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## CVD synthesis and optical study of bandgap-tunable Sn-doped monolayer molybdenum disulfide†

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Two-dimensional transition metal dichalcogenides (TMDCs) have attracted extensive interest in next-generation optoelectronic devices and energy-harvesting absorbers due to their fascinating optical and electronic properties. It is of great interest to engineer the electronic structure of TMDCs to attain more intriguing physical properties. Here, we introduce SnCl<sub>2</sub> as a low-cost, environmentally friendly dopant to simultaneously engineer the band structure of monolayer MoS<sub>2</sub> and this is an easily scalable and high-quality, efficient one-step CVD method, revealing that the tensile strain induced by the different bond lengths of Sn–S and Mo–S can directionally modulate the electronic state of monolayer MoS<sub>2</sub> and lead to bandgap reforming, providing a feasible way for bandgap engineering. Our work demonstrates the effective modulation of TMDC's bandgap to expand the novel optoelectronic properties of 2D materials.

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### Introduction

Two-dimensional transition metal dichalcogenides have promising potential for diverse applications in optoelectronic devices,<sup>1</sup> quantum information science,<sup>2</sup> biomedicine,<sup>3</sup> and integrated circuits<sup>4,5</sup> because of their thickness-dependent bandgaps and unique electronic and optical properties. Among them, single-layer TMDCs as direct bandgap semiconductors,<sup>6</sup> such as monolayer molybdenum disulfide (MoS<sub>2</sub>), are pertinent candidates for next-generation optoelectronic and valleytronic devices.<sup>7</sup> Currently, both top-down and bottom-up preparation techniques are developed to produce monolayer TMDCs, including mechanical cleavage,<sup>7</sup> liquid phase exfoliation,<sup>8</sup> physical vapor deposition (PVD),<sup>9,10</sup> molecular beam epitaxy (MBE)<sup>11</sup> and chemical vapor deposition (CVD).<sup>12,13</sup> Nevertheless, CVD is considered to be the most effective approach for large-scale and high-quality growth of 2D TMDCs.<sup>14,15</sup>

Two-dimensional semiconductors have tunable intermediate physical properties between insulators and conductors.<sup>16</sup> Chemical doping, a process that introduces charge carriers into semiconductors, is considered to be an effective way to

control the optical and electronic performances of 2D materials.<sup>17,18</sup> In the case of surface chemical doping, the dopant is usually introduced into the 2D semiconductor through physical or chemical interactions without destroying the structure.<sup>19,20</sup> This is usually achieved by chemical treatments or solvent-based intercalation methods, and the choice of dopant can be generic, including small molecules, ions, and particles.<sup>21,22</sup> However, doped structures lack a covalent connection between the dopant and the TMDC, and may be in a metastable state that does not permanently maintain the endowed properties.<sup>23</sup> In contrast, substitutional doping, in which some of the sites in the original 2D lattice are exchanged by exogenous atoms, has been widely used in the engineering of band structures and phase transitions. Generally, it is achieved by employing a powder vaporization chemical vapor deposition (CVD) method and introducing all the reactant precursors together during the growth of crystals.<sup>24</sup> This integrated approach results in stable substitutional doped structures, but the challenge is to produce high-quality homogeneous single crystals due to the different crystallization temperatures of the target 2D materials and the evaporation rates of each precursor.

Many efforts have been made to find high-quality 2D single crystals, including the employment of sodium halides to passivate defects and enhance photoluminescence,<sup>25</sup> the salt-assisted CVD growth to modulate the defects of sulfur vacancies in MoS<sub>2</sub>,<sup>26</sup> spontaneous n-doping caused by alkali metal compounds,<sup>27</sup> thermal oxidation-induced doping and etching in monolayer TMDs,<sup>28</sup> *in situ* gold chloride doping to

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modulate the photo-responsive performance,<sup>29</sup> Nb doping to create a monolayer p–n diode,<sup>30</sup> vanadium doping to fabricate specific transistors<sup>31</sup> *etc.* It is worth noting that Sn has been proven to be an effective doping candidate.

Chang *et al.* used SnS as a precursor to post-substitute CVD-grown WS<sub>2</sub> to obtain a series of Sn/W/S composite 2D materials, which enables direct selective layer doping in bilayer crystals.<sup>32</sup> Olding *et al.* utilized pulsed MOCVD for low-temperature epitaxial growth of *ortho*-eutectic SnS on hexagonal MoS<sub>2</sub> and found the preference of layer-by-layer 3D growth with prolonging purge time between alternating precursor doses, thus providing good control over the film thickness.<sup>33</sup> Fu *et al.* used a NaCl-assisted space-confined CVD method to obtain a MoS<sub>2</sub>/SnS<sub>2</sub> bilayer heterostructure and found the maximum responsivity of 9611 A W<sup>-1</sup> under visible light irradiation and the minimum response time of ~510 μs.<sup>34</sup> However, most of the current progress has focused on combining Sn with 2D materials using a two-step method to modify the lattice structure to tune the photoluminescence characteristics and electrical properties. Therefore, is it possible to incorporate Sn and TMDC in a one-step CVD process to generate a Sn-doped TMDC with unique optical properties?

