

Improved Strain Engineering of Monolayer Transition Metal Dichalcogenides via van der Waals Epitaxy on Graphene/SiC(0001)

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ABSTRACT

Engineering thermal strain is crucial for tuning the properties and functionalities of transition metal dichalcogenides (TMDs). Thermal strain arises from the thermal expansion coefficients (TEC) mismatch between TMDs and substrates, but conventional substrates often induce inhomogeneous broadening in the electronic structure mainly due to surface roughness and charged impurities. Here, we demonstrate uniform thermal strain in monolayer WSe₂ via van der Waals epitaxy on graphene/SiC(0001) substrates. Compared to WSe₂ grown on graphite, its photoluminescence peaks show a redshift and linewidth narrowing of about 30%. These results suggest that uniform tensile strain is introduced to WSe₂ due to the small TEC of SiC, and interfacial graphene suppresses the inhomogeneous broadening. Furthermore, tensile-strained monolayer MoS₂ grown on graphene/SiC exhibits enhanced catalytic activity for the hydrogen evolution reaction. Our findings highlight the potential of graphene/SiC substrate as a platform for improved strain engineering in TMDs, enabling future applications in electronics, optoelectronics, and

electrocatalysis.

KEYWORDS: transition metal dichalcogenide, graphene/SiC, van der Waals epitaxy, strain engineering, photoluminescence, hydrogen evolution reaction

MAIN TEXT

Two-dimensional transition metal dichalcogenides (TMDs) have attracted significant attention for their physical properties and electronic applications.¹⁻⁵ A key feature of TMDs is their direct bandgap in monolayer form, which becomes indirect bandgap in multilayers.^{1, 6} The direct bandgap in monolayers leads to strong photoluminescence (PL),^{1, 6, 7} making them ideal candidates for optoelectronic applications. Importantly, the PL properties of TMDs can be modulated by applying strain to their lattice. For instance, applying a tensile strain of approximately 2% to a WSe₂ crystal through mechanical bending strongly enhances the PL from the *A* exciton and narrows its linewidth from 42 meV to 24 meV at room temperature.⁸ These significant changes in PL properties are attributed to strain-induced band structure modifications, which alter exciton-phonon interactions.⁸⁻¹⁰ In addition, strain can modulate other key properties of TMDs, including bandgap,^{11, 12} carrier mobility,^{13, 14} and catalytic reactivity.^{15, 16} Thus, strain engineering is crucial for advancing the functional development of TMDs.

To date, the lattice strain to TMDs has been introduced by mechanical bending or thermal shrinkage mismatch of the substrate. The mechanical bending technique usually requires transferring TMDs onto a flexible substrate.^{8, 9} This technique is useful for investigating the physical properties of micrometer-sized samples, because of strain tunability. On the other hand, the thermal shrinkage mismatch is particularly important when TMDs are grown directly on substrates. For example, chemical vapor deposition (CVD),¹⁷⁻¹⁹ a widely used technique for growing TMDs directly on arbitrary substrates, offers an alternative approach to strain engineering. During CVD growth, the difference in thermal expansion coefficient (TEC) between the TMD and the substrate induces strain in the TMD because both materials contract at different rates during the cooling process. This method facilitates the introduction of built-in thermal strain in large-area TMD films without the need for external mechanical bending. In a notable study, Ahn *et al.* demonstrated that thermal strain in monolayer WSe₂ can be systematically tuned by choosing different substrate species for its growth, which results in varying PL peak positions associated with the bandgap modulation.¹⁹ This strain engineering via CVD is critical for optimizing the physical and chemical properties of TMDs.

A challenge in CVD-based strain engineering is that substrate surface imperfections including roughness, charged impurities, and dangling bonds typically induce inhomogeneous broadening in the

electronic structure of TMDs. For example, WS₂ monolayers grown on SiO₂ and sapphire substrates show relatively broad PL peaks, whereas sharp peaks are observed for these grown on atomically-flat graphite and hBN substrates.^{17, 18} To suppress the inhomogeneous broadening in CVD-grown strained TMDs, we focused on using graphene as an intermediate layer between TMD and substrate. In this study, we report a remarkably narrow PL linewidth in tensile-strained monolayer WSe₂ grown via van der Waals epitaxy on a graphene/SiC(0001) substrate. We found that WSe₂ on graphene/SiC exhibits the PL peaks with a redshift and linewidth narrowing of about 30% compared to that grown on conventional bulk graphite. These results suggest that WSe₂ is subjected to tensile strain due to the small TEC of SiC, even with graphene present as an interlayer. We also grew tensile-strained monolayer MoS₂ on the graphene/SiC substrate, which exhibited remarkable catalytic activity for the hydrogen evolution reaction (HER).

