referred as configurational entropy, in a material system increases due to

## 1. Introduction


2D transition metal dichalcogenides (TMDs) are intrinsically piezoelectric due to the broken inversion symmetry along the

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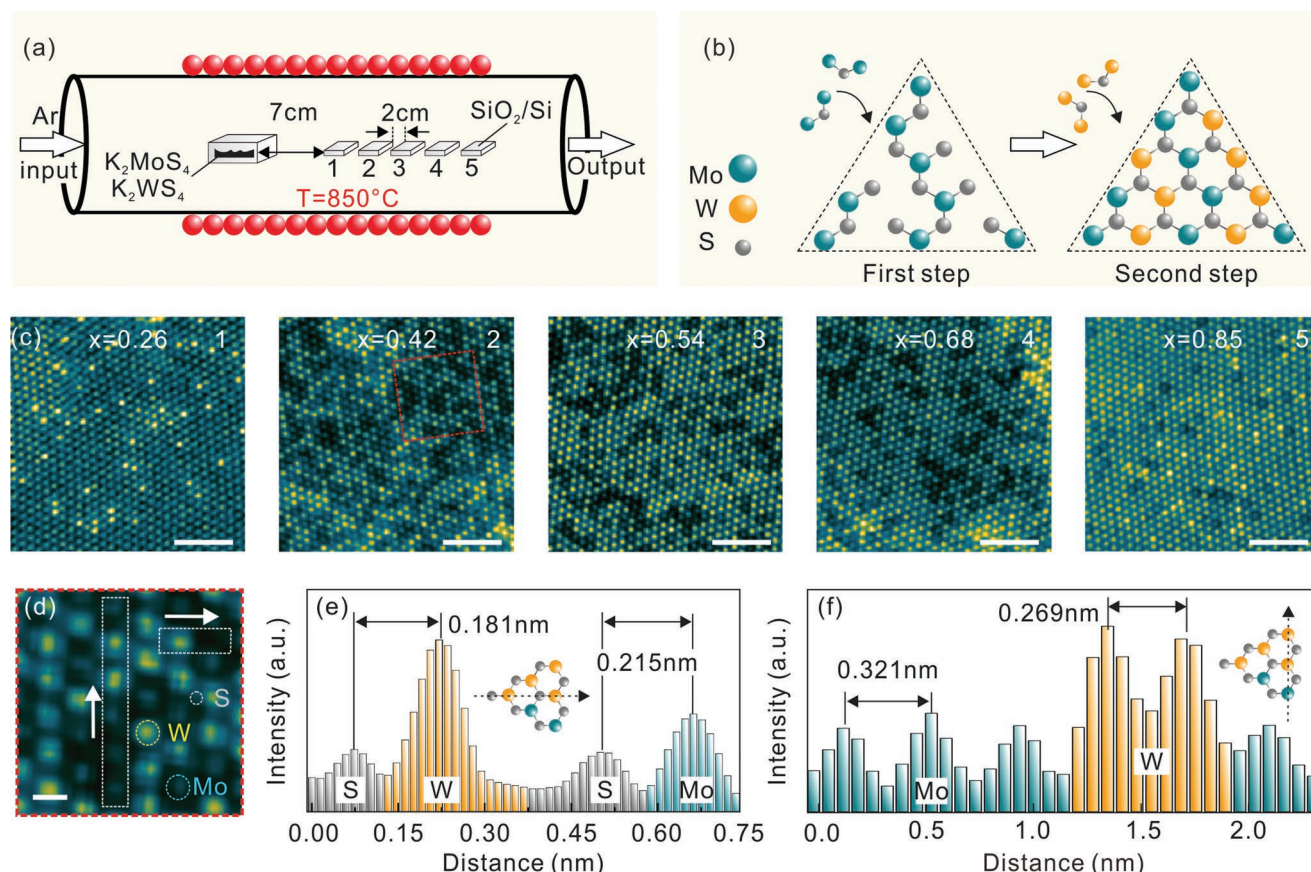
the lattice distortion of atomic configurations.<sup>[18]</sup> Due to the increment of configurational entropy, the alloys with a high piezoelectric response could be obtained when the number of substituted components is optimized.<sup>[19–22]</sup> As a result, by doping 2D-TMDs, enhanced piezoelectricity may be realized. However, enhanced piezoelectricity has not been observed from increased entropy 2D-TMDs alloys so far and the related sensing devices have not been reported.

Herein, in order to improve the piezoelectric properties, ternary TMDs of  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  with variable W concentrations are synthesized. By adopting a solution-based precursor technique,<sup>[23]</sup> the low-supersaturation process enables precise control of the W concentration in the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloy. X-ray photoelectron spectroscopy, Raman scattering, photoluminescence, and electromechanical assessment reveal that the piezoelectric coefficient of the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy ( $x = 0.54$ ) has the similar fraction of Mo and W atoms and the highest configurational entropy, it exhibits the best piezoelectric coefficient of  $4.22 \text{ pm V}^{-1}$  among all five  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys with different compositions. The output current of 150 pA at 0.24% strain is also higher than that of binary 2D materials and it can be further increased by array integration. As a result of the high piezoelectric response and

excellent mechanical durability, a mechanical sensor based on the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy is fabricated and demonstrated for real-time health monitoring.