In this work, we innovatively introduce anhydrous stannous chloride (SnCl<sub>2</sub>) as a dopant for monolayer MoS<sub>2</sub> growth *via* a simple and efficient one-step CVD method, and low-cost, environmentally friendly, easily scalable and high-quality Sn-doped MoS<sub>2</sub> monolayer single crystals are synthesized. The study of these systems will help us to establish a more comprehensive theoretical model of MoS<sub>2</sub> doping, develop doping materials with unique functionalities, and expand the applications of MoS<sub>2</sub> in emerging fields such as spintronics and quantum devices.

## Results and discussion

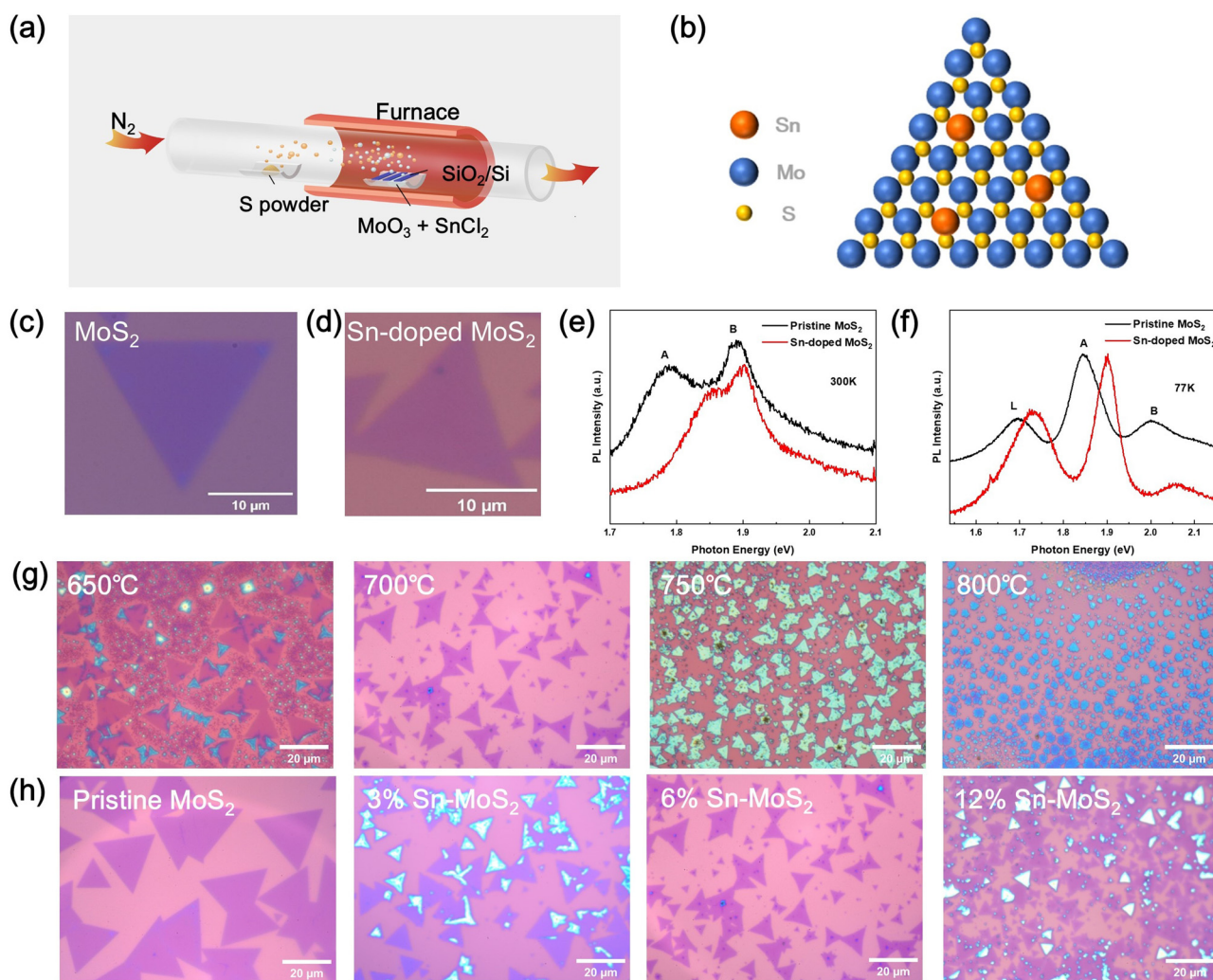
### Synthesis of Sn-doped monolayer MoS<sub>2</sub>

Molybdenum disulfide (MoS<sub>2</sub>) has a distinctive layer structure, high photoluminescence and low dark current; moreover, the bandgap can be restructured by layer thickness.<sup>35</sup> Pristine MoS<sub>2</sub> and 6 wt% SnCl<sub>2</sub>-doped monolayer MoS<sub>2</sub> (Sn-doped MoS<sub>2</sub>) were synthesized using a 2-inch tube furnace as shown in Fig. 1(a and b). The detailed synthesis procedure can be referred to the Methods section. Fig. 1(c) and (d) show the optical images of pristine and Sn-doped monolayer MoS<sub>2</sub> single crystals, both of which exhibit apparently triangular shapes, reflecting the 3-fold rotation symmetry and the high-quality single crystal nature. We first characterized the PL spectra of pristine MoS<sub>2</sub> and Sn-doped MoS<sub>2</sub> at room temperature and low temperature (77 K) as shown in Fig. 1(e) and (f), respectively, in which the pristine and Sn-doped MoS<sub>2</sub> manifest distinct emission features. At room temperature (~300 K, Fig. 1(e)), the A exciton of Sn-doped MoS<sub>2</sub> experiences a significant blueshift with an energy difference of ~60 meV from 1.783 eV to 1.856 eV, while the B exciton undergoes a relatively slight blueshift with an energy difference of ~10 meV from

