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# Stress-induced bandgap renormalization in atomic crystals

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ABSTRACT

Single atomic layers of two-dimensional (2D) transition metal dichalcogenides (TMDs) are promising candidates for integration of optical and electronic circuits due to their extraordinary optical oscillator strength and large exciton binding energy. Customizing the exciton energy of the TMDs is a direct way to control the light-matter interaction. Here we demonstrate that the electronic band gap of tungsten diselenide $WSe_2$ can be tuned continuously with the application of the uniaxial tensile strain. The energy is redshifted with a rate of ~62.5 meV/% strain for exciton A, determined by photoluminescence spectroscopy along with Finite Element Method modeling using the commercial software ANSYS. The uniaxial bandgap deformation potential (DP) of the electronic bandgap of monolayer $WSe_2$ can be computed directly from our measurements and is about $-6.3 \pm 0.5$ eV. Our results agree well with first-principles calculations. The ability to control the renormalization of the bandgap in 2D materials with strain could be used in flexible electronics or optoelectronic devices such as a TMDs based microcavity.

## 1. Introduction

Transition metal dichalcogenides (TMDs) have emerged as a new class of two dimensional materials and have attracted intense attention starting in 2010 because of their potential applications in electronics and optoelectronics [1–4]. In contrast to graphene, which is a gapless semimetal, hindering its application in optoelectronics, TMDs such as $WS_2$, $MoS_2$, $WSe_2$ and $MoSe_2$ have a direct bandgap in the visible region when their thickness is thinned down to an atomic scale [5,6]. Moreover, TMDs have been demonstrated as good candidates for allowing integration with solids and have extraordinary exciton-photon coupling strengths and ultra large excitonic binding energy (0.3–0.5 eV) [7,8]. These properties allow for room temperature exciton-polaritons, spontaneous coherence and strong optical nonlinearity. Though strong coupling has been observed at room temperature in 2014 [9], demonstrating that this polariton system is suitable for realizing polariton condensation and superfluidity, it is difficult to take the next step, partly due to the limited tunability of the cavity photon in resonance to the exciton energy of TMDs. However, the electronic bandgap is tunable by applying external mechanical strain.

Because of the unique property of ultra-strength, TMDs can in principle be stretched to very high strain, leading to large bandgap shift. This motivated several studies of the bandgap shift [10–13]; a numerical study of the deformation potential has been performed [14] but has not yet been directly compared to experiment. The experimental methods reported by the other groups involved transferring the monolayer to a "soft" substrate, so that the strain could be applied to the flake by bending the substrate. Here we report a method that uses a "hard," thick substrate. This ability is crucial for tuning the band gap of TMD materials embedded inside an optical microcavity, in which it is necessary to tune the energy of the cavity mode and the exciton mode relative to each other to achieve strong coupling. The stress-induced strain is demonstrated here to modify the band gap of the TMDs through the 500 $\mu$m of quartz, and results in energy shifts of up to 20 meV, allowing the possibility of tuning the exciton energy inside of the microcavity.

In this paper, we also report a systematic experimental study of the dependence of the deformation potential (DP) of monolayer $WSe_2$ on strain. The DP relates the first derivative of the band energy to the strain at equilibrium. DPs are often used to describe the electron-phonon interactions. A uniaxial tensile strain was applied to the sample by applying stress, and the strain was determined by a Finite Element Method with commercial software ANSYS (Release 19.0). The continuously tunable electronic band gap was investigated by the photoluminescence (PL) spectroscopy. Under the small strain on the sample, the energy shifted linearly with a rate of ~62.5 meV/% strain for

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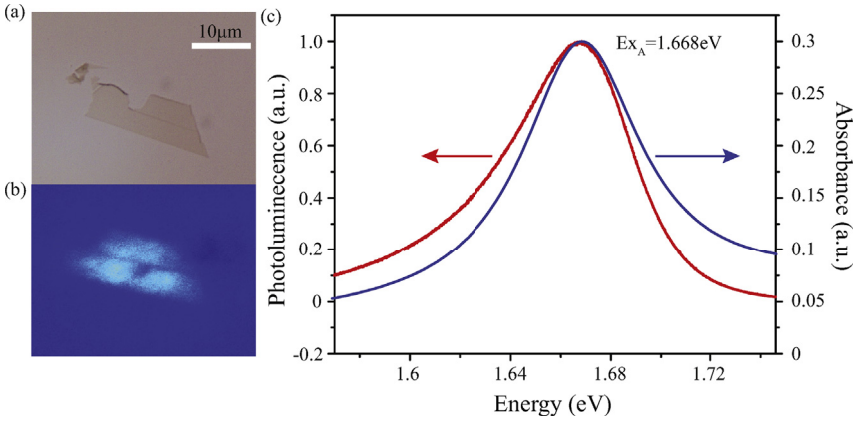


**Fig. 1.** (a) Optical microscope image of $WSe_2$ in Reflectance and (b) is the PL. The monolayer region is lightened up under the intense illumination. (c) A dominant peak corresponds to exciton A at center of 1.668 eV (743 nm) is shown in the typical photoluminescence and absorption spectrum.

exciton A and the DP was determined to be $-6.3 \pm 0.5$ eV, in agreement with prior experimental results [15] and with first-principles calculations [14].