## 2. Results and Discussion

The solution-based precursor technology is a new strategy to synthesize TMDs monolayer crystals because the supersaturation level of all the precursors can be controlled.<sup>[23]</sup> However, control of the composition is rather challenging since only one type of TMD with certain composition ratio can be obtained by optimizing the relative ratio of the amount of the precursors each time. Here, we design a low-supersaturation synthesis process to produce various TMDs alloys with controlled compositions simultaneously. In this method, a relatively low supersaturation state is produced from the vapor reactants leading to a reduced nucleation density essential for alloy growth. Moreover, the supersaturation state can be easily controlled by optimizing the distance between the precursor source and substrate, so that TMDs with diverse compositions can be fabricated. Details about the synthesis process can be found in **Figure 1a**, Experimental Section, as well as Figure S1 in the Supporting Information.



**Figure 1.** Synthesis and characterization of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys. a) Schematic view of the low supersaturation CVD growth system consisting of five substrates with different supersaturation levels attached to the  $\text{K}_2\text{MoS}_4$  and  $\text{K}_2\text{WS}_4$  sources. b) Alloying of the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloy. c) HR-TEM images of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys (scale bar: 2 nm). d) Magnified image of the region marked by the red square in (c-2) (scale bar: 0.3 nm). e, f) Intensities of W, Mo, and S (e) and W and Mo (f) of the areas demarcated by the short and long white dashed lines in (d), respectively.

The  $\text{K}_2\text{MoS}_4$  and  $\text{K}_2\text{WS}_4$  precursors with a ratio of 1:1 are mixed and loaded into the CVD chamber. Five substrates are placed at different locations from the source so that the supersaturation levels can be adjusted. Owing to the lower volatilization temperature of  $\text{K}_2\text{MoS}_4$ , the sublimed S and Mo atoms are first transported downstream by the carrying gas of Ar at 750 °C to nucleation sites on the nearby substrates. According to previous reports, the distribution and density of nucleation depend on the supersaturation level.<sup>[24]</sup> In the first growth step shown in the left panel in Figure 1b, the small amount of Mo in the solution-processed precursors produces significantly lower supersaturation level and a small density of Mo-related nucleation on the substrate. The supersaturation level decreases further when the distance between the sources and substrates increases. Therefore, the nucleation density is larger on the substrate closer to the source and vice versa. In the second step (shown in the right panel in Figure 1b), the temperature increases rapidly to 850 °C.  $\text{K}_2\text{WS}_4$  vaporizes to form W-related nucleation sites which merge with the Mo nucleation sites. Because of the similar covalent lattices (138 pm for Mo and 137 pm for W) and the same crystalline structure ( $P6_3/mmc$  symmetry point group) of  $\text{MoS}_2$  and  $\text{WS}_2$ , the Mo and W atoms randomly share the metal atom sites to form the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloy without clustering. Consequently, the value of  $x$  can be tuned by optimizing the distance of the substrate.

High-resolution transmission electron microscopy (HR-TEM) images are acquired from the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys synthesized at different locations in the furnace as shown in Figure 1a,c. The corresponding fast Fourier transform patterns and the deduced interplanar spacing parameters are illustrated in Figure S2 in the Supporting Information. The thickness of  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  is about 0.9 nm as determined by AFM (shown in Figure S3 in the Supporting Information) and it has a single-layer nature.<sup>[25]</sup> The single-crystal  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  with a regular triangular feature is illustrated by the HR-TEM image and the selected-area electron diffraction (SAED) pattern in Figure S4 in the Supporting Information. Due to a large difference in the atomic number between W ( $Z = 74$ ) and Mo ( $Z = 42$ ), brighter and darker spots can be resolved from the HR-TEM images, but S is not visible because of the possible inclination of the layers with respect to the direction of the incident electron beam.<sup>[20]</sup> The fraction of brighter spots corresponding to W atoms increases monotonically with larger distance between the substrate and precursor boat. The concentration of W in  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  is quantified to be  $x = 0.26$  for the closest substrate and gradually increases to  $x = 0.85$  for the farthest substrate. The  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy ( $x = 0.54$ ) exhibits the highest random degree and configurational entropy.

