Lattice strain effects on the optical properties of MoS$_2$ nanosheets

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"Strain engineering" in functional materials has been widely explored to tailor the physical properties of electronic materials and improve their electrical and/or optical properties. Here, we exploit both in plane and out of plane uniaxial tensile strains in MoS$_2$ to modulate its band gap and engineer its optical properties. We utilize X-ray diffraction and cross-sectional transmission electron microscopy to quantify the strains in the as-synthesized MoS$_2$ nanosheets and apply measured shifts of Raman-active modes to confirm lattice strain modification of both the out-of-plane and in-plane phonon vibrations of the MoS$_2$ nanosheets. The induced band gap evolution due to in-plane and out-of-plane tensile stresses is validated by photoluminescence (PL) measurements, promising a potential route for unprecedented manipulation of the physical, electrical and optical properties of MoS$_2$.

Transition metal dichalcogenides, such as MoS$_2$, have attracted considerable attention for their potential advantages in catalysis$^{14-17}$, transistors$^{18-20}$, batteries$^{21-22}$, gas sensors$^{23}$, photodetectors$^{24}$, and other optoelectronic devices$^{25}$. Bulk crystals of MoS$_2$, with an indirect band-gap of 1.3 eV, possess strong intra-layer sulfur-metal covalent bonds where the metal atoms are sandwiched by sulfur atoms but their interlayer stacking is weakly supported by van der Waals forces$^{26}$. Single-layer MoS$_2$, however, shows distinctly promising semiconductive properties with a direct band-gap of 1.9 eV$^{27}$, exhibiting strong photoluminescence$^{28}$, high in-plane carrier mobility (200–500 cm$^2$/V·s)$^{29}$ and robust mechanical properties$^{30}$. Interestingly, such indirect-to-direct band gap transition from the bulk form to the monolayer form due to quantum confinement leads to strong enhancement of photoluminescence (PL) from MoS$_2$$^{14}$, therefore creating a series of promising applications for two-dimensional (2D) material-based optoelectronics$^{31-34}$. This is afforded through the large yield of monolayer MoS$_2$ synthesis by chemical vapor deposition (CVD) that has been utilized to build up atomically thin optoelectronic devices$^{35-37}$. Moreover, it would be desirable to achieve a wider optical spectral response if the band gap of layered MoS$_2$ can be systematically controlled. "Strain engineering" has been shown to exert a profound impact on the properties of MoS$_2$$^{38-40}$. Since MoS$_2$ can endure large strains before breaking$^{41,42}$, tuning the MoS$_2$ band gap by lattice strain becomes an important strategy to enhance the performance of nanodevices made from MoS$_2$. In this work, we systematically investigated the effects of in-plane and out-of-plane tensile strains of MoS$_2$ nanosheets and explored the associated strain engineering of their band gap. The lattice strains in as-synthesized MoS$_2$ nanosheets were quantified using the X-ray diffraction (XRD), cross-sectional high-resolution transmission electron microscope (TEM) analysis and Raman spectroscopy. The band gap evolution of MoS$_2$ nanosheets induced by the strains was validated by PL measurements, which is qualitatively consistent with our theoretical analysis using density functional theory (DFT) calculations.

The phase of MoS$_2$ nanosheets synthesized using a hydrothermal method (Fig. S1) is confirmed to be a hexagonal structure of MoS$_2$ with space group P 63/mmc as indexed by JCPDF card number 37-1492. Particularly, the peak of (002) plane (c-axis) shifts to a smaller angle while the peak of (100) plane shifts to a larger angle, indicating that there is an expansion along [001] direction and in-plane compression in the as-synthesized MoS$_2$ nanosheets. The atomic plane spacing in the MoS$_2$ nanosheets can be calculated from the XRD pattern using the Bragg equation$^{26}$:

$$2d \sin \theta = n \lambda$$

(1)
where \( d \) is the atomic plane spacing, \( \theta \) is the Bragg scattering angle, \( n \) is the diffraction order and \( \lambda \) is the wavelength of incident X-ray. Using Equation (1), the XRD result showed a calculated interlayer spacing ((002) Miller indices spacing) of 6.1924 Å for the as-synthesized MoS\(_2\) nanosheets that is larger compared to that of bulk MoS\(_2\) (6.1554 Å)\(^{27}\). The observed difference in the (002) plane spacing causes a uniaxial tensile strain along [001] direction in the as-synthesized MoS\(_2\) nanosheets. By tuning the PH value in the reaction solution, the lattice strains in as-synthesized MoS\(_2\) nanosheets could be modified (Supporting Information, Figure S2). The morphology of the as-synthesized MoS\(_2\) nanosheets was characterized by scanning electron microscopy (SEM), showing that the 2D MoS\(_2\) nanosheets rolled up and thus formed a three-dimensional (3D) network with highly curved walls (Figure S3). From the high resolution TEM (HRTEM) image of the basal plane of the as-synthesized MoS\(_2\) nanosheets shown in Figure 1b, we can see hexagonal rings of alternative molybdenum and sulphur atoms in each unit, meaning that the MoS\(_2\) nanosheets are of high quality with defect-free atomic lattices. The corresponding zone axis is along [001] direction as confirmed using the fast Fourier transform (FFT) shown in the inset of Figure 1b. We also applied HRTEM to image the cross-section of the MoS\(_2\) nanosheets (Figure 1c). Typical nanosheets consist of 5, 6, 9, and 10 layers, from which the interlayer spacing can be measured accordingly (Supporting Information). The average of the measured interlayer spacing is 6.2282 Å in the as-synthesized MoS\(_2\) nanosheets (Figure 1d), which is about 1% larger than the bulk interlayer spacing (6.1554 Å) indicating an out-of-plane uniaxial tensile strain along [001] direction, consistent with the XRD results discussed above. These results confirm that the as-synthesized MoS\(_2\) nanosheets contain an out-of-plane uniaxial tensile strain and an in-plane biaxial compressive strain as depicted in Figure 1e.

Figure 2a shows Raman spectra of as-synthesized MoS\(_2\) nanosheets (grown from pH = 7 and pH \( < 7 \) solutions, respectively), strain-partially released MoS\(_2\) nanosheets (grown at pH \( < 7 \) and transferred by solution method to SiO\(_2\)/Si substrate, see supporting information), bulk MoS\(_2\) (SPI Supplies) and monolayer MoS\(_2\) (CVD growth on SiO\(_2\)/Si substrate). Compared with bulk MoS\(_2\), there is a red shift of A\(_{1g}\) mode observed in the monolayer MoS\(_2\) with \( \Delta \omega = 3 \) cm\(^{-1}\), and for E\(_{1g}\) mode, a blue shift (\( \Delta \omega = 2 \) cm\(^{-1}\)) exists in the monolayer MoS\(_2\). In the Raman spectra of MoS\(_2\) nanosheets grown from pH = 7 solution and PH \( < 7 \) solution, only red shifts for both E\(_{1g}\) and A\(_{1g}\) modes were observed, compared to bulk MoS\(_2\). Compared to as-synthesized MoS\(_2\) nanosheets, blue shifts of both E\(_{1g}\) and A\(_{1g}\) modes in the strain-released MoS\(_2\) nanosheets were observed. Figure 2b shows the frequencies of E\(_{1g}\) and A\(_{1g}\) modes of MoS\(_2\) nanosheets extracted from Figure 2a. The largest red shifts of both
E\textsubscript{1g} and A\textsubscript{1g} modes are observed in the MoS\textsubscript{2} nanosheets grown from PH = 7 solution. The strain-caused band-gap shift was also validated as shown in Figure 2c where PL spectra are plotted for bulk MoS\textsubscript{2}, monolayer MoS\textsubscript{2}, strain-partially released MoS\textsubscript{2} nanosheets and as-synthesized MoS\textsubscript{2} nanosheets. From the PL spectra of the as-synthesized MoS\textsubscript{2} nanosheets, two peaks at 693.9 nm (1.787 eV) (in blue) and 684 nm (1.813 eV) (in pink) were clearly observed, corresponding to a direct transition between the top valence band K point and the bottom conduction K points in the Brillouin zone\textsuperscript{14}. In comparison with MoS\textsubscript{2} nanosheets grown from PH = 7 solution, a blue shift (26 meV) of the direct band transition was observed in MoS\textsubscript{2} nanosheets grown from PH = 5 solution synthesized MoS\textsubscript{2} nanosheets, while a red shift (21 meV) of the direct band transition was observed in the strain-partially released MoS\textsubscript{2} nanosheets. In monolayer MoS\textsubscript{2}, most of the excited electrons and holes recombine with each other through direct band-to-band transition at the K point in the Brillouin zone, leading to strong photoluminescence near 1.87 eV. A weak feature was also observed at 613 nm (2.023 eV as noted) due to direct-gap hot luminescence\textsuperscript{14}. For bulk MoS\textsubscript{2}, an indirect band gap transition at 924.7 nm (1.341 eV) was observed, which is a transition between the top valence band \Gamma point and the bottom conduction band halfway between \Gamma and K points in the Brillouin zone\textsuperscript{29}. The band-gap shifts due to different strain effects in MoS\textsubscript{2} that were extracted from Figure 2c are shown in Figure 2d.