As illustrated in Figure 1a, we first prepared a homogeneous graphene/SiC substrate by the thermal decomposition method.²⁰⁻²³ Subsequently, WSe₂ crystals were grown on the graphene/SiC substrate by salt-assisted CVD method using a two-zone electric furnace.^{18, 24, 25} For comparison, we also grew WSe₂ crystals on bare SiC, bulk graphite, amorphous SiO₂, and sapphire substrates under the same condition (Figure S1). Figure 1b shows an optical image of triangular shaped WSe₂ crystals grown on a graphene/SiC substrate. These crystals tend to align in two opposite directions due to van der Waals (vdW) epitaxial growth on graphene surface.^{17, 18, 26, 27} Figure 1c illustrates the orientation relationship between WSe₂ and the underlying graphene layer. We note that thick multilayers of WSe₂ were grown on a bare SiC substrate (Figure S1), likely due to the difference in surface energy.²⁶ Figure 1d displays a cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the monolayer WSe₂ crystal indicated by arrows in Figure 1b (lower magnification images are provided in Figure S2). The electron incidence was parallel to the $[1\bar{1}00]_{\text{SiC}}$ direction, which is also parallel to the $[11\bar{2}0]_{\text{Gra.}}$ direction.²² The monolayer WSe₂ is uniformly formed on top of the bilayer graphene/SiC. The lattice of WSe₂ can be resolved with reduced contrast (inset), indicating an orientation relationship of $[11\bar{2}0]_{\text{WSe}_2} // [11\bar{2}0]_{\text{Gra.}} // [1\bar{1}00]_{\text{SiC}}$. This observation further supports van der Waals epitaxy of WSe₂ on graphene/SiC. The energy dispersive X-ray spectroscopy (EDS) line profiles obtained from this cross section also confirm the formation of WSe₂ on graphene/SiC. Importantly, the signal for Se was also detected at the graphene/SiC interface across the observation area, with Se distributed two-dimensionally as a bright contrast in the image. This suggests that intercalation of Se into the graphene/SiC interface occurred during the CVD process. Such intercalation phenomenon has been reported for various other elements such as H,^{28, 29} O,³⁰ S,³¹ Ga,³² and Pb,³³ which terminate interfacial Si atoms by penetrating the graphene/SiC interface. The detailed characterization of this two-dimensional Se will be reported

elsewhere.

We then examined the PL properties of the WSe₂ monolayer, as shown in Figure 1e. Interestingly, a very narrow linewidth of approximately 28 meV was observed for WSe₂ grown on the graphene/SiC substrate. To the best of our knowledge, PL linewidths as narrow as 28 meV at room temperature have not been previously reported for CVD-grown WSe₂.^{19, 24, 26, 34, 35} The peak center was located at about 1.60 eV. In contrast, monolayer WSe₂ grown on graphite exhibited a broader peak with a linewidth of approximately 42 meV, positioned at 1.63 eV. Furthermore, the peak intensity for WSe₂ on graphene/SiC was more than twice than that on bulk graphite. These results clearly demonstrate the strain-induced modulation of the electronic structure by the graphene/SiC substrate.

