Curvature-Controlled Band Alignment Transitions in 1D van der Waals Heterostructures

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(Dated: September 7, 2022)

One-dimensional (1D) van der Waals (vdW) heterostructures, formed between coaxial nanotubes of transition metal dichalcogenides (TMDCs), have emerged as a new area of endeavor in nanoscience. A key to designing and engineering the properties of such 1D vdW heterostructures lies on understanding the band alignment of coaxial nanotubes in the heterostructures. However, how curvature, tube diameters, and intertube coupling affect the band-edge levels and band alignment of TMDC nanotubes in 1D vdW heterostructures remains unknown. Here, through comprehensive first-principles calculations and analyses, we establish a complete framework of band alignment in 1D vdW heterostructures of TMDC nanotubes. We reveal that, as the diameter of a TMDC nanotube decreases, the combined effects of curvature-induced flexoelectricity and intrinsic circumferential tensile strain cause a rapid and continuous lowering of the conduction band minimum (CBM), whereas the valence band maximum (VBM) exhibits an initial lowering before rising, which originates from a change in the orbital character of the VBM. The transition in the orbital character of VBM also leads to direct-to-indirect bandgap transition in small-diameter armchair and chiral nanotubes, as well as photoluminescence quenching in zigzag nanotubes. As individual TMDC nanotubes form coaxial 1D vdW heterostructures, the effect of intertube coupling via flexovoltage effect can result in a transition of intertube band alignment from Type II to Type I in multiple heterostructural systems, including large-diameter MoSe2@WS2, MoTe2@MoSe2, and MoTe2@WS2 heterostructures. These results lay down a foundation for the rational design of 1D vdW heterostructures.

INTRODUCTION

Band alignment and band energy diagram are core concepts of semiconductor physics that explain a wide range of phenomena underlying applications such as transistors and quantum well lasers [1, 2]. The key ingredients for determining the band alignment at a semiconductor interface include the energy levels of the valence band maximum (VBM) and conduction band minimum (CBM) of each semiconductor, as well as possible interfacial coupling effects. In addition to successes in studying bulk semiconductor interfaces, band alignment has demonstrated its predictive power in the study of low-dimensional semiconductor heterostructures such as stacked two-dimensional (2D) materials [3], where interlayer excitons were observed in van der Waals (vdW) heterostructures of 2D transition metal dichalcogenides (TMDC) with a staggered (Type II) band alignment [4-6]. Recently, one-dimensional (1D) vdW heterostructures of coaxial nanotubes have emerged as an intriguing new class of nanomaterials [7-12]. Single-walled, single-crystal MoS2 nanotubes with diameters as small as 3.9 nm have been grown on single-walled carbon nanotubes (SWCNTs) and boron-nitride (BN) nanotubes using chemical vapor deposition [7]. This provides a fresh new ground for discovering unique phenomena and functionalities in these novel heterostructures. Understanding the band alignment between coaxial nanotubes in 1D vdW heterostructures will be a critical step in this endeavour.

A prerequisite to determining the band alignment in 1D vdW heterostructures lies on resolving the diameter-dependent evolution of the band-edge levels of individual nanotubes. In this respect, although there have been abundant studies of the diameter-dependent electronic properties of SWCNTs [13-21], similar investigations of TMDC nanotubes are surprisingly limited [22-32]. In particular, a systematic understanding of the curvature- and diameter-dependent band-edge energy levels and characters of TMDC nanotubes is still lacking.

