Experimental Demonstration of Continuous Electronic Structure Tuning via Strain in Atomically Thin MoS$_2$

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Abstract: We demonstrate the continuous tuning of the electronic structure of atomically thin MoS$_2$ on flexible substrates by applying a uniaxial tensile strain. A redshift at a rate of $\sim$70 meV per percent applied strain for direct gap transitions, and at a rate 1.6 times larger for indirect gap transitions, has been determined by absorption and photoluminescence spectroscopy. Our result, in excellent agreement with first principles calculations, demonstrates the potential of two-dimensional crystals for applications in flexible electronics and optoelectronics.

Keywords: Transition metal dichalcogenide, strain, absorption, photoluminescence, second harmonic generation, crystallographic orientation

The ability to continuously tune a material’s properties is one of the most unique features of two-dimensional (2D) crystals. Because of their atomic thickness, the electronic and optical properties of these materials are highly sensitive to external perturbations. The 2D atomic membranes are also known as “ultrathin materials” with high elasticity and Young’s modulus. They can even be strained to the intrinsic limit of $\sim$25%, as recently demonstrated in both monolayer graphene and MoS$_2$. The elastic strain field has thus been proposed as an effective approach for continuous band structure tuning in 2D crystals.

The strain effect on the electronic and vibrational properties of graphene has been extensively investigated. Noneffect of the high symmetry of the graphene honeycomb structure, makes band gap opening by strain difficult. In contrast, atomically thin MoS$_2$, a semiconducting transition metal dichalcogenide (TMD) with lower symmetry, offers an excellent opportunity for band structure tuning via strain engineering. Monolayer MoS$_2$ consists of hexagonal planes of S and Mo atoms in a trigonal prismatic structure. Several distinctive electronic and optical properties including a crossover from an indirect gap to a direct gap in the limit of monolayer thickness, strong excitonic effects, and the possibility of full optical control of the valley and spin occupation have been recently demonstrated in this material. The observed changes in the nature of the band gap and its size as a function of layer thickness are a direct consequence of the changes in orbital interactions along the out-of-plane direction. This result also suggests that strain can be similarly employed to tune the in-plane orbital interactions, thus affecting the electronic structures in 2D MoS$_2$.

Furthermore, since the direct gap is only slightly lower in energy compared to the indirect gap in monolayer MoS$_2$, relatively small tensile strains are expected to be adequate to cause a direct to an indirect gap transition ($\sim$2% uniaxial strain) and even a semiconductor-to-metal transition ($\sim$10% biaxial strain).

A great number of first principles calculations have been recently reported on the effect of strain on the electronic, vibrational, and chemical properties of 2D MoS$_2$ and other semiconducting TMDs. Although the details and magnitude of the predicted effect depend on the level of approximations involved, these calculations all predict a redshift of the gap energy with tensile strain. This result can be qualitatively understood as a result of reduced orbital overlap and hybridization due to weakened atomic bonds. The calculations also show the possibility of reducing the effective carrier masses by tensile strain, which can be explored to improve the carrier mobility and the transport characteristics. While the strain effect on the vibrational properties of 2D semiconducting TMDs has been studied experimentally, an experimental study of the strain dependence of their electronic properties, however, remains unavailable.

In this Letter, we report a systematic experimental study of the electronic structure as a function of strain in both monolayer and bilayer MoS$_2$. A uniaxial tensile strain was applied to the samples using a cantilever device, and the strain dependence of
their electronic structure was investigated by optical absorption and photoluminescence (PL) spectroscopy. Under relatively small strains, a redshift of \( \sim 70 \) meV/% strain was observed for the direct-gap excitons for both mono- and bilayer MoS\(_2\), and a slightly larger (\( \sim 1.6 \) times) redshift rate was observed for the indirect-gap transitions in bilayer MoS\(_2\). These results are in excellent agreement with first principles calculations.\(^{32-42}\) Furthermore, no dependence of the effect on strains applied along the zigzag and armchair crystallographic orientation was observed. This is consistent with the isotropic in-plane elasticity predicted by the 3-fold symmetry of MoS\(_2\).\(^{32,36}\) Our investigation paves the way to mechanically engineer the electronic and optical properties of atomically thin MoS\(_2\) and other TMDs, which have emerged as a new class of 2D semiconductors.