1.889 eV to 1.901 eV compared with pristine MoS<sub>2</sub>. At 77 K, the linewidth of exciton peaks becomes narrow and each exciton peak can be separately resolved (Fig. 1(f)), in which both the A and B excitons of Sn-MoS<sub>2</sub> show a 60 meV blueshift compared to pristine MoS<sub>2</sub>. In addition, the peak located at ~1.728 eV is attributed to the localized defect-related exciton feature, which also presents a 20 meV blueshift. The results obviously indicate that the introduced SnCl<sub>2</sub> plays a vital role in the band structure renormalization of monolayer MoS<sub>2</sub>. Therefore, we performed a systematic study of the influence of temperature and doping concentration on the CVD growth of Sn-doped MoS<sub>2</sub>.

As shown in Fig. 1(g), 6 wt% SnCl<sub>2</sub> doped MoS<sub>2</sub> crystals were prepared at the temperatures of 650 °C, 700 °C, 750 °C and 800 °C, respectively. At 650 °C, Sn-doped MoS<sub>2</sub> crystals mainly show triangular shapes with obvious crystal boundaries and the lateral dimension of the nanosheet is ~10 μm. However, the low reaction temperature leads to relatively insufficient sulfur vapor for reaction with the MoO<sub>3</sub> vapor, which results in the incomplete growth of the crystal edges. When the temperature is increased to 700 °C, the deposited Sn-doped MoS<sub>2</sub> single crystals also show relatively uniform triangular shapes, but the nucleation density of the grown crystals is significantly reduced and the boundaries are smooth with an average lateral size up to ~13 μm. However, when the temperature is further increased to 750 °C, the nucleation density begins to increase and the growth starts to turn into the vertical direction with the increasing thickness of growth crystals. If the temperature is increased to 800 °C, the generated crystals show a cluster-like structure with prominent surface roughness, indicating too rigorous growth conditions for the MoS<sub>2</sub> single crystal. Therefore, we selected the growth temperature of 700 °C to explore the influence of SnCl<sub>2</sub> concentration on the properties of Sn-doped MoS<sub>2</sub>.

Fig. 1(h) presents the optical images of pristine MoS<sub>2</sub> and 3 wt%, 6 wt% and 12 wt% Sn-doped MoS<sub>2</sub> (percentage of precursors) prepared at a temperature of 700 °C. Both the pristine MoS<sub>2</sub> and Sn-doped MoS<sub>2</sub> display relatively uniform triangular shapes. However, with the increasing SnCl<sub>2</sub> concentration, the morphologies of MoS<sub>2</sub> experience dramatic variations. Compared with the pristine MoS<sub>2</sub>, the lateral dimensions of the crystals continuously shrink with the increase of SnCl<sub>2</sub> concentration, which might originate from the relatively huge difference of lattice constants between SnS (SnS<sub>2</sub>) and MoS<sub>2</sub>, limiting the growth of large areas of the single crystals. In addition, when the doping concentrations are 3 wt% and 12 wt%, most of the growth crystals undergo secondary growth accompanied by more Sn atoms adsorbed on the crystal surface, which might affect the overall growth efficiency and the physical properties of MoS<sub>2</sub>. Nevertheless, the crystals grown from 6 wt% SnCl<sub>2</sub> doped MoS<sub>2</sub> exhibit homogeneous surface morphologies similar to pristine MoS<sub>2</sub> with an average crystal size of ~10 μm. It can be seen that the doping concentration of SnCl<sub>2</sub> greatly imposes the growth behaviors of MoS<sub>2</sub>, thus might induce significant modulation of the crystal structure and optoelectronic properties, evidenced by the promi-