The above considerations motivate us to establish a complete framework of band alignment in 1D vdW heterostructures of TMDC nanotubes. We first carry out a comprehensive investigation of the diameter-dependent electronic properties of SWCNTs [13-21], similar investigations of TMDC nanotubes are surprisingly limited [22-32]. In this respect, although there have been abundant studies of the diameter-dependent electronic properties of SWCNTs [13-21], similar investigations of TMDC nanotubes are surprisingly limited [22-32]. We employ density functional theory (DFT) calculations to determine the absolute energy levels of the VBM and CBM of TMDC nanotubes in reference to vacuum level. This common vacuum energy reference allows us to directly compare the band-edge levels of nanotubes of varying diameters. Our DFT calculations focus on zigzag and armchair nanotubes with diameters that ranges from 1.5 nm to 5 nm, the upper end of which exceeds those of experimentally synthesized

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We find that the band-edge levels of TMDC nanotubes exhibit a highly non-trivial dependence on the tube diameters. When the tube diameter is above 50 Å, curvature-induced flexoelectricity and its associated electrostatic potential effect is found to be the main reason that affects the band-edge levels of individual TMDC nanotubes. Below a diameter value of ~50 Å, the circumferential tensile strain inherent in TMDC nanotubes starts to play an increasingly important and eventually dominant role in the band-edge evolution, causing a rapid lowering of the CBM of TMDC nanotubes as well as a transition from downward to upward shifting in VBM levels as tube diameter decreases. The transition in diameter-dependent evolution of VBM levels is caused by a strain-induced change in the VBM character from in-plane to out-of-plane orbitals, and this transition has profound implications on the electronic and optical properties of TMDC nanotubes, including direct-to-indirect bandgap transition in armchair and chiral nanotubes, as well as photoluminescence quenching in zigzag nanotubes. Quantum confinement is found to play a negligible role on the band-edge evolution.

After obtaining an in-depth understanding of the band-edge evolution of individual TMDC nanotubes, we have studied the band alignment of coaxial TMDC nanotubes in 1D vdW heterostructures, taking into account of the effect of intertube electronic coupling. We find that the flexovoltage generated by the outer nanotube on the inner nanotube in a 1D vdW heterostructure plays a critical role in the band alignment of coaxial nanotubes. Combining the results on individual nanotubes and intertube coupling effects, we establish a complete framework of band alignment in all 1D vdW heterostructures formed between TMDC nanotubes, such as the WS$_2$@MoS$_2$ 1D vdW heterostructures illustrated in Figure 1a. We find that as the tube diameters of 1D vdW heterostructures decrease, a transition from Type II to Type I band alignment (Figure 1b) can occur in multiple heterostructural systems. In particular, Type II to Type I band-alignment transitions can occur in large-diameter MoSe$_2$@WS$_2$, MoTe$_2$@MoSe$_2$, and MoTe$_2$@WS$_2$ heterostructures, making these heterostructural systems attractive for nanoscale optoelectronic applications.
RESULTS AND DISCUSSION

We first present our results and analyses of the diameter-dependent band-edge level evolution in TMDC nanotubes. The DFT-calculated CBM and VBM levels of MoS$_2$ and WS$_2$ nanotubes are presented in Figure 1c,d. The results reveal that the CBM levels of MoS$_2$ nanotubes exhibit a continuous lowering with the decrease of tube diameter ($D$). In contrast, the VBM levels exhibit a more complex change. In the limit of infinitely large diameter, the tube curvature approaches zero and therefore the VBM level shall be equal to that of the corresponding monolayer. However, the VBM levels computed for MoS$_2$ and WS$_2$ nanotubes with diameters around 50 Å are lower than those of the corresponding monolayers, indicating an initial lowering of the VBM levels as the tube diameters decrease. The VBM of MoS$_2$ nanotubes already starts to show a slowly upward shift when the diameter is below $\sim$50 Å, whereas in WS$_2$ nanotubes, the upward shift becomes noticeable at a diameter of around 40 Å. When the tube diameter is below 30 Å, the CBM level lowers rapidly with a further reduction of the tube diameter, whereas the VBM level exhibits the opposite trend, raising in a fast pace with decreasing tube diameter. These trends are the same for both zigzag and armchair tubes, indicating weak chirality dependence of band-edge level evolution.