The unequal bond lengths between S–Mo and S–W result in structural asymmetry of  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ . The atomic distribution and intensity profiles for S, Mo, and W are presented in Figure 1d–f. Figure 1d shows the magnified HR-TEM image (Figure 1c-2) of  $\text{Mo}_{0.58}\text{W}_{0.42}\text{S}_2$ . There is a clear sixfold coordination symmetry and honeycomb-like structure in which S atoms have low contrast while W and Mo atoms are yellow and blue spots, respectively. As shown in Figure 1e, the intensities of S, Mo, and W from an area surrounded by a white-dashed shorter rectangle along the white arrow in Figure 1d reveals that S atoms are immediately adjacent to Mo and W atoms with distances of

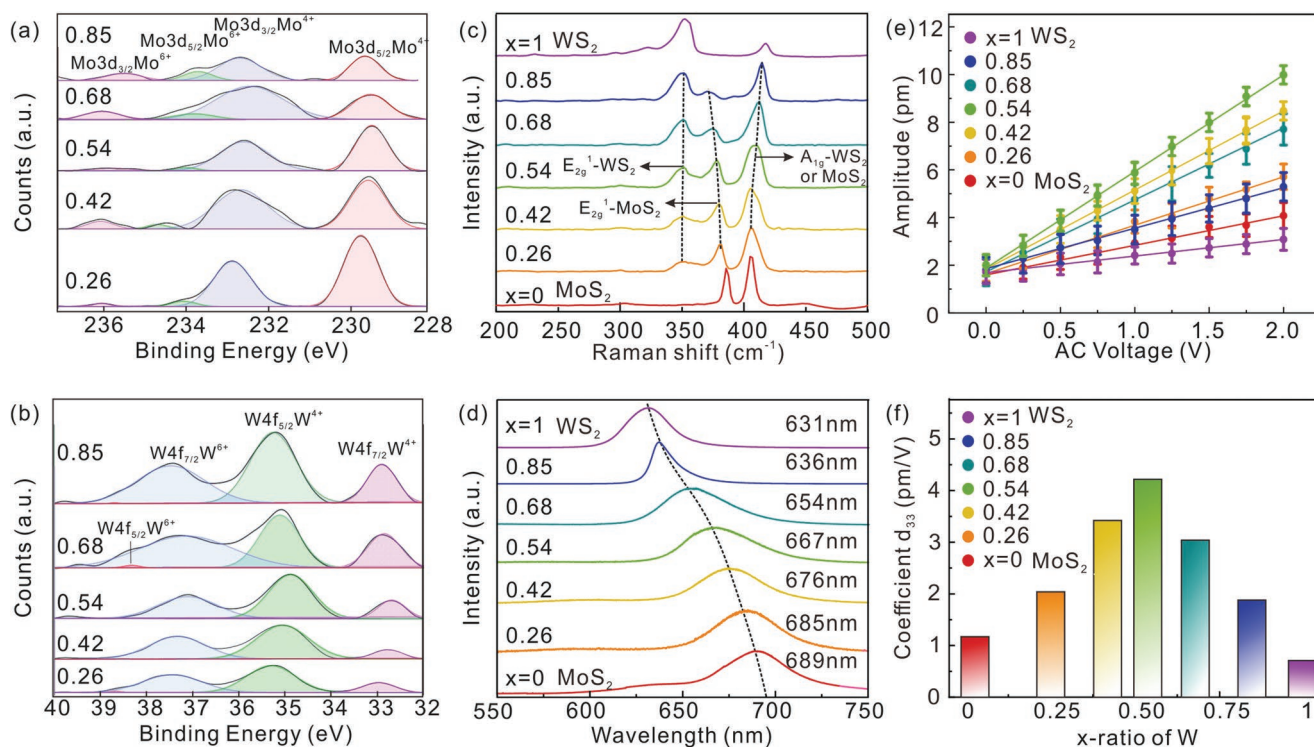
0.215 and 0.181 nm, respectively. The unequal S–Mo and S–W bond lengths break the reflection symmetry along the in-plane direction, resulting in a higher degree of asymmetry than the binary 2D-TMDs. To illustrate random substitution of Mo and W, the atomic composition of Mo and W in  $\text{Mo}_{0.58}\text{W}_{0.42}\text{S}_2$  from the white dashed longer rectangle along the white arrow in Figure 1d is shown in Figure 1f. Compared to W atoms, the number of Mo atoms is larger considering the atomic stoichiometry of the  $\text{Mo}_{0.58}\text{W}_{0.42}\text{S}_2$  alloy. The Mo–Mo distance is 0.321 nm, which is larger than that of W–W (0.269 nm). The intensity analysis suggests that the heteroatom-doping distribution of the  $\text{Mo}_{0.58}\text{W}_{0.42}\text{S}_2$  alloy is random and disordered, thus enhancing the entropy of the  $\text{Mo}_{0.58}\text{W}_{0.42}\text{S}_2$  alloy compared to pure  $\text{MoS}_2$  or  $\text{WS}_2$ .