To further illustrate the band-gap modulation by strain, we investigated the influence of in-plane uniaxial tensile strain on the phonon spectra and the band gap of exfoliated MoS\textsubscript{2} nanosheets. The exfoliated MoS\textsubscript{2} nanosheets were transferred onto a flexible substrate (details in Supporting Information). The solidification process for the polydimethylsiloxane (PDMS) flexible substrate caused the exfoliated MoS\textsubscript{2} nanosheets to strongly adhere to the surface of PDMS (Figure S7). Upon bending the PDMS substrate, an in-plane uniaxial tensile strain is exerted at the top-most plane containing the exfoliated MoS\textsubscript{2} nanosheets. As shown in Figure 3a, the applied strain significantly causes blue shifts in A\textsubscript{1g} and E\textsubscript{1g} modes of the exfoliated MoS\textsubscript{2} nanosheets. Assuming that the bending induced strain is entirely transferred to exfoliated MoS\textsubscript{2} nanosheets, we estimated the in-plane uniaxial tensile strain \( \varepsilon \) existing in the exfoliated MoS\textsubscript{2} nanosheets by calculating the ratio of the PDMS substrate thickness \( d \) to twice the radius of the curvature \( R \) as \( \varepsilon = d/2R \). Figure 3b shows the frequencies of E\textsubscript{1g} and A\textsubscript{1g} modes of the exfoliated MoS\textsubscript{2} nanosheets with different local strains extracted from Figure 3a. In Figure 3c prior to bending the PDMS substrate, the exfoliated MoS\textsubscript{2} nanosheets exhibit a PL peak at 880.1 nm (1.409 eV), which is similar to the indirect band transition in bulk MoS\textsubscript{2}. We also observed...
another direct band transition PL peak at 695.1 nm (1.784 eV), corresponding to the same direct band-to-band transition as observed in as-synthesized MoS2 nanosheets. With the in-plane uniaxial tensile strain, red shifts of direct band-to-band transition and indirect band transition are observed by bending the PMDS substrate. Figure 3d shows the PL peaks of the exfoliated MoS2 nanosheets with different local strains extracted from Figure 3c.

MoS2 consists of weak bonds between different S-Mo-S layers as illustrated in the stacked structure of Figure 4a. Each layer is electrically neutral, such that nature of the forces between adjacent layers is van der Waals’ type31. The van der Waals forces between S atoms in adjacent layers dominates the interlayer forces. Figure 4b shows atomic displacements of the four Raman-active modes. In the out-of-plane A1g mode, the restoring force is primarily due to interlayer van der Waals interaction32. With increasing the number of layers, the additional “spring” between S atoms in neighboring layers enhances the restoring force, resulting in an increase of the A1g mode frequency. The in-plane E2g mode is a symmetric mode, which vibrates out of phase as sketched in Figure 4b. The presence of the interlayer interactions can also increase the effective restoring force acting on the basal plane atoms33–35. It has been demonstrated that in bulk graphite, this kind of inter-layer interactions affect the intra-layer bonding and stiffen the in-plane lattice vibrations34. Similarly, with an increase of number of layers in MoS2, there is an increase in the frequency of the in-plane E2g mode. Compared to the Raman spectrum of bulk MoS2, red shifts are observed for both A1g and E2g modes of the as-synthesized MoS2 nanosheets. As characterized above, there is a uniaxial tensile strain along [001] direction in the as-synthesized MoS2 nanosheets grown from PH7 solution. The out of plane uniaxial tensile strain weakens the interlayer interactions, leading to a decrease in frequencies of both A1g and E2g modes.