The general trend of the variation in the VBM and CBM levels of MoSe$_2$, WSe$_2$, and MoTe$_2$ nanotubes are similar to MoS$_2$ and WS$_2$, but the non-monotonic change of their VBM is even more evident, as shown in Figure 2a–c. Notably, the VBM of the three Se- and Te-based TMDC nanotubes do not rise until the tube diameter is below $\sim$30 Å. The transition diameters are $\sim$30 Å, 28 Å, and 30 Å for MoSe$_2$, WSe$_2$, and MoTe$_2$ nanotubes, respectively. The maximum lowering of the VBM in reference to the corresponding monolayers, reached at the “transition diameters”, are on the order of 0.2 eV.

Since VBM and CBM correspond to the edges of the valence and conduction bands, respectively, it is informative to inspect the electronic band structures of TMDC nanotubes. The atomic structures of zigzag and armchair nanotubes are illustrated in Figure 2d. The calculated electronic band structures of a zigzag MoSe$_2$ nanotube with diameter $D = 41$ Å and an armchair MoSe$_2$ nanotube of $D = 44$ Å are shown in Figure 2e,f. At these diameter values, both zigzag and armchair MoSe$_2$ nanotubes are direct bandgap semiconductors. In the zigzag MoSe$_2$ nanotubes, both the VBM and CBM reside at the $\Gamma$ point, whereas in the armchair nanotubes, the band edges are located at around 2/3 of the path from $\Gamma$ to $X$, where $X$ is the 1D Brillouin zone boundary. DFT-calculated results indicate that, as the tube diameters are reduced further, zigzag nanotubes will remain their direct-bandgap nature. By contrast, a direct-to-indirect bandgap transition will occur in armchair nanotubes, due to the relative upward shift of the electronic states near $\Gamma$ (Figure S1). The direct-to-indirect bandgap transition is observed in all armchair nanotubes of Mo- and W-dichalcogenides (MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, and WSe$_2$). Such a transition has previously been observed in MoS$_2$ and MoSe$_2$ nanotubes, where the diameters corresponding to the transitions were determined to be 52 Å and 33 Å, respectively, in close agreement with our results [32, 34].

To investigate the origin of the diameter-dependent band-edge levels of TMDC nanotubes, we note that when a TMDC monolayer is wrapped into a nanotube, three distinct factors could affect the band-edge levels: (i) The electron orbitals are spatially confined along the circumferential direction due to the small tube diameter, leading to possible quantum confinement effect. (ii) The radial curvature of the nanotube can generate flexoelectricity and flexoelectric potential [19, 35, 36] inside the nanotube, which could shift the energy levels of the electronic states. (iii) The bending of a 2D sheet into a nanotube and the subsequent structural relaxation alter the crystal symmetry and generate internal tensile and bending strains in the nanotube, which change the electron orbital hybridization and thus the band-edge levels.

Quantum Confinement Effect (QCE). We first consider the effect of circumferential QCE in TMDC nanotubes by using the Brillouin-zone-folding scheme that was originally developed for studying QCE in SWCNTs [20]. QCE has been shown to have a strong influence on the band-edge levels of SWCNTs [13–17, 19]. In Mo- and W-dichalcogenide 2D semiconductors, QCE in the layer-normal direction is also the key factor that drives indirect-to-direct bandgap transition from bulk to monolayer [37, 38].

From structural perspective, a TMDC nanotube can be thought of as derived from a monolayer TMDC, which is rolled up and seamed to form a tubular structure with a finite radial curvature. The direction of rolling and the circumference of the resultant tube form a tubular structure with a finite radial curvature. The direction of rolling and the circumference of the resultant tube are determined by the “chiral vector” $C_h = na_1 + ma_2$, where $a_1$ and $a_2$ are the 2D primitive lattice vectors of the corresponding TMDC monolayers [20], as illustrated in Figure 3a. The two integer indices $n$ and $m$ form a pair $(n, m)$ that specifies the chirality of the tube, with $(n, n)$ corresponding to armchair tubes, $(n \neq 0, m = 0)$ and its symmetric pair $(n = 0, m \neq 0)$ zigzag tubes, and other cases of $(n \neq m, m \neq 0)$ being chiral tubes. The translational vector $T$, which is parallel to the tube axis and normal to $C_h$, reflects the 1D translational symmetry of the nanotube.