To investigate the relationship between the atomic stoichiometry and piezoelectricity of  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloy, X-ray photoelectron spectroscopy (XPS), Raman scattering, PL, and electromechanical measurements are conducted, as illustrated in Figure 2. The XPS spectra of Mo 3d and W 4f of the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys with different compositions are shown in Figure 2a,b. The W 4f peak intensity increases with larger W concentration ( $x$ ) but that of the Mo 3d peak decreases or vice versa. The strong peaks at 229.5 and 232.7 eV in Figure 2a are the Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> peaks of  $\text{Mo}^{4+}$ , respectively, and the weak peaks at 234.0 and 235.9 eV are the Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> peaks of  $\text{Mo}^{6+}$ , respectively. The weak peaks of  $\text{Mo}^{6+}$  are mainly due to the trace amount left from incomplete decomposition of  $\text{K}_2\text{MoS}_4$  on the substrate. As for the W 4f peaks, there are two valence states of  $\text{W}^{4+}$  (32.8 and 35.1 eV) and  $\text{W}^{6+}$  (37.4 and 38.5 eV) as shown in Figure 2b. Since the decomposition temperature of  $\text{K}_2\text{WS}_4$  is higher than that of  $\text{K}_2\text{MoS}_4$ , the residual hexavalent W concentration is larger accordingly. In addition, the concentration of S in the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys does not change appreciably as shown by the similar S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> peaks (Figure S5, Supporting Information). The XPS results are consistent with that provided by HR-TEM (Figure 1c).

Raman scattering spectroscopy is performed to characterize the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys as shown in Figure 2c. Prior to Raman measurement, monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys pre-cleaned by deionized water to remove the possible  $\text{K}_2\text{WS}_4$  and  $\text{K}_2\text{MoS}_4$  residue during the transfer process (Figure S6, Supporting Information). In the pure monolayer  $\text{MoS}_2$ , the Raman spectrum shows the in-plane vibrational  $E_{2g}^1$  ( $\Gamma$ ) mode at 385 cm<sup>−1</sup> and an out-of-plane  $A_{1g}$  ( $\Gamma$ ) mode at 405 cm<sup>−1</sup>.<sup>[26]</sup> As for the pure monolayer  $\text{WS}_2$ , the strong peak at 350 cm<sup>−1</sup> is the in-plane vibration  $E_{2g}^1$  ( $\Gamma$ ) mode and the weak peak at 419 cm<sup>−1</sup> is attributed to the out-of-plane  $A_{1g}$  ( $\Gamma$ ) mode.<sup>[27]</sup> The positions of the  $E_{2g}^1$ - $\text{MoS}_2$  and  $A_{1g}$  peaks of the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys exhibit red and blue shifts with increasing W concentration, respectively, but the position of the  $E_{2g}^1$ - $\text{WS}_2$  peak does not change. The shifts are caused by lattice distortion from substitution between W and Mo atoms and are summarized in Figure S7 in the Supporting Information.<sup>[28]</sup> In the monolayer  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy, Raman mapping of three characteristic modes suggests that the distribution of Mo and W is rather uniform across the triangular flake, as shown in Figure S8 in the Supporting Information.

The PL spectra of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys in Figure 2d show that the emission energy level is closer to that of the monolayer  $\text{WS}_2$  (631 nm, 1.98 eV) with increasing W





**Figure 2.** Relationship between the atomic stoichiometry and piezoelectricity of the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloy. a,b) XPS spectra of Mo-3d (a) and W-4f (b) of  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys with different compositions. c) Raman scattering and d) PL spectra of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ . e) Average piezoresponse amplitude and f) piezoresponse coefficients of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  samples with different compositions.