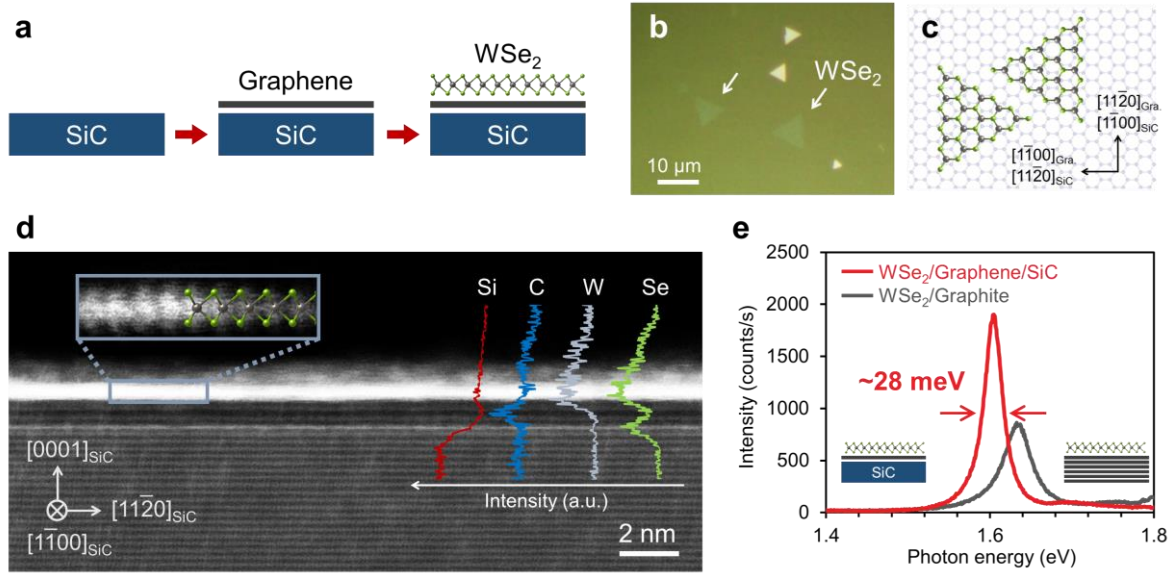


Figure 1. (a) Schematic illustration on the growth procedure of graphene and WSe₂ on a SiC substrate. (b) Optical image of WSe₂ crystals grown on graphene/SiC. (c) Crystallographic orientation relationship between WSe₂ and graphene, with the orientations of the underlying graphene and SiC indicated by arrows. (d) Cross-sectional HAADF-STEM image of the WSe₂/graphene/SiC stack, with overlaid EDS spectra for Si, C, W, and Se. The inset shows an enlarged image taken at lower contrast, where the WSe₂ lattice is visible. (e) Typical PL spectra for monolayer WSe₂ grown on graphene/SiC (red) and on graphite (gray).

To investigate the remarkable PL properties of WSe₂ grown on graphene/SiC, we conducted PL mapping measurements. Figures 2a, 2b, and 2c show the PL intensity, peak energy, and full width at half maximum (FWHM) maps obtained over a single grain of monolayer WSe₂ grown on graphene/SiC, respectively. Additionally, spectra extracted from three different points are presented in Figure 2d.

Although redshifted peaks with narrow linewidths were observed in most parts of the grain, variations in peak characteristics were evident, as shown in Figure 2d. Specifically, the peak intensity and position depend on the locations. In contrast, monolayer WSe₂ grown on graphite exhibited less variation in peak features, as shown in Figures 2e–2h. To further elucidate the PL results, plots of intensity versus energy and FWHM versus energy extracted from the map data are displayed in Figures 2i and 2j, respectively. In Figure 2j, data obtained from monolayer WSe₂ grown on SiO₂ and sapphire substrates are also plotted (see Figure S3 for their map images and spectra). Figure 2i shows a negative correlation between PL intensity and peak energy. This negative correlation was also reported in a previous study that investigated PL inhomogeneity in WSe₂, where the variation is attributed to strain differences in the WSe₂ lattice.³⁶ On the other hand, as shown in Figure 2j, the FWHM shows a positive correlation with peak energy, whereby the FWHM decreases as the peak energy decreases. Previous studies demonstrated that when WSe₂ is subjected to uniaxial or biaxial tensile strain via mechanical bending, the FWHM decreases, and a redshift occurs as the tensile strain increases, which will be explained later.^{8, 9, 37} From these observations, we conclude that the WSe₂ crystal grown on graphene/SiC has more pronounced built-in tensile strain than that on graphite and sapphire. Specifically, the typical peak position of 1.60 eV observed in WSe₂ on graphene/SiC corresponds to a tensile strain of about 0.4%, based on the discussion in Ref. 19. Furthermore, the narrow PL linewidth suggests that, at least within the laser spot size ($\sim 1 \mu\text{m}^2$), the tensile strain is uniformly applied to WSe₂ and the inhomogeneous broadening is significantly suppressed, likely due to the atomically-flat and clean surface of graphene.³⁸ A detailed discussion on the strain direction is provided in Supporting Information.

The changes in PL spectra can be understood by the strain-induced modification of the band structure of monolayer WSe₂. As schematically illustrated in Figure 2k, tensile strain induces the upshift of the *Q* valley in the conduction band and the decrease of direct band gap at the *K-K* valley.^{8, 9, 37} The former suppresses intervalley scattering of the direct *K-K* exciton, thereby enhancing the radiative transition probability. Consequently, the PL spectra exhibit a redshift, a narrowing of the linewidth, and an increase in peak intensity.