## 2. Experimental results

An isolated monolayer of $WSe_2$ with a typical size of $10 \times 25\,\mu m^2$ was mechanically exfoliated and transferred to the surface of a piece of transparent thin quartz. The thickness of the quartz was 500 $\mu$m (Fig. 1a). Two typical modes $E^1_{2g}$ (353 $cm^{-1}$) and $A^1_{1g}$(417 $cm^{-1}$) were characterized respectively by micro-Raman spectroscopy to help to determine the thickness of the sample. Fig. 1 shows images taken using an optical microscope. The top image shows the large exfoliated $WSe_2$ flake in reflectance and the bottom image shows the photoluminescence (PL, bottom) under 632 nm He-Ne laser excitation with a large Gaussian spot.

The PL spectra were collected by the same objective and directed to a grating spectrometer equipped with a charge coupled device (CCD). The monolayer region is lightened up because of its direct band gap transition around the K point in the Brillouin zone. A typical monolayer PL spectrum is shown in Fig. 1c with a dominant single peak of exciton A centered at 1.689 eV (743 nm) with a FWHM of 50 meV. These values vary slightly along the sample, presumably due to substrate adhesion, surface charge density, defects and fluctuations in strain.

In the experiment, the stress was loaded on the back of the substrate with the help of stress setup built by us. A sharp needle was mounted in a tube with a spring connected to its front and back. The entire apparatus was installed on an x-y-z translation stage. The tube was oriented in the z direction and attached to the micrometer. The top face of the substrate was stuck to a piece of metal with a small hole drilled through. The monolayer $WSe_2$ was located within that hole. The load of the stress could be continuously tuned by changing the micrometer. The stressor was aligned behind the 2D material by a long working distance objective (X50, NA = 0.75), using the method of Ref [16].

A 10 meV redshift was observed in the peak position of the photoluminescence of monolayer $WSe_2$ with the applied strain up to 0.16%, as shown in Fig. 2(b). The stress induced the reduction of the electronic band gap, in agreement with the theoretical predictions of Refs. [17–24] since the tensile strain softens the atomic bonds and results in reduced orbital overlap and hybridization.

To determine the absolute deformation potentials, we needed to calibrate the strain. This was done by calibrating the force applied to the sample and calculating the strain for that force using a numerical model. We mounted the micrometer stressor assembly to a board with a SHIMPO 20 Newton force gauge. We then measured the applied force over a full range of micrometer settings. The resulting force curve was linear with a vertical offset; the vertical offset occurred because the stressor has an inner spring which never compresses after initial contact is made, while the outer spring continues to behave in accordance with Hooke's law. The fit of these data to a straight line gave us a calibration function for how much force we are applying for a given micrometer setting during our experiments. Then the applied strain $\varepsilon$ through the substrate was computed by finite element method using the commercial software ANSYS, the details can refer to the supplementary information, with the input of the load of the stress. To build up the model, we assumed that the $WSe_2$ adhered to the substrate without slipping. We found that we had a maximum strain in our sample of 0.16%. For small strains, the hydrostatic strain is dominant in modifying the electronic bandgap and the shear deformation is negligible, independent of its direction, which is consistent with the isotropic in-plane elasticity expected for a crystal with D3h symmetry [25].

The PL spectrum corresponding to each stress was measured, and the energy shift of the monolayer $WSe_2$ as a function of the strain is illustrated in Fig. 3. The energy of exciton A exhibits a continuous redshift as more stress is loaded. The result indicates a linear relation for a small strain and a redshift rate at about 62.5 meV/%, which is in close agreement with previous calculations, which lie in the range 40–100 meV/% strain [17–23]. First-principles calculations indicate that the effect of the strain on the binding energy of the excitons is negligible, even though there are strong excitonic effects in monolayer TMDs [17,26]. Thus, the measured excitonic energy shift as a function of the strain can be used to describe the electronic band gap change directly. For 2D materials with stoichiometry of $MX_2$, the bands in vicinity of Fermi level are made of d orbitals of M atoms and p orbitals of X atoms, and the electronic bandgap originates from the d orbitals splitting because of the trigonal prismatic structure and M-d, X-p orbital hybridization. The applied uniaxial tensile strain in the experiment elongates the bond length of M-M and M-X, while decreases the X-X distance, resulting in the reduction of the bandgap and giving rise to the redshift of the resonant energy.