Without loss of generality, here we use MoS$_2$ as a representative to discuss the effect of QCE on the band-edge level evolution of TMDC nanotubes. In the zone-folding scheme [20], we first calculate the 2D electronic band structure of monolayer MoS$_2$, as shown in Figure 3b,c. Bloch electron wavevectors that satisfy the periodic boundary conditions imposed by the formation of nanotubes are then determined, which leads to the discretization of monolayer Brillouin zone into 1D line segments. From the discretized Brillouin zone, the 2D electronic states are mapped to 1D, resulting in the 1D band-
structures of nanotubes within the zone-folding scheme.

In more technical terms, a nanotube can be unrolled into a hypothetical curvatureless nanoribbon. In this unrolled ribbon, the Bloch wavefunction $\Psi_k(r)$ must find itself after traveling a distance corresponding to the chiral vector $C_h$, that is, $\Psi_k(r + C_h) = \Psi_k(r)$, where $k$ is a 2D crystal momentum. In combination with the Bloch’s theorem, the boundary conditions require that the phase of electron wavefunctions gained due to a translation of $C_h$, that is, $\exp(ik \cdot C_h)$, be unity. This leads to $k \cdot C_h = 2\pi \mu$, where $\mu$ is an integer.

The reciprocal vectors $K_1$ and $K_2$ that correspond to $C_h$ and $T$ can be defined by following standard orthogonality relations between real and reciprocal lattices: $K_1 \cdot C_h = 2\pi$, $K_1 \cdot T = 0$, $K_2 \cdot C_h = 0$, and $K_2 \cdot T = 2\pi$. Using these relations, the crystal momentum $k$ that satisfies $k \cdot C_h = 2\pi \mu$ can be written in terms of $K_1$ and $K_2$ as:

$$k = k \frac{K_2}{|K_2|} + \mu K_1,$$

where $k$ is a continuous real number. Due to the translational symmetry of nanotubes along $T$, the value of $k$ in eq. 1 can be restricted between $-|K_2|/2$ and $|K_2|/2$, that is, between $-\pi/T$ and $\pi/T$, where $T$ equals $|T|$. Furthermore, denoted by $N$ the number of TMDC formula units within the area enclosed by $C_h$ and $T$, it can be proven that $NK_1$ corresponds to a reciprocal lattice vector of the 2D monolayer [20]. As wavevectors differ by a reciprocal lattice vector are equivalent, the choices of $\mu$ can be restricted to between 0 and $N - 1$. These considerations lead to the following formula for mapping the hypothetical 1D band structure $E_{1D}(k)$ of a nanotube from the 2D band structure $E_{2D}(k)$ of monolayer [20]:

$$E_{1D}^\nu(k) = E_{2D}(k \frac{K_2}{|K_2|} + \mu K_1),$$

$$(-\frac{\pi}{T} < k < \frac{\pi}{T}, \mu = 0, ..., N - 1).$$

For each 1D crystal momentum $k$, there are $N$ branches. Each branch represents a slice of the corresponding 2D band structure.

We can further express $K_1$ and $K_2$ in the above equation (eq. 2) in terms of the 2D reciprocal lattice vectors of monolayer, namely $b_1$ and $b_2$. It can be proven [20] that for a zigzag $(n, 0)$ nanotube, $N = 2n$, $K_1 = (2b_1 + b_2)/N$, and $K_2 = -b_2/2$, as illustrated in Figure 3d. On the other hand, for an armchair nanotube with the chiral index $(n, n)$, $N$ is still equal to $2n$, but $K_1 = (b_1 + b_2)/N$, and $K_2 = (b_1 - b_2)/2$, as shown in Figure 3g.