In our experiment, we used PMMA (ePlastics) as a flexible and transparent substrate to apply controllable and reproducible strains on the samples. Atomically thin MoS\(_2\) samples of well-defined crystallographic orientation were deposited directly on PMMA by mechanical exfoliation\(^{44}\) (Supporting Information S1) of bulk crystals (SPI). Regions of mono- and bilayers were identified by their optical contrast (inset of Figure 1a) and were further confirmed by absorption and PL spectroscopy\(^{20}\) (Figure 1b). Their crystallographic orientation was inferred from the rotational anisotropy of the second harmonic generation (SHG) process\(^{35,46}\) (Figure 1c). Details on the determination of the sample thickness and crystallographic orientation will be described below.

Strain was applied to the samples through van der Waals coupling at the sample–substrate interface along either the armchair or zigzag direction of the crystal by bending the flexible substrate in two perpendicular directions using the cantilever setup (Figure 1a).\(^{35}\) The applied strain \( \varepsilon \) is calibrated according to the deflection of the cantilever \( \delta \) as \( \varepsilon = (3h/2L)(1 - (x/L)) \) for small deflections.\(^{47}\) Here \( L \) is the length of the cantilever, \( x \) is the distance from the sample to the clamped edge of the cantilever, and \( t \) is the thickness of the substrate. To avoid sample slippage, we have kept the strain below 0.5%. A thin layer of PMMA can also be deposited on top of the samples. We have also studied a large number of samples (Supporting Information S2) and assumed the above strain calibration to be accurate only for those samples, which showed large and repeatable strain effects.

The absorption spectrum of atomically thin MoS\(_2\) samples was measured using broadband radiation from a supercontinuum laser, which was focused onto the samples with a
50x microscope objective. The reflected light from the MoS₂ samples on the PMMA substrate \( (R_{\text{MoS₂+sub}}) \) and from the bare substrate \( (R_{\text{sub}}) \) was collected by the same objective and directed to a grating spectrometer equipped with a charge-coupled device (CCD). The sample absorbance \( A \) at photon energy \( \hbar \omega \) is then determined from the reflectance contrast \( (R_{\text{MoS₂+sub}} - R_{\text{sub}})/R_{\text{sub}} = (4/(n_{\text{sub}}^2 - 1))A(\hbar \omega) \), where \( 4/(n_{\text{sub}}^2 - 1) \) is a local field factor with \( n_{\text{sub}} \) as the refractive index of PMMA.\(^{48}\) PL was measured simultaneously using the same optical setup by exciting the samples with a single-mode solid-state laser centered at 532 nm. The laser power on the samples was kept below 1 and 50 \( \mu W \), respectively, for absorption and PL measurements to avoid sample heating. The typical data acquisition time is 5 and 20 s for absorption and PL measurements, respectively.

The absorption and PL spectrum of both mono- and bilayer MoS₂ under zero strain are shown in Figure 1b. In the energy range of 1.55–2.30 eV, two characteristic absorption features, known as the A (\( ~1.90 \) eV) and B (\( ~2.05 \) eV) excitons, were observed. They are associated with the direct gap transitions around the K-point of the Brillouin zone. The absorbance of the bilayer sample is about 2 times of the absorbance of the monolayer sample outside the region of the exciton resonances, which serves as an unambiguous determination of the bilayer thickness.\(^{20}\) In the PL spectra, often only the A exciton emission associated with the lowest energy direct gap transitions is seen for monolayer samples. In contrast, a characteristic low-energy emission feature (I) near 1.55 eV is observed for bilayer samples. This feature is associated with the indirect-gap transitions\(^{20,21}\) and is absent in monolayer MoS₂, which is a clear indication of a crossover from an indirect gap to a direct gap semiconductor in the limit of monolayer thickness.