In-plane uniaxial tensile strain (%)

In-plane uniaxial tensile strain (%)

Figure 3 | (a) Raman spectra of the exfoliated MoS2 nanosheets on PDMS flexible substrate. The insets in (a) show the schematic illustrations of the exfoliated MoS2 nanosheets on flexible substrate undergoing strain effect. The in-plane uniaxial tensile strain was introduced by bending the PDMS flexible substrate. (b) The frequencies of E2g and A1g modes extracted from (a). The Raman peak shift error bar indicates the spectrometer resolution. (c) The PL spectra of exfoliated MoS2 nanosheets on 0% (in black), 0.47% (in red), 1.21% (in blue) in-plane uniaxial tensile strain. (d) The PL peaks of exfoliated MoS2 nanosheets on flexible substrate extracted from (c). The band-gap is decreases by an increase of in-plane uniaxial tensile strain.
morphology similar to broken-bamboos (Figure S8, Supporting Information). Note that the increase in frequency of the $A_{1g}$ mode from the monolayer to the bulk MoS$_2$ is 3 cm$^{-1}$. One might expect that the additional interlayer van der Waals interactions should raise the frequency of $E_{12g}$ mode with an increase of number of layers. However, according to our experimental results shown in Figure 2a, the $E_{12g}$ mode in bulk MoS$_2$ has a lower frequency ($\sim 2$ cm$^{-1}$) than in monolayer MoS$_2$. This frequency decrease of the $E_{12g}$ mode is possibly due to the long range Coulomb interactions from the coupled dipoles induced from Mo-S bonds. The Coulomb interactions tend to decrease the frequencies of both $E_{12g}$ and $E_{11u}$ (TO) modes from the coupled dipoles induced from Mo-S bonds. The Coulomb interactions dominate the Raman peak shifts. In this case, an in-plane tensile strain effect can lead to a red shift in Raman peaks as reported by Conley et al., resulting from the increase of the Coulomb interactions. In monolayer or few layered samples, the interlayer interactions become stronger and surpass the Coulomb interactions. In fewer layers samples, the Coulomb interactions dominate the Raman peak shifts. In this case, an in-plane tensile strain effect can lead to a red shift in Raman peaks. The in-plane uniaxial tensile strain can enhance the interlayer interactions in the exfoliated MoS$_2$ nanosheets, leading to stronger in-plane and out-of-plane effective restoring forces acting on the atoms. Therefore, higher frequencies of $A_{1g}$ and $E_{12g}$ modes are observed in the exfoliated MoS$_2$ nanosheets with an in-plane uniaxial tensile strain.

It has been established that the energy states of the valence band and conduction band mainly originate from the 3p orbital of S atoms and 4d orbital of Mo atoms. The interatomic distance change due to the strain effect can lead to a different superposition of those atomic orbitals. The variations in the overlap between the 3p orbital of S and 4d orbital of Mo cause shifts in the energy states of the valence band and conduction band. The presence of the lattice strains therefore modifies the overlap between the S orbital and the Mo orbital, which results in an energy shift in the band gap. The presence of in-plane uniaxial tensile strain, the direct band gap is tailored by a rate of $\sim 35$ meV per 1%, while the indirect band gap is less sensitive to this tensile strain. The strain is employed to tailor the band gap by modifying the curvature of the bands, reflecting in a change in the effective masses of electrons and holes. For MoS$_2$, the location shift of conduction band extremum generally occurs for much smaller strain than the location shift of the valence band extremum. Therefore, the strain-induced change in the effective mass of the electron in the conduction band extremum halfway between $\Gamma$ and K points in the Brillouin zone can reflect the indirect bang-gap evolution of MoS$_2$. As subjected to in-plane uniaxial tensile strain, the effective mass of
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Acknowledgments

This work was supported by National Natural Science Foundation of China (NSFC) (21373196), the Recruitment Program of Global Experts, the Fundamental Research Funds for the Central Universities (WK2060140014, WK2340000050), and a faculty start-up grant for S.A.D. at the University of California San Diego.

Author contributions

B.X. and J.Z. initiated the study. B.X. designed the experiment. L.Y., M.S. and S.Z. performed the experiments. X.C. and K.W. carried on theoretical calculations. B.X., J.Z., S.D. and I.F. analyzed the data. B.X., L.Y., J.Z., S.D. and L.F. prepared the manuscript. All the authors contributed to discussions of the project.