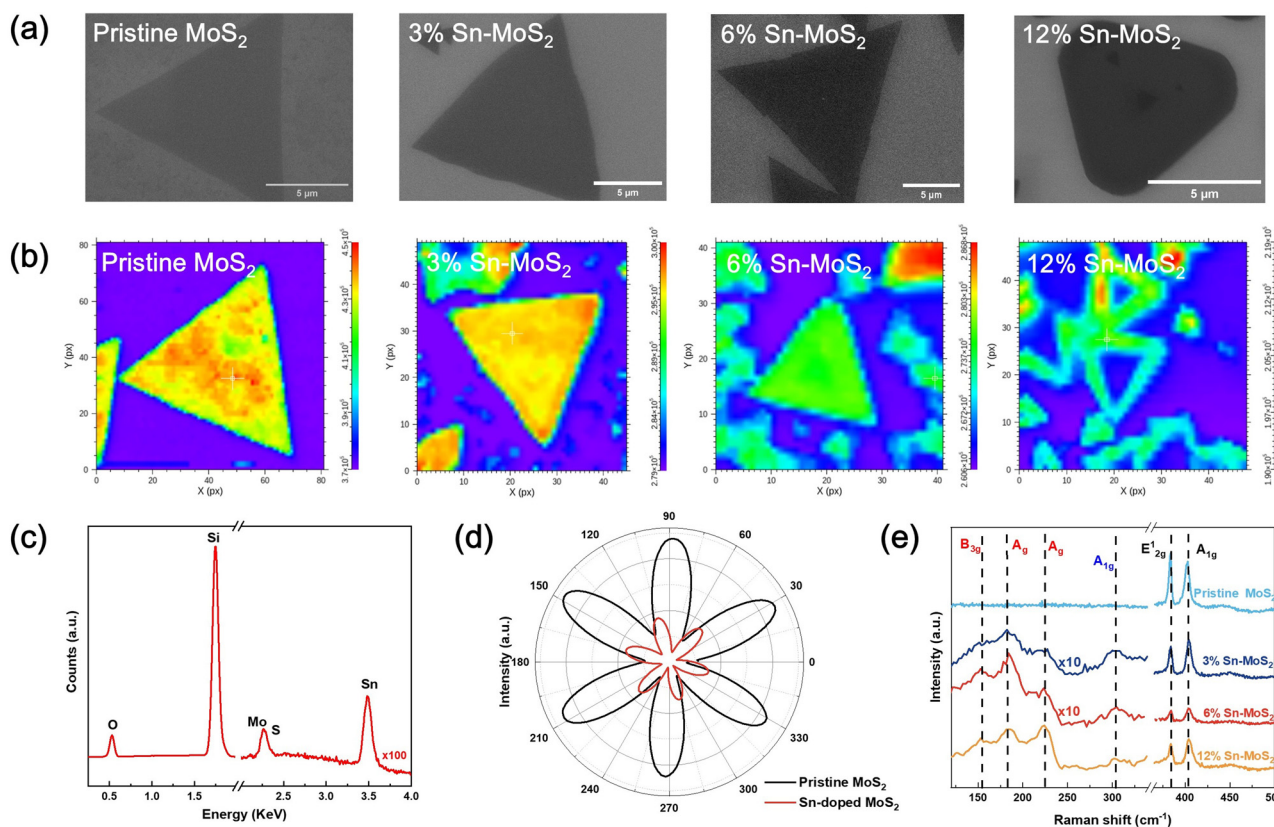
**Fig. 1** Synthesis of Sn-doped monolayer MoS<sub>2</sub> single crystals. (a) Illustration of the CVD setup for the synthesis of Sn-doped MoS<sub>2</sub>. (b) Schematic of an Sn-doped MoS<sub>2</sub> structure. (c and d) Optical images of pristine MoS<sub>2</sub> and Sn-doped MoS<sub>2</sub>, respectively. (e) PL spectra of pristine MoS<sub>2</sub> and Sn-doped MoS<sub>2</sub> at room temperature (532 nm CW laser, 100 μW). (f) PL spectra of pristine MoS<sub>2</sub> and Sn-doped MoS<sub>2</sub> at 77 K (532 nm CW laser, 100 μW). (g) Optical images of 6 wt% SnCl<sub>2</sub>-doped MoS<sub>2</sub> at the growth temperatures of 650 °C, 700 °C, 750 °C and 800 °C, respectively. (h) Optical images of pristine MoS<sub>2</sub>, 3 wt% Sn-doped MoS<sub>2</sub>, 6 wt% Sn-doped MoS<sub>2</sub> and 12 wt% Sn-doped MoS<sub>2</sub> at 700 °C.

ment blueshift of the PL emissions from different excitonic states as shown in Fig. 1(e and f). Hence, we conducted further spatial homogeneous measurements to identify the Sn-doped MoS<sub>2</sub>, including SEM-EDS, SHG, AFM, Raman, PL and broadband reflectance contrast.

### Characterization of Sn-doped MoS<sub>2</sub>

The spatial homogeneity of pristine MoS<sub>2</sub> and 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub> was identified with scanning electron microscopy (SEM) and PL mapping, respectively. As shown in Fig. 2(a), the pristine MoS<sub>2</sub> crystals have clear boundaries and smooth surfaces, which coincide with the observations of optical images. For 3 wt% Sn-doped MoS<sub>2</sub>, the boundary of the crystals changes from a straight line to an irregular convex edge, which indicates that the Sn-doping induces strong strain during the chemical vapor deposition process.

When the doping concentration is increased to 6 wt%, the boundaries of MoS<sub>2</sub> crystals become rough, which may be related to the edge growth kinetics.<sup>36,37</sup> However, when the doping concentration reaches 12 wt%, the three corners of the triangular shapes of MoS<sub>2</sub> crystals become rounded, and small nucleation centers in the center of the MoS<sub>2</sub> crystals could be observed. PL mapping images in Fig. 2(b) further demonstrate the high-quality and relatively homogeneous nature of the monolayer single crystals formed. Compared with the pristine MoS<sub>2</sub>, the 3 wt% and 6 wt% Sn-doped MoS<sub>2</sub> crystals manifest more excellent homogeneity of PL emissions across the whole sheet of flakes. However, the PL mapping image of 12 wt% Sn-doped MoS<sub>2</sub> shows PL emission concentrated at the edge but weak emission at the center part, suggesting that the high doping concentration leads to the damage of the crystals during the CVD growth. In addition, the PL emission intensity



**Fig. 2** (a) SEM images corresponding to pristine MoS<sub>2</sub> and 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub>. (b) PL mapping images corresponding to pristine MoS<sub>2</sub> and 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub>. (c) EDS spectrum of 6 wt% Sn-doped MoS<sub>2</sub>. (d) Second harmonic generation (SHG) intensity of pristine MoS<sub>2</sub> and 6 wt% Sn-doped MoS<sub>2</sub>. (e) Raman spectra of MoS<sub>2</sub> with different Sn-doping concentrations.

