Bandgap engineering of rippled MoS$_2$ monolayer under external electric field

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In this letter we propose a universal strategy combining external electric field with the ripple of membrane to tune the bandgap of semiconducting atomic monolayer. By first-principles calculations we show that the bandgap of rippled MoS$_2$ monolayer can be tuned in a large range by vertical external electric field, which is expected to have little effect on MoS$_2$ monolayer. This phenomenon can be explained from charge redistribution under external electric field by a simple model. This may open an avenue of optimizing monolayer MoS$_2$ for electronic and optoelectronic applications by surface patterning. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4803803]

In recent years, motivated by the discovery of graphene, two dimensional (2D) materials have attracted more attention for their physics and potential application in next-generation electronics and optoelectronics. Although graphene is the most studied 2D crystal, its lack of bandgap hampers its application in semiconducting and photonic devices. This fact has motivated the research in other 2D crystals with a large intrinsic bandgap, such as atomically thin MoS$_2$. Recently, monolayer MoS$_2$ transistors have shown large in-plane mobility and high current on/off ratio making this material of great interest for electronic devices and sensors. Especially, monolayer MoS$_2$ is a direct bandgap semiconductor, being attractive for optoelectronic application, although bulk MoS$_2$ is an indirect bandgap semiconductor. Further, the ability to manipulate the bandgap could lead to other functionalities in these materials. Several strategies have been employed to engineer bandgaps. For example, tensile strain can be applied to tune bandgap of monolayer MoS$_2$. But, a direct-to-indirect bandgap transition occurs at only strain of 1%. Applying external electric field is another strategy to tune electronic properties of materials. It has been shown that an external electric field normal to flat monolayer MoS$_2$ sheet cannot change its bandgap. Although theoretical studies show that the bandgap of double-layer MoS$_2$ sheets can be modulated by applying vertical external electric field, double-layer MoS$_2$ is itself an indirect gap semiconductor, and indirect-to-direct transition cannot occur under external electric field. It would, therefore, be highly desirable to have capabilities to continuously control the bandgap of large monolayer MoS$_2$ and at the same time preserve the direct-gap character. This may open an avenue of optimizing monolayer MoS$_2$ for optoelectronic applications and shed light on the effect of

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(a) Monolayer MoS$_2$ ripple structure. Band structures of zigzag (b) and armchair (c) monolayer MoS$_2$ ripple structures along y direction under different external electric field (0.0, 0.1, 0.2 V/Å) from first-principles DFT calculation.
surface roughness, as represented by the nanopattern, on electronic properties of thin films via surface wrinkling.

First, we take monolayer MoS2 as an example to show our strategy. Experimentally spontaneous ripples have been observed for monolayer MoS2.23 Here, we built a monolayer MoS2 periodic ripple structure, as shown in Fig. 1(a). Period length (l) of ripple structure along x direction is about 9.5 nm and ripple height (h) along z direction is about 2 nm. The lattice constant (c) along y direction (zigzag direction in hexagonal lattice) is 3.16 Å (experimental value of bulk MoS2). MoS2 ripple structures along armchair direction in hexagonal lattice is similar to zigzag ripple structure, and lattice constant along y direction is 5.473 Å. Experimentally, periodic ripple structure can be fabricated and controlled by putting MoS2 monolayer on a wavy substrate, similar to graphene case.24 First-principles density-functional theory (DFT) calculations were performed in a supercell configuration using the Vienna ab initio simulation package (VASP).25 We employed projector augmented-wave (PAW) method,26 the general gradient approximation (GGA)27 of exchange-correlation functionals, an energy cutoff of 400 eV for the plane-wave basis, and 1 × 21 × 1 Monkhorst-Pack k-points. Geometry optimizations were performed with a criterion of the maximum residual force less than 0.02 eV/Å without any symmetry constraints. The supercell was adjusted to maintain a sufficiently large separation between adjacent layers (>20 Å from surface to surface). A supercell used in calculation is shown by dashed line in Fig. 1(a).

We apply an external electric field on monolayer MoS2 ripple structure. External electric field is along z direction. The most important finding is that the bandgap of MoS2 ripple structure reduces rapidly with increasing the strength of electric field, although bandgap of flat monolayer MoS2 cannot be changed under vertical external electric field. In Figs. 1(b) and 1(c) we show, respectively, band structures of zigzag and armchair monolayer MoS2 ripple structures under different strength of electric field. For example, a 0.2 V/Å of electric field strength can reduce the bandgap from 1.76 to 1.0 eV, and at the same time the direct gap character is preserved. Furthermore, we also found that the decrease of bandgap is linear with the strength of electric filed, shown in Fig. 2. These results indicate that the combination of electric field and ripple is an effective strategy to tune bandgap of monolayer MoS2.