One may think that the shift of the E' mode in Raman spectrum can also be utilized to investigate the strain in WSe₂. However, the E' mode of WSe₂ on graphene/SiC exhibits nearly uniform characteristics across the grain, and its Raman shift is indistinguishable from that of WSe₂ on graphite (Figures S4 and S5). Thus, it is difficult to quantify strain using our Raman measurement system, primarily due to the limitation in wavenumber resolution (see Supporting Information for details). In contrast, the PL signal is more sensitive to strain in WSe₂ compared to the Raman signal, making it more suitable for strain evaluation. Indeed, in Refs. 19 and 36, the authors assessed the strain in WSe₂ based on the shift of the PL

154 peak rather than that of the Raman signal.^{19, 36}

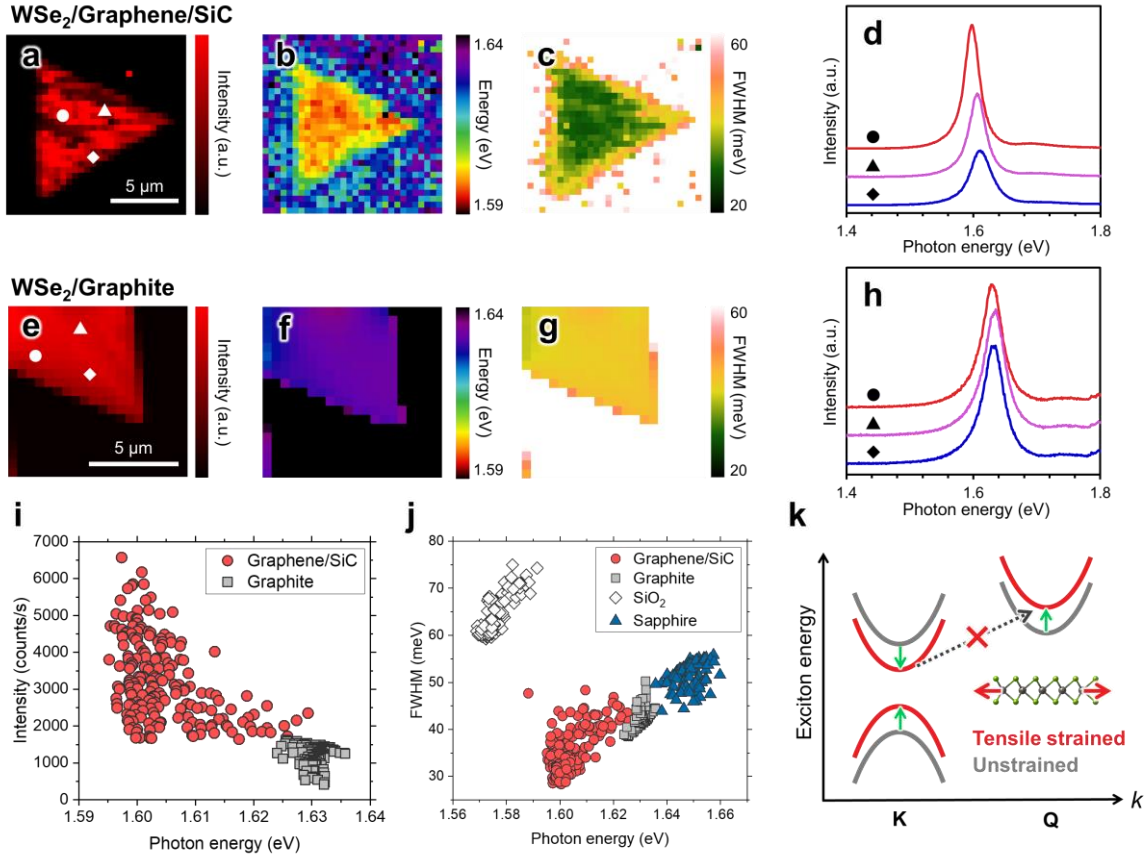


Figure 2. (a) PL intensity, (b) peak energy, and (c) peak FWHM maps of monolayer WSe₂/graphene/SiC. (d) PL spectra at three different points indicated by symbols in (a). (e) PL intensity, (f) peak energy, and (g) peak FWHM maps of monolayer WSe₂/graphite. (h) PL spectra at three different points indicated by symbols in (e). (i) Plot of PL intensity versus peak energy and (j) plot of peak FWHM versus peak energy, both extracted from the map data. For peak fitting, we basically used a single Voigt function component, except for the sample grown on the sapphire substrate, which required two components. (k) Schematic band diagram of tensile-strained and unstrained monolayer WSe₂. Tensile strain results in a narrowing of the band gap at the *K-K* valley and the reduction in intervalley scattering owing to the upshift of the conduction band at the *Q* valley.