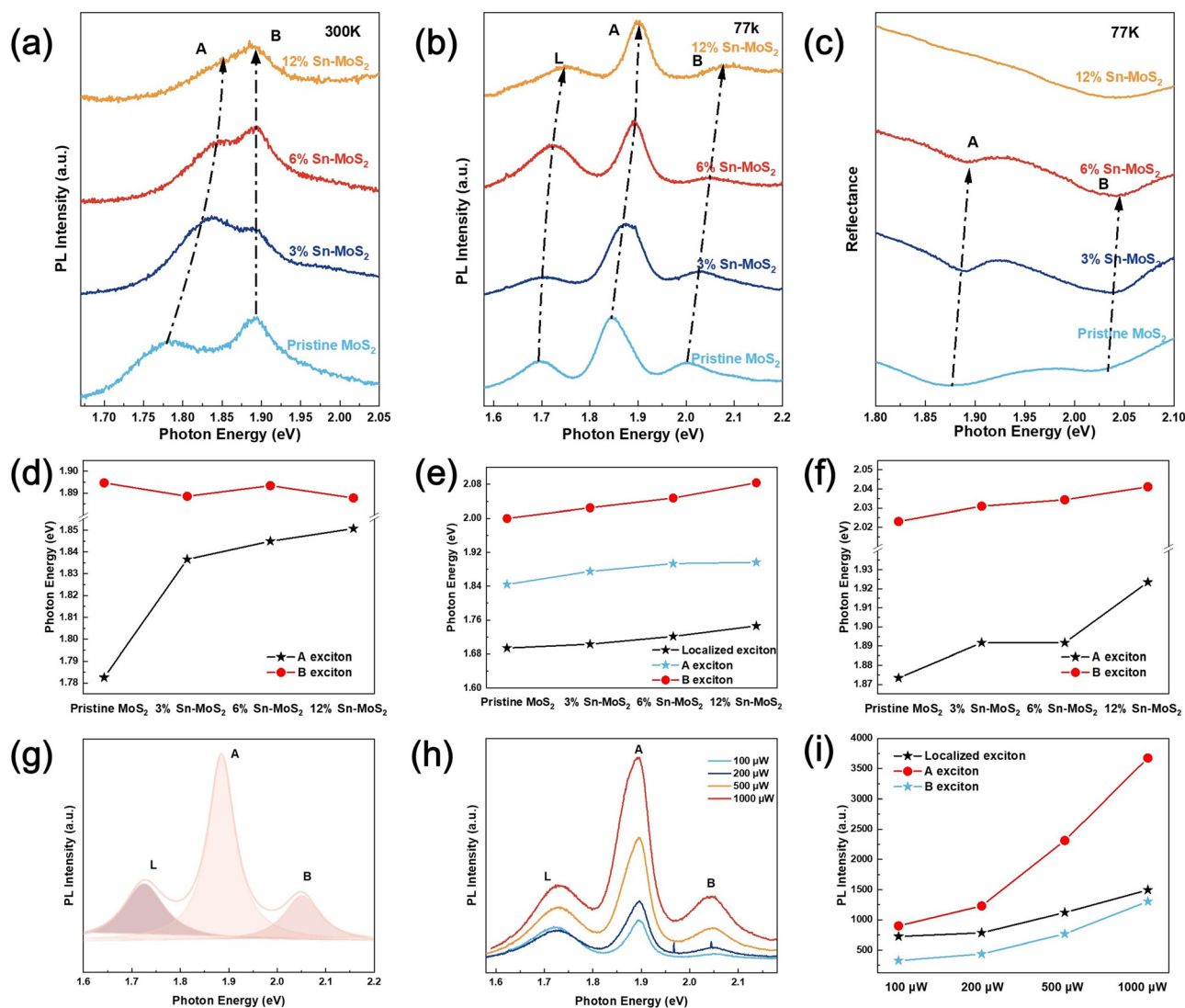
of the Sn-doped MoS<sub>2</sub> crystals experiences an attenuation trend with the increase of doping concentration.

We performed EDS analysis to confirm the doping of Sn in the Sn-doped MoS<sub>2</sub> crystal. As shown in Fig. 2(c), the Mo and S elements are located at  $\sim 2.5$  keV, and the peak of  $\sim 3.6$  keV corresponds to the Sn element, indicating the successful introduction of Sn into the monolayer MoS<sub>2</sub> nanosheet to generate the Sn-doped MoS<sub>2</sub> single crystal, and the doping concentration of the Sn element shows a gradient increase with the increase in the proportion of the precursor (the atomic percentage of Sn rises from 0.29 at% to 0.39 at%), while the total atomic percentages of Mo and S does not fluctuate significantly (Fig. S1†). In order to further probe the lattice symmetry of the Sn-doped MoS<sub>2</sub> crystals, polarization-resolved SHG measurement was performed on the pristine and 6 wt% Sn-doped MoS<sub>2</sub> crystals (Fig. 2(d)). It is shown that both the pristine MoS<sub>2</sub> and Sn-doped MoS<sub>2</sub> have a six-fold polarization symmetry of the SHG signal, which is consistent with the three rotational symmetry of a monolayer MoS<sub>2</sub> single crystal. 3 wt% and 12 wt% Sn-doped MoS<sub>2</sub> are presented in Fig. S2,† also indicating that Sn-doping does not impose the crystal symmetry of MoS<sub>2</sub>. It is worth noting that the Sn-doped MoS<sub>2</sub>'s SHG intensity shrinks compared to the pristine MoS<sub>2</sub>, which might be due to the strain induced by Sn-doping.<sup>38</sup> Raman