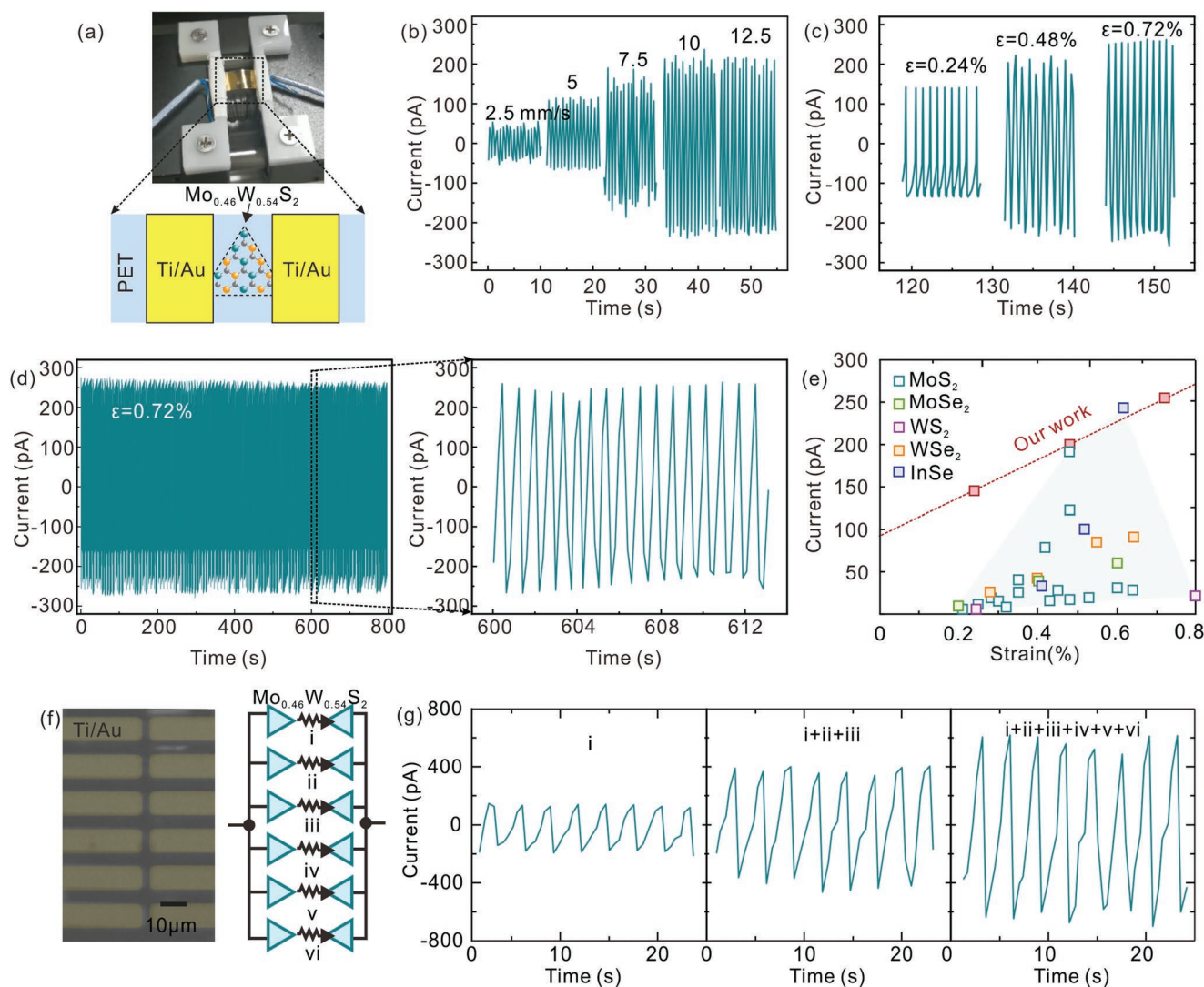
concentration and vice versa. The emission energy level is closer to that of the monolayer  $\text{MoS}_2$  (689 nm, 1.8 eV) with decreasing W concentration. The relationship between the bandgap and W concentration is illustrated in Figure S9 (Supporting Information), which is consistent with previous results.<sup>[28]</sup>

Piezoelectricity is generated by electric polarization in a non-centrosymmetric crystal structure with the symmetry broken in the lateral direction.<sup>[16,17]</sup> Owing to the structural asymmetry, a nonzero dipole moment is created in an asymmetrical order unit cell and forms a macroscopic potential difference along the lateral direction when strain is applied. This dipole moment is coupled to the materials lattice and changes in the lattice such as defects, vacancies, and doping, which can enhance electric polarization. It is expected that the piezoelectric signal from binary 2D-TMDs such as  $\text{MoS}_2$  and  $\text{WS}_2$  is weaker than that from a heteroatom-doped 2D-TMDs alloy ( $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ ). In our case, though the interplanar spacing parameters for the heteroatom-doped  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys with different compositions barely change (Figure S2, Supporting Information), the presence of S–Mo and S–W bonds with unequal dipole leads to a larger net dipole moment than that of the binary 2D-TMDs, thus inducing higher piezoelectric performance. Moreover, by increasing the doping-compositional space disorder, referred to as distortion-driven entropy enhancement, the heteroatom-doping-induced piezoelectric performance can be further enhanced. The preliminary density functional theory (DFT) calculation results also suggest that the entropy, especially the configurational entropy contributes to the piezoelectric effect in the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy (detail shown in Figure S10 in the

Supporting Information). As a result, the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy with  $x$  close to 0.5 (that is, almost equiatomic W and Mo) has the highest entropy and piezoelectric currents as shown in Figure S11 in the Supporting Information. The piezoelectric properties of the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys are analyzed quantitatively by piezoresponse force microscopy (PFM) as shown in Figures S12 and S13 (Supporting Information) and the variations in the PFM amplitude versus AC voltage are presented in Figures S14–S20 (Supporting Information), as summarized in Figure 2e. As expected, the maximum PFM amplitude is observed from the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy with the maximum entropy. In our quantitative analysis, the effective piezoelectric coefficient,  $d_{33}^{\text{eff}}$  of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys is calculated using the following equation<sup>[29,30]</sup>

$$d_{33}^{\text{eff}} = \frac{A_p(\text{pm})}{V_{\text{AC}}(\text{V})} \quad (1)$$

where  $A_p(\text{pm})$  is PFM amplitude and  $V_{\text{AC}}(\text{V})$  is the amplitude of the AC voltage. The piezoresponse coefficients of monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  with different compositions can be calculated from the slope of the linearly fitted curve in Figure 2e, as summarized in Figure 2f. Because of the higher asymmetric degree in the in-plane atomic structure, the ternary  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys have larger  $d_{33}^{\text{eff}}$  than both the binary  $\text{MoS}_2$  or  $\text{WS}_2$ . The monolayer  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  has the maximum  $d_{33}^{\text{eff}}$  of 4.22 pm V<sup>−1</sup>, while  $\text{MoS}_2$  and  $\text{WS}_2$  have the  $d_{33}^{\text{eff}}$  values of 1.25 and 0.71 pm V<sup>−1</sup>, respectively. All in all, XPS, Raman scattering, PL, and electromechanical evaluation reveal that the low-supersaturation