To gain insight into the origin of the tensile strain in WSe₂ on graphene/SiC, we examined the Raman spectra of graphene. Figure 3a shows typical Raman spectra of graphene obtained before and after the CVD growth of WSe₂. For clarity, the contribution of the SiC substrate was subtracted from both spectra

(the original spectra are shown in Figure S6). In the spectrum before WSe₂ growth (gray), the FWHM of the 2D peak was 38 cm⁻¹, which is characteristic of monolayer graphene.^{23, 39, 40} Also, as indicated by the arrows, several broad peaks originating from the interfacial carbon layer (so-called zero-layer graphene (ZLG)) between graphene and SiC were observed.^{23, 29, 41} The 2D peak was positioned at 2712 cm⁻¹, blue-shifted from that of pristine graphene (~2680 cm⁻¹), suggesting that the graphene layer is compressively strained.⁴² This compressive strain is commonly explained by the TEC mismatch between graphene and SiC.⁴² Overall, these observations are consistent with the typical characteristics of monolayer graphene grown directly on SiC.^{22, 23, 42} After the CVD growth of WSe₂, notable changes occurred in the spectrum. The characteristic features of the ZLG diminished, and the FWHM of the 2D peak increased to 65 cm⁻¹, which corresponds to the formation of bilayer graphene.^{29, 39, 40} This spectral change suggests that intercalation of a foreign element into the graphene/SiC interface occurred during the CVD process, and ZLG was converted to graphene.²⁸⁻³³ In fact, as described above, the intercalation of Se and the presence of bilayer graphene were confirmed by the STEM observation in Figure 1d. Here, the 2D peak remained at 2719 cm⁻¹, indicating that the graphene layers are still compressively strained after the CVD growth, as illustrated in the inset. The persistence of compressive strain suggests a strong interaction between graphene and SiC substrate, even after the Se intercalation.

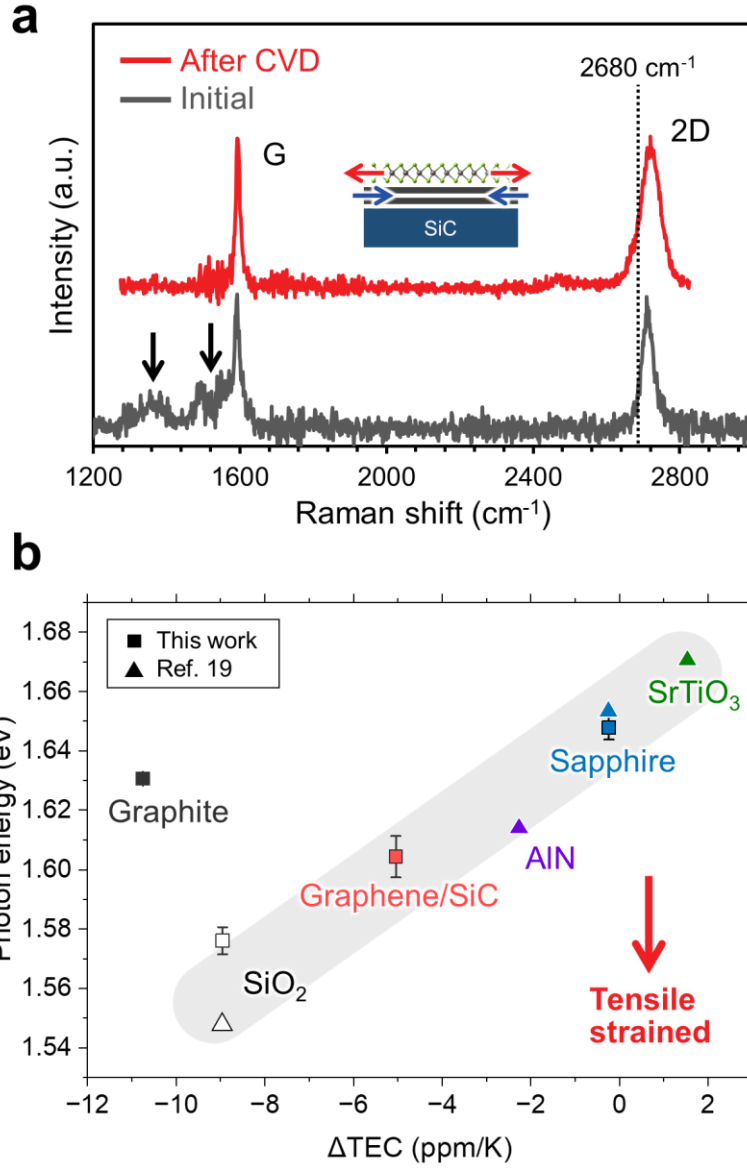


Figure 3. (a) Raman spectra of graphene before and after the CVD growth of WSe₂. For clarity, the contribution of the SiC substrate was subtracted from both spectra. The inset illustration represents the tensile strain in WSe₂ and the compressive strain in the graphene layers. (b) Relationship between the PL peak energy of monolayer WSe₂ and the TEC difference between WSe₂ and the growth substrates. Data extracted from Ref. 19 are also plotted as triangles. For WSe₂ grown on graphene/SiC, data point is plotted based on the TEC of SiC.