spectroscopy was employed to identify the Raman characteristic modes of pristine MoS<sub>2</sub> and different concentrations of SnCl<sub>2</sub>-doped MoS<sub>2</sub> single crystals (Fig. 2(e)). The pristine MoS<sub>2</sub> shows two apparent peaks located at 383.8 and 403 cm<sup>-1</sup>, ascribed to E<sup>1</sup><sub>2g</sub> and A<sub>1g</sub> characteristic phonon modes of MoS<sub>2</sub>. As for the different Sn-doped MoS<sub>2</sub> crystals, the E<sup>1</sup><sub>2g</sub> and A<sub>1g</sub> peaks exhibit characteristic blue-shifts (Fig. S3†). The subtle variations in peak separation ( $\Delta \sim 0.74$  cm<sup>-1</sup>) likely arise from competing effects of localized lattice distortion induced by dopant atoms, non-uniform charge redistribution between Mo and S atoms, and strain field heterogeneity at different doping levels. At 3 wt% doping, sparse Sn distribution induces localized lattice distortions amplified by size mismatch and synergistic interactions with point defects, leading to significant but spatially confined tensile effects. At 12 wt% doping, accumulated lattice mismatch and strain between aggregated dopants dominate, with potential phase transitions further releasing transient strain. In contrast, the 6% dosage achieves optimal balance: uniform Sn distribution minimizes local strain while compensating intrinsic defects (*e.g.*, sulfur vacancies), thereby suppressing detectable global peak shifts. In particular, four relatively weak peaks, located at 154.1, 182.4, 223.9 and 302.3 cm<sup>-1</sup>, emerge in all of the Sn-doped MoS<sub>2</sub> crystals, corresponding to the B<sub>3g</sub> and A<sub>g</sub> peaks of SnS and the A<sub>1g</sub> peak

of SnS<sub>2</sub>, which indicates that the SnCl<sub>2</sub>-dopant has decomposed and the Sn element has occupied some positions of Mo in the lattice point to form SnS and SnS<sub>2</sub> in Sn-MoS<sub>2</sub>. It is worth noting that the peak intensities increase with the increasing concentration of SnCl<sub>2</sub>. Compared with pure SnS single crystals,<sup>39</sup> the B<sub>3g</sub> and A<sub>g</sub> peaks of SnS have distinct red shifts of 4.5 and 5.7 cm<sup>-1</sup>, respectively; instead, the higher wavenumber peak of A<sub>g</sub> has a blueshift of 7.2 cm<sup>-1</sup>, which manifests that strong strain exists in the Sn-doped MoS<sub>2</sub> crystal. This originates from the relatively huge difference in lattice constants between SnS (SnS<sub>2</sub>) and MoS<sub>2</sub>. In addition, the wavenumber differences for E<sup>1</sup><sub>2g</sub> and A<sub>1g</sub> of the pristine

MoS<sub>2</sub> and 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub> are all ~19 cm<sup>-1</sup>. AFM characterization (Fig. S4†) shows some variation from the theoretical monolayer thickness (~0.65 nm), but they all remain below the bilayer threshold (~1.2 nm). The increased thickness in doped samples likely stems from three factors: (1) local lattice expansion due to Sn incorporation, (2) surface adsorbates from the doping process, and (3) slight out-of-plane distortions induced by strain. Crucially, this interpretation is strongly supported by Raman (Fig. S3†) and PL spectra (Fig. 3), which collectively verify the monolayer nature across all samples, suggesting that the nature of monolayer MoS<sub>2</sub> crystals retain a high quality and less damage after Sn-doping.



**Fig. 3** Optical properties for different concentrations of SnCl<sub>2</sub>-doping MoS<sub>2</sub>. (a) PL spectra of pristine MoS<sub>2</sub> and 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub> at room temperature (532 nm CW laser, 100 μW, 30 s). (b) PL spectra of pristine MoS<sub>2</sub> and 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub> at 77 K (532 nm CW laser, 200 μW, 30 s). (c) Reflectance spectra of pristine MoS<sub>2</sub> and 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub> at 77 K. (d) Photon energies of A excitons and B excitons as a function of doping concentration at room temperature extracted from (a). (e) Photon energies of localized defect excitons, A excitons and B excitons as a function of doping concentration at 77 K extracted from (b). (f) Absorption photon energies of A excitons and B excitons as a function of doping concentration at 77 K extracted from (c). (g) Lorentzian fitting for different excitonic states of 6 wt% Sn-doped MoS<sub>2</sub> at 77 K. (h) PL spectra of 6 wt% Sn-doped MoS<sub>2</sub> with incident power values of 100, 200, 500 and 1000 μW at 77 K. (i) Integrated PL intensities of localized defect excitons, A excitons and B excitons of 6 wt% Sn-doped MoS<sub>2</sub> as a function of incident power at 77 K.