**Figure 3.** Characteristics of the piezoelectric nanogenerator based on  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  with increased entropy (IE-PNG). a) Photograph of the mechanical loading equipment and schematic of the IE-PNG. b,c) Output currents of the IE-PNG at different strain rates (b) and strain values (c). d) Durability of the IE-PNG under cyclic loading of up to  $0.72\%$  strain at a  $10 \text{ mm s}^{-1}$  strain rate. e) Comparison of the output currents of the binary 2D materials PNG and IE-PNG. f) SEM image of the integrated array consisting of six IE-PNGs. g) Output currents of parallel connection of one, three, and six IE-PNGs from left to right, respectively.

process is capable of tuning the elemental concentration in the 2D-TMDs flexibly and controllably. Moreover, the compositional space disorder and configurational entropy correlate with metal doping, and the piezoelectric properties can be optimized in  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy with the highest configurational entropy.

Since  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  with increased entropy delivers the best piezoelectric performance, a piezoelectric nanogenerator (IE-PNG) is fabricated on PET, as described in Experimental Section and Figure S21 (Supporting Information) and illustrated in Figure 3a. By using this piece of equipment, the applied strain and strain rate can be programmed for periodical stretching and release of the PET substrate. The applied strain is first fixed at  $0.48\%$  to investigate the relationship between the current and strain rate. The output currents of the IE-PNG under different strain rates from  $2.5$  to  $12.5 \text{ mm s}^{-1}$  are shown in Figure 3b. The output voltages of IE-PNG based on  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  under

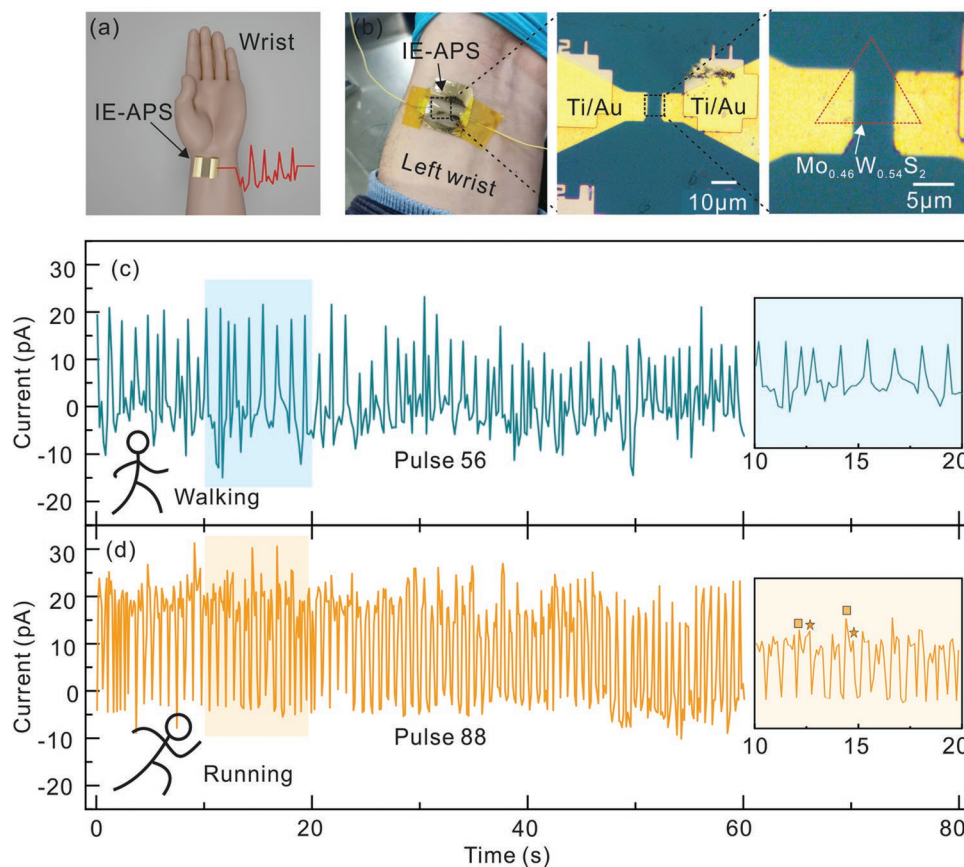
different load resistances or different strain rates are shown in Figure S22 in the Supporting Information. As the strain rate increases from  $2.5$  to  $10 \text{ mm s}^{-1}$ , the current increases linearly from  $50$  to  $200 \text{ pA}$  and the linear increase is consistent with the strain-induced current equation of  $I = d_{33}EA\dot{\epsilon}$ , where  $I$  is the output current,  $d_{33}$  is the piezoelectric charge constant,  $E$  is Young's modulus,  $A$  is the cross-sectional area, and  $\dot{\epsilon}$  is the applied strain rate.<sup>[31]</sup> For certain materials,  $d_{33}$ ,  $E$ , and  $A$  are constant and a linear relationship between  $I$  and  $\dot{\epsilon}$  can be obtained. The linear relationship is observed for strain rates below  $10 \text{ mm s}^{-1}$  and the output current is saturated when the strain rate is larger than  $10 \text{ mm s}^{-1}$ . This phenomenon arises from layer separation between the triboelectric layer and PET substrate at the high strain rate and therefore, the generated charges cannot be derived completely. The correlation between the piezoelectric output current and the layer number of  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$