Based on the above results, we now discuss the origin of the tensile strain in WSe₂ grown on graphene/SiC. As mentioned previously, the built-in strain in CVD-grown WSe₂ is governed by the TEC of the underlying substrate. Figure 3b shows the relationship between the PL peak energy of WSe₂ (vertical axis) and the TEC difference between WSe₂ and the substrates (horizontal axis). In addition to the results obtained in our study, results in Ref. 19 are also plotted as triangles. The most significant tensile strain was observed on the SiO₂ substrate, as evidenced by the pronounced redshift of the PL peak. This can be attributed to a large TEC difference between WSe₂ (~9.5 ppm/K¹⁹) and SiO₂ (0.55 ppm/K¹⁹). On the other hand, since the TEC of sapphire substrate is close to that of WSe₂, little strain was introduced and the PL peak energy was close to that of unstrained WSe₂ (1.65 eV^{7, 19}). The PL peak energy and the TEC difference have therefore a linear correlation. Here, when the PL peak position on the graphene/SiC substrate is plotted based on the TEC of SiC (~4.5 ppm/K⁴³), it aligns well with this correlation. In other words, the tensile strain in WSe₂ grown on graphene/SiC can be explained by the TEC of SiC. Notably, as mentioned above, the underlying graphene layers remain under compressive strain. Therefore, we infer that, after the CVD process, graphene experienced compressive strain due to the contraction of the SiC substrate, while WSe₂ underwent tensile strain as it contracted more, owing to its larger TEC compared to SiC.

In the following, we further discuss the narrow PL linewidths in WSe₂ grown on the graphene/SiC substrate. As shown in Figure 3b, WSe₂ grown on SiO₂ experienced strong tensile strain. Given the band modulation induced by this strain, a significant narrowing of the PL linewidth would be expected in this sample. However, the actual PL linewidths were more than 60 meV, as shown in Figure 2j. In contrast, WSe₂ grown on graphene/SiC exhibited a much narrower linewidth of about 28 meV, despite experiencing less strain than the sample on SiO₂. These results suggest that graphene with the atomically smooth surface and negligible charged impurities effectively suppressed the inhomogeneous broadening of the PL peak.^{17, 18} This highlights that the flatness and cleanliness of the substrate surface are other critical factors in the CVD-based strain engineering.

The tensile strain observed in WSe₂ on graphene/SiC suggests the presence of an interaction between them. However, little strain was introduced in WSe₂ grown on graphite flakes, despite the large TEC difference (Figure 3b). As reported previously,^{17, 18} this observation indicates that the interaction between WSe₂ and graphite is minimal, likely due to the chemical inertness of the highly crystalline graphite surface. One possible origin of the interaction between WSe₂ and graphene/SiC is the chemical bond formation between dangling bonds at the WSe₂ edges and the underlying graphene or SiC (see Supporting Information for a detailed discussion, including Figures S7 and S8). Further investigation into the origin of the strain will be the subject of future work.

The characteristic thermal strain in TMD grown on the graphene/SiC substrate can potentially affect properties other than PL. We thus investigated the catalytic activity for the HER in monolayer MoS₂ grown on graphene/SiC using high-resolution scanning electrochemical cell microscopy (SECCM).⁴⁴ MoS₂ was chosen due to its particularly high catalytic activity among various TMDs.⁴⁵ We also characterized monolayer MoS₂ grown on graphene/SiC and confirmed the introduction of tensile strain (see Figures S9–S12). In contrast to WSe₂, the PL peak of MoS₂ on graphene/SiC exhibited a broadening of linewidth along with a redshift (Figure S11). This opposite trend is due to the band structure of MoS₂, where the intervalley scattering becomes more pronounced with increasing tensile strain.^{9, 37} The observed tensile strain in MoS₂ can similarly be explained by the same rationale as for WSe₂, where the strain arises from the relatively large TEC of MoS₂ (~7.5 ppm/K⁴⁶) compared to that of SiC (~4.5 ppm/K⁴³).