Since Sn-doping dramatically imposes the growth behavior and the homogeneity of MoS<sub>2</sub>, it is important to further reveal the effect of Sn-doping on the electronic states, thus renormalizing the band structure of MoS<sub>2</sub>. In Fig. 3(a and b), the PL spectra of Sn-doped MoS<sub>2</sub> at room temperature and 77 K show a blueshift compared to that of pristine MoS<sub>2</sub>, in which the photon energies of A and B and localized defect exciton states continuously increase with the increasing Sn-doping concentration. The photon energy of A excitons of MoS<sub>2</sub> is blueshifted from 1.783 eV to 1.850 eV with increasing doping concentration with an energy difference of ~70 meV, whereas the effect on B excitons is not obvious at room temperature. The low-temperature environment significantly reduces the lattice vibration and thermal dissociation effects, allowing the radiative recombination process of localized excitons to dominate, thus their corresponding luminescence peaks are significantly enhanced in intensity, the spectral line widths are narrowed, and the positions of the characteristic peaks are more pronounced. Therefore, the peak-resolved spectra at 77 K provide better accuracy in extracting the photon energy blue shifts of A exciton, B exciton and localized defect exciton states at 50 meV, 80 meV and 50 meV, respectively. In addition, we also obtained the broadband reflectance contrast for pristine MoS<sub>2</sub>, 3 wt%, 6 wt%, and 12 wt% Sn-doped MoS<sub>2</sub> as shown in Fig. 3(c). It is obvious that the absorptions for A excitons and B excitons also experience a blueshift in photon energy, which further confirms that the blueshift of all exciton energies comes from the renormalization of the band structure with Sn-doping. As shown in Fig. 3(g-i), we used Lorentzian peak fitting of the PL spectra of 6 wt% Sn-doped MoS<sub>2</sub> at 77 K to extract the integrated PL emission intensities for different excitonic states as a function of excitation power. It reveals that the PL intensities of all exciton states show a superlinear enhancement as a function of the incident power. The excitation power dependent PL spectra for pristine MoS<sub>2</sub> and 3 wt% and 12 wt% Sn-doped MoS<sub>2</sub> both at room temperature and 77 K

can be found in Fig. S6 and S7 in the ESI,<sup>†</sup> which display similar superlinear enhancement behavior.

The variation of PL intensity with the doping concentration of SnCl<sub>2</sub> at room temperature and 77 K is shown in Fig. S5,<sup>†</sup> where not only the photon energy of each exciton state retains the blueshift response but also the PL intensity monotonically decreases with the increasing doping concentration, consistent with PL spectra in Fig. 3 and the PL mapping images shown in Fig. 2(b). These phenomena further prove that the Sn-doping effect remarkably imposes the electronic structure of MoS<sub>2</sub> with the enlargement of the bandgap and the possible transformation from a direct bandgap to an indirect bandgap, which will be further discussed in the following section.

## Discussion

Based on the above growth characterization and the optical properties of pristine and Sn-doped MoS<sub>2</sub>, we can derive the effect of SnCl<sub>2</sub>-doping on monolayer MoS<sub>2</sub> single crystals as follows<sup>40</sup> (Fig. 4(a)): first, the SnCl<sub>2</sub> dopant decomposes into a free Sn atom and chlorine gas upon heating to a temperature of 247 °C,<sup>41</sup> which deposits on the 300 nm SiO<sub>2</sub>/Si substrate as the nucleating point for the imminent growth of MoS<sub>2</sub>. As the temperature increases to 500 °C (S powder at a temperature of 120 °C) and the sulfur vapor starts to be conveyed to the deposition site<sup>42,43</sup> to react with the vapor of the precursor MoO<sub>3</sub>, forming Sn-doped MoS<sub>2</sub> crystals at the nucleating points of Sn atoms,<sup>44,45</sup> demonstrated by the coexistence of Raman characterization modes for SnS, SnS<sub>2</sub> and MoS<sub>2</sub> as shown in Fig. 2(e). Meanwhile, the bond length of Sn-S (2.59 Å) is longer than that of the Mo-S bond (2.41 Å),<sup>46</sup> resulting in the different lattice constants of SnS, SnS<sub>2</sub> and MoS<sub>2</sub>, which have ~15.7% lattice mismatch between SnS<sub>2</sub> and MoS<sub>2</sub> and ~16.8% between SnS and MoS<sub>2</sub>, respectively.<sup>47,48</sup> As shown in Fig. 4(b), the lattice mismatch between SnS/SnS<sub>2</sub> and MoS<sub>2</sub> gives rise to a

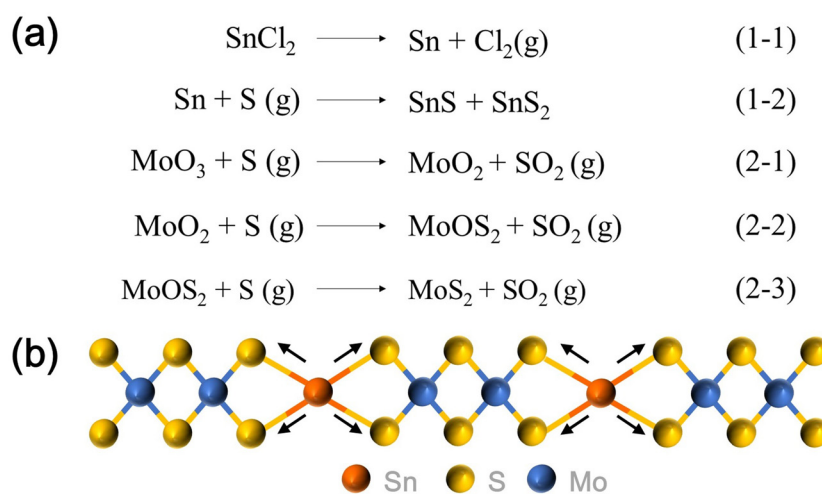


Fig. 4 (a) Reaction formulae involved in the CVD synthesis of molybdenum disulfide. (b) Schematic representation of the mechanism of Sn-doped monolayer MoS<sub>2</sub>.