is also investigated, as shown in Figure S23 in the Supporting Information. Different from two-layer binary 2D-TMDs such as  $\text{MoS}_2$ , in which the piezoelectric behavior disappears due to a symmetric cancellation of alternating orientations between the adjacent layers,<sup>[1]</sup> the two-layer  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  still exhibits a weak piezoelectric signal arising from the out-of-plane asymmetry of adjacent layers, though the intensity is attenuated considerably.

The relationship between the current and strain is investigated for a fixed strain rate of  $10 \text{ mm s}^{-1}$ , as shown in Figure 3c. The output current increases when the strain increases from 0.24% to 0.72%. According to the piezoelectric theory, the distance between the positive charge and negative charge, which correlates with the strain, determines the polarization and bound charges.<sup>[31]</sup> However, if the applied strain exceeds 0.96%, an unstable output current is observed due to significant slippage between the IE-PNG and PET substrate (see Figure S24 in the Supporting Information). The durability test results in Figure 3d indicate that the response of the IE-PNG is stable with time for cyclic loading up to 0.72% strain (more details shown in Figure S25 in the Supporting Information) at a  $10 \text{ mm s}^{-1}$  strain rate for 800 s. The output current is rather stable confirming the excellent mechanical stability. In addition, the output current is a key parameter to evaluate the performance of piezoelectric nanogenerators (PNGs), the output currents of the PNG with the binary monolayer 2D materials

and compared to those of our IE-PNG composed of the monolayer  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy are shown in Figure 3e.<sup>[1,10,11,29,32–37]</sup> In our case, the output current increases linearly with the applied strain and is always higher than that of the other binary 2D materials at the similar strain state. For instance, at a low strain of 0.24%, our IE-PNG shows an output current of 150 pA that is an order of magnitude larger than those of  $\text{MoS}_2$ ,  $\text{MoSe}_2$ ,  $\text{WS}_2$ ,  $\text{WSe}_2$ , and  $\text{InSe}$ . The output current reaches 200 pA for 0.48% strain that is also higher than that of other binary 2D materials. For a strain above 0.6%, the monolayer  $\text{InSe}$ , a group-III monochalcogenide, shows a higher output current due to the largest clamped-ion piezoelectric coefficients.<sup>[38]</sup> To further improve the properties of the IE-PNG, multiple IE-PNGs can be integrated in parallel on the PET substrate to obtain an enlarged output current, as shown in Figure 3f. As expected, piezoelectric output currents with 150, 400, and 600 pA are observed from the single, triple, and sextuple IE-PNGs, respectively, when connected in parallel (Figure 3g).

Benefiting from the linear relationship between the output current and strain (shown in Figure 3e), a flexible mechanical sensor constructed with the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  alloy is applied to monitor the human arterial pulse. The real-time arterial pulse sensor uses  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  flake (IE-APS) on the soft PDMS and the IE-APS is attached to the skin at the left wrist as schematically shown in Figure 4a. The optical microscopy image of



**Figure 4.** Characteristics of the real-time arterial pulse sensor based on  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  (IE-APS). a) Schematic diagram of the IE-APS placed on a human wrist. b) Optical microscopy image of the IE-APS. c,d) Output currents of two different physical modes: c) walking and d) running; the insets show the magnified pulses in the colored rectangles.



the IE-APS is shown in Figure 4b and the output currents of two different physical modes, walking and running, are presented in Figure 4c,d, respectively. The pulse rate is 56 bpm in the walking mode and increases to 88 bpm in the running mode. The peak value of the positive pulses is always slightly higher than that of the negative pulses because of the difference in the strain rates between systolic and diastolic blood pressure, implying that the time for systole is shorter than that during diastole.<sup>[39]</sup> The magnified line signals from 10 to 20 s are shown in the insets in Figure 4c,d. Compared to single peak originating from one pulse in the walking mode, two peaks denoted by square and star symbols are distinguishable in a running model, which is caused by superposition of the incoming blood wave ejected from the left ventricular and reflected wave from the lower body.<sup>[32]</sup> The capability of resolving the left ventricular and reflected wave from the incoming blood wave confirms that the IE-APS based on  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  with increased entropy has very high sensitivity in pressure detection. The fast response and high sensitivity of the self-powered mechanical sensor render it an ideal flexible device in practice.