Figures 4a and 4b show typical HER current mapping images for monolayer MoS₂ grown on graphene/SiC and graphite, respectively. Notably, MoS₂ on graphene/SiC exhibited exceptionally high catalytic activity near the edges of the grain (see also Figure S13). Figure 4c shows current profiles across the MoS₂ grains, where the current around the edges of MoS₂ on graphene/SiC (red) is an order of magnitude higher than that from the edges of MoS₂ on graphite (blue). Also, the broad distribution of active sites near the edges of MoS₂/graphene/SiC is evident. Figures 4d and 4e display overpotential and Tafel slope at various positions, estimated from linear sweep voltammetry. The overpotential at 10 mA/cm² and the Tafel slope at the edge of MoS₂ on graphene/SiC (red) reach 550 mV and 124 mV/dec, respectively. On the other hand, for the edge of MoS₂ on graphite (blue), these values were 570 mV and 153 mV/dec, respectively. The lower overpotential and smaller Tafel slope at the edge of MoS₂/graphene/SiC indicate better catalytic performance.

It is well known that the edges of MoS₂ exhibit high HER activity,^{44, 45} as confirmed by the current mapping image of MoS₂ on graphite (Figure 4b). However, in the MoS₂/graphene/SiC sample, active sites are more broadly distributed near the edges (Figure 4a). According to a previous study, in addition to the presence of defects, band modulation induced by tensile strain further enhances the catalytic activity of MoS₂.¹⁵ Therefore, the built-in tensile strain in MoS₂ grown on graphene/SiC may contribute to its enhanced catalytic performance. Another possibility is that the strain facilitated the formation of defects in MoS₂, increasing the number of active sites.¹⁶ A more detailed investigation into the distribution of defects and strain is necessary to fully elucidate the origin of the high HER activity. Overall, these results further support the versatility of the graphene/SiC substrate for the growth and strain engineering of TMDs.

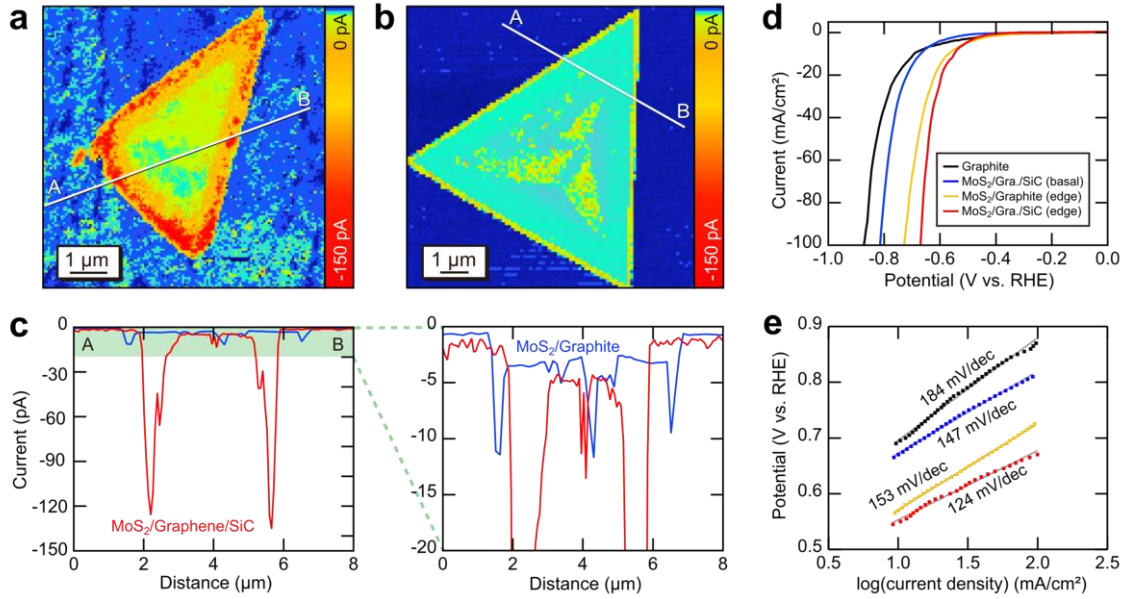


Figure 4. HER current mapping images of monolayer MoS₂ grown on (a) graphene/SiC and (b) graphite, taken at applied potentials of -0.84 V and -0.79 V versus reversible hydrogen electrode (RHE), respectively. (c) Electrochemical current profiles along the white lines in (a) and (b), highlighting the distinct current values for the MoS₂/graphene/SiC sample. (d) Overpotential and (e) Tafel slope for graphite (black), basal plane of MoS₂ on graphene/SiC (yellow), edge of MoS₂ on graphite (blue), and edge of MoS₂ on graphene/SiC (red).