We note that there is a finite Stokes shift for the PL due to factors such as unintentional doping and shallow traps, which could also be strain dependent. As we show below, this effect is also sample dependent. \( W \), therefore, rely primarily on absorption spectroscopy to determine the exciton energies. PL is used to determine the indirect gap transitions since their absorption is extremely weak.

The crystallographic orientation of monolayer MoS₂ samples was determined by second harmonic generation (SHG) rotational anisotropy.\(^{45,46}\) SHG is allowed in monolayer MoS₂ since it is noncentrosymmetric while the process is forbidden in bilayer MoS₂ since inversion symmetry is restored. In our experiment, linearly polarized optical pulses from a modelocked Ti:Sapphire oscillator centered at 800 nm were used to excite monolayer MoS₂ samples under normal incidence. The reflected SH intensity polarized along the pump polarization direction was monitored while the samples were rotated about their surface normal. A typical angular dependence with a characteristic 6-fold pattern is illustrated in Figure 1c, which arises from SHG in crystals with \( D₃h \) symmetry. The symmetry of the atomic structure also predicts that the polarized SH intensity is maximized for excitation polarized along the armchair direction and zero along the zigzag direction. The crystallographic orientation of bilayer samples was inferred from the orientation of the attached monolayer regions.

We illustrate in Figure 1d the absorption spectrum of a monolayer sample under tensile strains up to 0.52% along the zigzag direction. The dashed blue and red lines are guide to the eye of the redshift of the peaks. The black dashed line at 1.96 eV is the PMMA Raman line at 2954 cm⁻¹, which is strain independent for the range of strains applied in this work. (b) Strain dependence of the A and B peak energies from the absorption measurement and the A peak energy from the PL measurement (symbols). Lines are linear fits to the data.

Figure 2. (a) Absorption (left panel) and PL (right panel) spectrum of a monolayer MoS₂ sample under tensile strains up to 0.52% along the zigzag direction. The dashed blue and red lines are guide to the eye of the redshift of the peaks. The black dashed line at 1.96 eV is the PMMA Raman line at 2954 cm⁻¹, which is strain independent for the range of strains applied in this work. (b) Strain dependence of the A and B peak energies from the absorption measurement and the A peak energy from the PL measurement (symbols). Lines are linear fits to the data.

normalized to the A exciton peak. Both the A and B exciton absorption peaks redshift with increasing strain. Figure 2b summarizes the exciton absorption peak energies as a function of strain. For the relatively small strains investigated here, a linear dependence is observed. A redshift rate of 64 \( \pm 5 \) and 68 \( \pm 5 \) meV/% strain is extracted for the A and B exciton, respectively. Within experimental accuracy, the A-B exciton splitting remains \( \sim 146 \) meV for the entire range of applied strain in this work. The A exciton PL peak shows a similar strain dependence and a redshift rate compared to the A exciton absorption peak, which suggests that the Stokes shift in this sample is largely strain independent.

To understand qualitatively the experimental results, we note that although the excitonic effects are particularly strong in...
atomically thin MoS$_2$ due to reduced dielectric screening$^{22-25}$ the exciton binding energies have been shown by first principles calculations to be almost strain independent.$^{36,42}$ The measured strain dependence of the excitonic resonance energies can thus be related directly to the changes in the electronic band structure. The bands near the Fermi energy in MoS$_2$ are composed primarily of the Mo 4d and S 3p atomic orbitals, and the nature of the band gap and its size is determined by the d-manifold splitting due to the crystal field of the trigonal prismatic structure and Mo 4d$^-$S 3p orbital hybridization. Application of tensile strains increases the Mo$-$Mo and Mo$-$S bond length (and decreases the S$-$S layer distance due to Poisson contraction).$^{32}$ The net effect is a reduction in the orbital hybridization and d-bandwidth, which is revealed as the reduced band gap and red-shifted exciton resonance energies. The observed magnitude of the effect ($\sim 70$ meV/% uniaxial strain) is also in good agreement with ab initio calculations ($40-100$ meV/%).$^{32-42}$ Furthermore, the A$-$B exciton splitting in monolayer MoS$_2$ corresponds mainly to the spin$-$orbit splitting of the lowest energy valence bands. The insensitivity of the latter to small strains is expected since the spin$-$orbit interactions arise from the inner parts of the atoms and are insensitive to the atomic bond lengths.