lateral strain to induce a local out-of-plane curvature, which will dramatically impose the renormalization of the band structure,<sup>49</sup> consistent with previous theoretical and experimental results.<sup>46</sup> The blue shift and intensity weakening observed in the PL spectra after Sn doping of MoS<sub>2</sub> might have originated from the combined effect of the direct-to-indirect band structure transition and tensile strain.

First, it can be seen from Fig. S3† that the introduction of Sn doping leads to blue shifts of E<sub>12g</sub><sup>1</sup> and A<sub>1g</sub> in MoS<sub>2</sub>, and with 3 wt% Sn-MoS<sub>2</sub>, the sparsely distributed dopant atoms cause local lattice distortions and defect effects, leading to significant tensile strains. For 12 wt% Sn-MoS<sub>2</sub>, a large number of dopant atoms exacerbate the lattice mismatches and strain accumulations, and may even induce a phase transition or structural remodeling, further increasing the strains. This tensile strain changes the Mo–S bond length and bond angle, thus regulating its energy band structure (Fig. 4(b)). This tensile strain not only increases the bandgap but also may lead to the transformation of MoS<sub>2</sub> from a direct bandgap semiconductor to an indirect bandgap semiconductor (Fig. S8†). The direct-to-indirect band structure transition makes the electron–hole recombination require phonon participation, which significantly reduces the radiative recombination efficiency and leads to a weakening of the PL intensity. In addition, the defects introduced by Sn doping (*e.g.*, sulfur vacancies or Sn atom substitution sites) act as nonradiative recombination centers, increasing the nonradiative recombination probability of electron–hole pairs and further decreasing the PL intensity. In summary, after Sn doping of MoS<sub>2</sub>, the effects of tensile strain and defect states lead to a change in the energy band structure, which transforms MoS<sub>2</sub> from a direct bandgap to an indirect bandgap semiconductor, and thus induces a blue shift in the PL spectra and a reduction in the intensity.

## Conclusions

In summary, we have developed a new method using SnCl<sub>2</sub> as an efficient dopant to grow a Sn-doped MoS<sub>2</sub> monolayer. The Sn-doped MoS<sub>2</sub> monolayer dramatically imposes the growth behavior and the electronic state of MoS<sub>2</sub> due to the lattice mismatch between SnS (SnS<sub>2</sub>) and MoS<sub>2</sub>, resulting in the renormalization of the band structure with the enlargement of the bandgap and the possible shift from a direct bandgap to an indirect in the monolayer MoS<sub>2</sub>. The developed Sn-doping method could serve as an effective approach to tailor the band structure and explore a plethora of fascinating optical and electronic properties in 2D TMDCs, paving the way for the next generation of optoelectronic devices.

## Methods

### CVD growth

Sn-doped MoS<sub>2</sub> was synthesized by an atmospheric pressure CVD method in a single temperature tube furnace as depicted

in Fig. 1(a). A mixture of 14 mg MoO<sub>3</sub> with SnCl<sub>2</sub> powder (0.5 mg, 1 mg, 2 mg) was placed in a quartz boat. The SiO<sub>2</sub>/Si substrate was inverted onto a quartz boat and placed at the center of the tube furnace. Another quartz boat containing 120 mg of sulfur powder was placed around 16 cm upstream of the molybdenum oxide precursor. The CVD process was carried out at ambient pressure and high-purity N<sub>2</sub> was used as the carrier gas. The furnace temperature was raised to 700 °C at a rate of 14 °C min<sup>-1</sup> and held for 5 min with the carrier gas flow rate maintained at 10 sccm. Then, the furnace was rapidly cooled down to room temperature at a carrier gas flow rate of 500 sccm and Sn-doped MoS<sub>2</sub> was obtained on the SiO<sub>2</sub>/Si substrate (Fig. S9†).

### Characterization of Sn-doped MoS<sub>2</sub> monolayers

SEM was performed using an Apreo 2S model from Thermo Fisher with an accelerating voltage of 15.00 kV. Raman and PL spectra of Sn-doped MoS<sub>2</sub> were collected with an Andor spectrometer using a 532 nm CW laser and the Raman signal was calibrated from the peak of silicon (520 cm<sup>-1</sup>). PL mapping images were obtained using a 532 nm CW laser with a 10 mW power for 0.1 s. The polarization-resolved SHG was evaluated using a home-built setup with the excitation wavelength of an 810 nm femtosecond pulse laser (Chameleon Ultra II, with a pulse width of 140 fs and a repetition rate of 80 MHz). The pulse laser was focused by a 40× objective, and the focused laser spot was about 2 μm.

## Data availability

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

## Conflicts of interest

The authors declare no competing financial interest.

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