In summary, we have demonstrated the potential of graphene/SiC substrate for improved strain engineering in TMDs. We successfully introduced uniform thermal strain in monolayer WSe₂ using the atomically-flat graphene interlayer between WSe₂ and SiC. The synthetic WSe₂ exhibited a significant redshift in PL peak and a narrow linewidth of about 28 meV, highlighting the ability of graphene to suppress the inhomogeneous broadening caused by the substrate surface. Furthermore, monolayer MoS₂ grown on graphene/SiC showed enhanced HER activity, showcasing the versatility of this substrate for applications beyond optoelectronics. These results underline the importance of substrate engineering in achieving both strain uniformity and improved functional properties in TMDs. Our findings provide valuable insights into the role of substrate surface and TEC mismatch in strain engineering, and show that graphene/SiC can overcome the limitations posed by conventional substrates. Our strategy can be extended to other 2D material/substrate systems, offering a general platform for strain engineering via interface modulation. As a future direction, studying the exciton dynamics of strained WSe₂ is of considerable interest, but the rapid non-radiative relaxation induced by graphene limits such investigation. Introducing

an atomically-thin insulating interlayer, such as hBN, may help overcome this challenge and allow clearer observation of exciton behavior under controlled strain conditions.

SUPPORTING INFORMATION

Experimental details; Supplementary notes on the strain direction in monolayer WSe₂, the limitation of wavenumber resolution in Raman spectroscopy, the origin of the interaction between TMDs and graphene/SiC substrate, and the effect of the step-terrace structure and graphene layer on the PL properties of WSe₂; Optical images of WSe₂ crystals grown on graphene/SiC, graphite, bare SiC, SiO₂, and sapphire substrates; Cross-sectional STEM images of WSe₂/graphene/SiC as well as in-plane view of the WSe₂ lattice; PL map and spectra obtained for monolayer WSe₂ grown on SiO₂ and sapphire substrates; E' Raman map and spectra for monolayer WSe₂ grown on graphene/SiC; E' Raman spectra for monolayer WSe₂ grown on graphene/SiC, graphite, SiO₂, and sapphire substrates; Raw Raman spectra of graphene/SiC; AFM topography images and height profiles for WSe₂ grown on graphene/SiC; PL map and graphene 2D FWHM map for a WSe₂/graphene/SiC sample; Optical images of MoS₂ crystals grown on graphene/SiC and graphite substrates; AFM topography images and height profiles for MoS₂ grown on graphene/SiC; PL spectra and strain analysis for monolayer MoS₂ grown on graphene/SiC; Raman spectra and strain analysis for monolayer MoS₂ grown on graphene/SiC; HER current mapping images for various monolayer MoS₂ grains grown on graphene/SiC.

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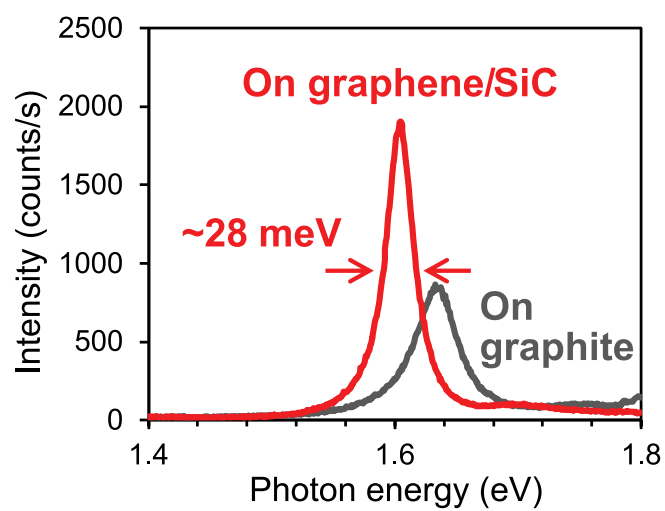
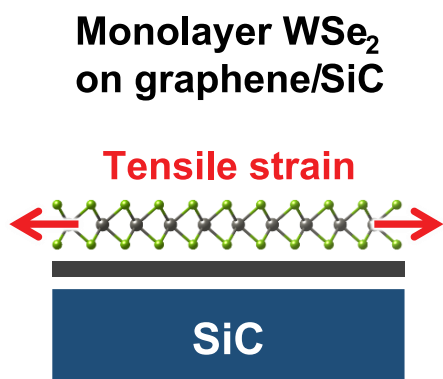
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