For comparison, we also investigate the strain effects on the electronic structure of bilayer MoS$_2$ (Figure 3). Similar strain effects are observed for the A and B exciton energies with a redshift rate of $71 \pm 5$ and $67 \pm 5$ meV/% strain, respectively, from the absorption measurements (Figure 3b). These values are comparable to that of monolayer MoS$_2$. The redshift rate of the A exciton energy extracted from the PL measurements (Figure 3c), however, is smaller ($48 \pm 5$ meV/%). Such a discrepancy indicates that the Stokes shift of the A exciton PL is strain dependent, likely due to strain-induced defects. The overall PL intensity (not shown in the normalized PL spectra of Figure 3a), as well as the relative strengths of the I and A feature, decreases with increasing strain, which is also consistent with the picture of strain-induced defects. Moreover, the PL feature I near 1.55 eV, corresponding to indirect gap transitions, is observed to redshift with a larger rate of $77 \pm 5$ meV/% strain than the A exciton PL energy (Figure 3c). If the strain dependence of the Stokes shift is similar for both the A and I emission features, the strain effect is about 1.6 times larger for the indirect gap transitions than for the direct gap transitions. Such a trend arises from the difference in orbital composition and the corresponding orbital hybridization as a function of strain at different points of the Brillouin zone. We note that for an accurate determination of the indirect gap energy and its strain dependence a direct absorption measurement, such as photoconductivity spectroscopy,$^{20}$ is needed.

In summary, we have demonstrated that both the direct and indirect band gaps of atomically thin MoS$_2$ can be efficiently tuned by applying a uniaxial tensile strain. For both monolayer and bilayer MoS$_2$ samples, a redshift rate of $71 \pm 5$ and $67 \pm 5$ meV/% strain, respectively, from the absorption measurements (Figure 3b). These values are comparable to that of monolayer MoS$_2$. The redshift rate of the A exciton energy extracted from the PL measurements (Figure 3c), however, is smaller ($48 \pm 5$ meV/%). Such a discrepancy indicates that the Stokes shift of the A exciton PL is strain dependent, likely due to strain-induced defects.

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In summary, we have demonstrated that both the direct and indirect band gaps of atomically thin MoS$_2$ can be efficiently tuned by applying a uniaxial tensile strain. For both monolayer
and bilayer samples, the A and B exciton resonance peaks, associated with direct gap transitions, redshift under tensile strains with similar rates, and a larger redshift rate is observed for the indirect band gap transitions in bilayer MoS₂. We also find that the uniaxial strain effect is independent of crystallographic orientation of the crystal within the range of 0.5% strain applied in this work. We note that the large strain effects observed in atomically thin MoS₂ have importance beyond this specific material. We anticipate that the elastic strain field can be used to tailor the electronic structure of other semi-conducting transition metal dichalcogenides with properties similar to MoS₂. Also, a spatially inhomogeneous strain field can be engineered to generate spatially varying band structures and mechanically induced photodiodes can be engineered, for instance, for solar energy harvesting. The compatibility of 2D atomic crystals with flexible substrates and their mechanically tunable electronic and optical properties open up a new opportunity for applications of 2D crystals in flexible electronics and optoelectronics.

ASSOCIATED CONTENT
2 Supporting Information
Description on exfoliation of atomically thin MoS₂ samples on PMMA cantilevers with well-defined crystallographic orientations and histogram of the strain effects in all atomically thin MoS₂ samples studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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