The bandgap absolute deformation potential can be calculated directly from our measurements. The DP is defined as the first derivative of the electronic bandgap energy as a function of strain at equilibrium. The bandgap DP can be derived from the DP of the valence and conduction band as [14,27,28]

$$D_{gap} = \frac{\delta E}{\delta V/V}, \tag{1}$$

where $D_{gap}$ is the absolute deformation potential of the bandgap, $\delta E$ is the band gap energy shift with the applied strain, and $\delta V/V$ is the relative change of the volume, which can be represented by the strain as: $\delta V/V = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$, where $\varepsilon_{xx}$, $\varepsilon_{yy}$, and $\varepsilon_{zz}$ are the normal strains along the x, y, and z directions, considering only hydrostatic strain for a small strain. We fit the bandgap shift as the function of strain linearly

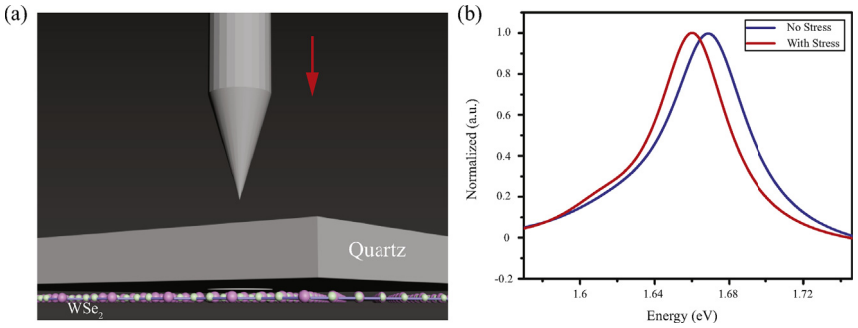


**Fig. 2.** ((a) Schematic of the homemade stress setup with a sharp needle installed on an x-y-z translation stage. The back of the needle connects to a spring which is adhered to one of the micrometers in the z direction. Thus, the stress can be tuned by changing the micrometer. (b) Typical photoluminescence spectroscopy of monolayer $WSe_2$ with tensile strain up to 0.16% (red) in comparison to that of without stress (blue); 10 meV redshift is observed from the spectrum. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

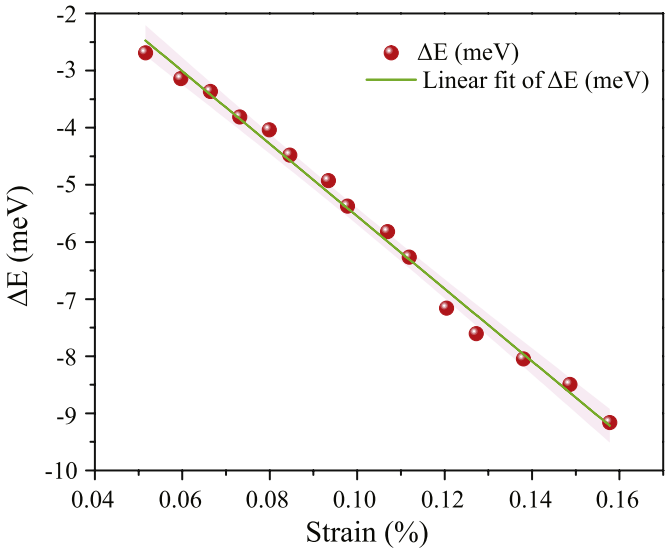


**Fig. 3.** The electric bandgap shift of the monolayer $WSe_2$ as a function of strain. The energy shift is determined by the PL and the corresponding strain is computed by the ANSYS. The result indicates a linear relation under a small strain with a gradient of 62.5 meV/% strain. The linear fit of the bandgap shift gives us a slope of $-6.3$ eV with the uncertainty of $\pm$ 0.5 eV.

with best-fit slope of $-6.3$ eV with the uncertainty about $\pm$ 0.5 eV. The fitting result agrees well with the first-principles calculation [14] $D_{gap}^{K-K} = -5.86$ eV.

## 3. Conclusion

In conclusion, we have observed strain-induced bandgap renormalization, that is, a redshift of the bandgap in monolayer $WSe_2$ with a rate of 62.5 meV/% strain, which corresponds to an absolute deformation potential of $-6.3 \pm 0.5$ eV with the strain up to 0.16%, in agreement with the theoretical result of $-5.86$ eV for $WSe_2$. The method of tuning the electrical band of the $WSe_2$ can be applied to the other transition metal dichalcogenides, and the ability to tune the band gap gives the possibility of observing the degeneracy of the spin valley coupling at cryogenic temperatures with large strain applied, since the shear effects can become important and lead to band crossings. This tuning ability can also be used to trap single-photon emitters in the TMDs by using a localized strain potential [29]. Moreover, the method to continuously tune the band structure of TMDs gives rise to the possibility of tuning the resonance of a polariton in a microcavity and could be the cornerstone for realizing polariton condensation at room temperature [30].

## Author contributions

D. S, Z. S and J. B initiated the project. Z. S, and J. B designed the experiments. H. CP.M, S.C, A.R and S.K.B prepared the monolayer $WSe_2$ sample and transferred to a quartz. Z. S and J. collected the data and Z. S and D.S analyzed the data. Z.S did the ANSYS modeling. All the authors contributed to the discussion of the results and the manuscript writing.

## Competing financial interests

The authors declare no competing financial interests.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ssc.2018.11.006.

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