In addition, we also should point out the effect of ripple on electronic properties of monolayer MoS2. Ripple introduces strain into structure, resulting in the change of bond angles, bond lengths, and curvature of atomic plane. Change of bond angles and bond lengths will influence the electronic properties of materials. We built several zigzag ripple structures with different curvatures, as shown in Fig. 3, and calculate their band structures. We found that the bandgap decreases gradually with

![FIG. 2. Bandgap versus applied electric field for zigzag monolayer MoS2 ripple structures with 19.5 and 23.5 Å of h and armchair monolayer MoS2 ripple structures with 18.8 Å of h. The fitted line is also shown. Bandgap decreases linearly with increasing the strength of electric field.](image1)

![FIG. 3. The band structures of zigzag monolayer MoS2 ripple structures with different curvatures. The bandgap decreases gradually with the increase of curvature, and a direct-to-indirect gap transition occurs when bandgap decreases to a certain value (about 1.73 eV).](image2)
the increase of curvature, and a direct-to-indirect gap transition occurs when bandgap decreases to a certain value (about 1.73 eV). Although the strain introduced by ripple is not homogeneous, its influence on electronic properties is similar to a homogeneous strain. Previous studies show that a direct-to-indirect bandgap transition occurs at only strain of 1%. This also indicates that strain engineering is not an applicable method to tune the bandgap for preserving direct-gap character. For armchair ripple structure, we do not find the direct-indirect gap transition at curvature range studied. This can be well understood from Brillouin zone (BZ) folding. As shown in Fig. 1(a), the supercell of rippled MoS2 monolayer has a large non-redundant lattice parameter (about 2 nm) along x direction, while the lattice parameter remains small (3.16 Å for zigzag ripple and 5.473 Å for armchair ripple) along y direction. Accordingly, the hexagonal BZ of perfect MoS2 monolayer is folded into rectangle for the supercell of rippled MoS2 monolayer, where the width in x direction is very narrow due to the corresponding large period length in the real space. The K and Γ points in original BZ are still well separated along y direction in the momentum space for the BZ of zigzag ripple, while these two points are adjacent with the same y-coordinate and a small shift in x direction for the BZ of armchair ripple. With strain, there is a transition from direct bandgap (K → K point) to indirect bandgap (Γ → K point) for perfect flat MoS2. The transition is also clearly seen for zigzag ripple with the increase of curvature in Fig. 3, due to well-separation of K and Γ point in the momentum space. However, there is not an apparent direct-to-indirect bandgap transition due to small dispersion between the adjacent K and Γ points for armchair ripple.

In the following, we will explain why the bandgap of rippled monolayer MoS2 can be tuned by vertical external electric field, which is invalid for flat monolayer MoS2. A schematic diagram for the decrease of gap under external electric field is shown in Fig. 4. Position of curvature maximum in monolayer MoS2 ripple structure is called peak or valley (marked in Fig. 4). Under external electric field along +z direction, the electrostatic energy felt by an electron at peak region becomes higher and that at valley region becomes lower. This makes the band energy of electrons in peak region rise and lower in valley region. Moving of energy bands in opposite direction results in the decrease of bandgap. Therefore, the Highest Occupied Molecular Orbital (HOMO) level of electrons in peak region and the Lowest Unoccupied Molecular Orbital (LUMO) level of electrons in valley region become HOMO and LUMO level of overall superstructure, respectively. According to this model, under electric field the HOMO and LUMO should locate at peak and valley regions of ripple, respectively. This is confirmed by charge density distribution of HOMO and LUMO from first-principles calculation, shown in Fig. 4(b). We also can see that LUMO is primarily of Mo \( d_{\alpha z} \) character, and HOMO is primarily of Mo \( d_{\alpha y} \) and \( d_{\alpha z} \) character. As a comparison, we should also point out that charge density distribution of HOMO and LUMO in the absence of external electric field is overlapped. The spatial separation of charge carriers in such field-induced semiconducting MoS2 ripple structure should give rise to interesting effects in transport measurements and hold the promise of a bright future for use in photovoltaics. Moreover, we anticipate similar effects in the presence of chiral rippled monolayer (that is, the ripples propagate along neither armchair nor zigzag direction), owing to the similar field modulation by the heights of sample in an external potential gradient. This is a universal strategy combining external electric filed with ripple of membrane to tune the bandgap in semiconducting atomic membrane.

According to above model, the change of bandgap can be expressed as \( \Delta E_g = \varepsilon S \Delta E_f (\langle \xi \rangle_{\text{HOMO}} - \langle \xi \rangle_{\text{LUMO}}) \), where \( \langle \xi \rangle_{\text{HOMO}} \) and \( \langle \xi \rangle_{\text{LUMO}} \) represent the distribution center of HOMO and LUMO along the direction of the applied external field (z direction in Fig. 1), \( E_f \) is the strength of applied external electric field, \( e \) is the electron charge, and \( S \) is the
brane to tune the bandgap of semiconducting atomic membrane by combining external electric field with ripple of monolayer MoS2. We find that the bandgaps of rippled monolayer MoS2 can be optimized for semiconducting atomic membrane. This may open an avenue of optimizing monolayer MoS2 for electronic and optoelectronic applications by surface patterning.

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