### 3. Conclusion

Heterodoping is a feasible way to increase the structural asymmetry, compositional space disorder, and entropy of TMDs. The entropy-enhanced  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  TMD delivers exceptional piezoelectricity performance such as a piezoelectric coefficient of  $4.22 \text{ pm V}^{-1}$  and output current of 150 pA at 0.24% strain. Furthermore, it can be integrated into a larger package to increase the output current to 600 pA to cater to self-powered applications. A mechanical sensor is fabricated with the  $\text{Mo}_{0.46}\text{W}_{0.54}\text{S}_2$  TMD to monitor human arterial pulse rates in real-time for different physical modes. Owing to the high piezoelectric sensitivity, the incoming blood wave and reflected wave manifest as two peaks in the running mode. Our results demonstrate the feasibility of optimizing the properties of the piezoelectric materials for high-performance energy generators and mechanical sensors by increasing the entropy of the alloy, and the novel strategy has large potential pertaining to the design of next-generation piezoelectric materials and self-powered wearable devices.

### 4. Experimental Section

**Sample Preparation:**  $\text{K}_2\text{MoS}_4$  and  $\text{K}_2\text{WS}_4$  synthesized from  $(\text{NH}_4)_2\text{MoS}_4$  powder (99.9%, Sigma Aldrich) and  $(\text{NH}_4)_2\text{WS}_4$  powder (99.9%, Sigma Aldrich)<sup>[40]</sup> were used as precursors in CVD using a movable single heating furnace. A quartz boat loaded with  $\text{K}_2\text{MoS}_4$  and  $\text{K}_2\text{WS}_4$  with a molar mass ratio of 1:1 was placed in a 2-inch quartz tube. The 300 nm  $\text{SiO}_2/\text{Si}$  ( $1 \times 1 \text{ cm}$ ) substrate was cleaned with acetone and methanol. The composition of the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys was controlled by varying the loading distance between the substrate and precursor boat. Before synthesis, the tube was evacuated to a pressure of 1 Pa and then filled with Ar gas to atmospheric pressure. The furnace put far away from the precursors was heated to  $850^\circ\text{C}$  for 60 min under 200 sccm Ar flow. Afterwards, the furnace was pushed to the precursors and maintained 10 min for the synthesis. The temperature of the precursors increased rapidly from room temperature to  $850^\circ\text{C}$  and after the synthesis, the

furnace was immediately pushed away from the precursor and the Ar flow rate was adjusted to 500 sccm to enable cooling.

**PFM Characterization:** The surface morphology of the monolayer alloys was examined on a commercial AFM system (Dimension Icon, Bruker) and the PFM mode was employed to detect the piezoelectricity with the aid of a conductive “SCM-PIT” tip coated by Pt/Ir. To avoid contact resonance at the tip-sample junction, the frequency of the applied AC voltage was 15 kHz which was far away from the contact resonance frequency (above 120 kHz).

**HR-TEM Characterization:** The atomic structure and crystallinity of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  samples were characterized by HR-TEM (JEOL, JEM-ARM 300F) at 80 kV.

**XPS Characterization:** The elemental composition of the  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  alloys was determined by X-ray photoelectron spectroscopy (Kratos AXIS Supra XPS equipped with a monochromatic Al  $K_{\alpha}$  source) referenced to the C1s peak at 284.8 eV.

**PL and Raman Scattering Characterization:** Photoluminescence and Raman scattering were conducted on the HORIBA Jobin Yvon HR800 with a 514 nm semiconductor laser with a spot size of  $1 \mu\text{m}$  in air under ambient conditions. High-resolution Raman mapping was performed using the confocal  $\mu\text{-PL}$  system (WITec, alpha-300) with a 532 nm wavelength laser and  $100\times$  (0.9 NA) objective lens. The grating was  $1800 \text{ g mm}^{-1}$ .

**Electrical Output Characterization:** The low-noise output currents of the monolayer  $\text{Mo}_{1-x}\text{W}_x\text{S}_2$  IE-PNGs were measured on a picoammeter (Keithley, 4200) and a bending machine was utilized to generate the programmed driving strain between the two electrodes.

**On-Body Experiments:** The left wrist of the volunteer (one of the authors of this paper) was cleaned with soap and water, and dried. The real-time arterial pulse sensor was attached onto the volunteer skin to monitor the actual pulses. The volunteer involved in this context gave written, fully informed consent before participation in the study. The experiments conducted in this study were not subject to ethical approval.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

2D alloys, entropy, nanogenerators, piezoelectricity, sensors

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