Eq. 2 now represents a complete formula for mapping the 1D band structure of a nanotube from that of a corresponding 2D monolayer. We shall emphasize that the
FIG. 3. Effect of circumferential quantum confinement on the band-edge levels of MoS$_2$ nanotubes. (a) Top view of the direct lattice of a monolayer MoS$_2$. The 2D primitive lattice vectors are indicated by $\mathbf{a}_1$ and $\mathbf{a}_2$. The chiral vector $\mathbf{C}_h$ and the corresponding translation vector $\mathbf{T}$ of zigzag nanotubes (shown in blue) and armchair nanotubes (shown in red) are illustrated. (b) 2D band structure of monolayer MoS$_2$. The relative contributions of the Mo $d_{\pi_z}$, $d_{\pi_z} + d_{\sigma_y}$, and $d_{\sigma_x} + d_{\sigma_y}$ orbitals to the electronic states are illustrated. (c) Full-zone 3D band structure of monolayer MoS$_2$. The reciprocal lattice vectors of monolayer MoS$_2$ are indicated by $\mathbf{b}_1$ and $\mathbf{b}_2$. $\mathbf{K}_1$ and $\mathbf{K}_2$ are the reciprocal lattice vectors of $\mathbf{C}_h$ and $\mathbf{T}$. The blue line segments correspond to the unique crystal momentums that satisfy the circumferential periodic boundary conditions of a zigzag nanotube. The separation between two segments equals $|\mathbf{K}_1|$, and the length of each line segment is $|\mathbf{K}_2|$. For a zigzag nanotube with chiral index $(n, 0)$, the number of line segments is $2n$. The hypothetical 1D band structure of a nanotube can be obtained by cutting the band structure of a 2D monolayer along the blue line segments and mapped to 1D along the direction of $\mathbf{K}_2$. (e) Mapped and DFT-calculated band structures of a zigzag (14,0) nanotube, shown as blue and gray curves, respectively. (f) The CBM and VBM levels of mapped 1D band structures are shown as open diamond markers. The DFT calculated results are represented by filled circles. (g,h,i) Similar to (d,e,f), but for armchair nanotubes with chiral indices $(n, n)$. The number of line segments in (g) is also $2n$.

band structure of nanotubes thus obtained only consider the effect of quantum confinement of electronic states along the circumferences of nanotubes. Following this scheme, we have calculated the mapped band structures of a zigzag (14,0) and an armchair (14,14) nanotubes, whose diameters are 15 Å and 25 Å, respectively. The results are shown in Figure 3e and Figure 3h, respectively. In these figures, DFT-calculated band structures are plotted together with the mapped ones for comparison. It can be seen that, although the mapped and DFT-calculated band structures share similar features in terms of band dispersion, the band-edge levels and bandgaps exhibit a significant difference. Furthermore, if we plot the band-edge levels obtained from the zone-folding scheme as a function of tube diameter, as shown in Figure 3f and Figure 3i, they exhibit little variation...
with respect to inverse diameter $1/D$. This indicates that QCE plays a negligible role in the band-edge level evolution of both zigzag and armchair nanotubes.

The above result can be understood on the basis of that, even for a zigzag (14,0) with a diameter as small as 15 Å, there are already 28 line segments ($N = 2n$) cutting through the 2D band Brillouin zone. Since monolayer MoS$_2$ and other 2D TMDCs are semiconductors with a bandgap around 1–3 eV as well as relatively large electron and hole effective masses [39, 40], the 1D line segments can sample 2D electron states whose energies are very close to the VBM and CBM of a 2D monolayer. In fact, for armchair $(n, n)$ nanotubes, it is can be seen from Figure 3g that one of the line segments is guaranteed to pass through both the K and $K'$ points of the 2D hexagonal Brillouin zone, where the CBM and VBM of monolayer TMDC reside. This results in exactly the same band-edge levels of the mapped 1D and the original 2D systems for armchair nanotubes. For zigzag nanotubes of very small diameters (15 Å), a very small amount of raising of CBM and lowering of the VBM is observable in Figure 3f, but the trend is opposite to the DFT-calculated results in this diameter regime.

Although the 2D-to-1D band-structure mapping leads to the conclusion that circumferential QCE has little influence on the band-edge levels of nanotubes, it does provide important insight into the electronic structure of TMDC nanotubes. As a key example, the band-structure mapping explains why in zigzag nanotubes, both the VBM and CBM are always located at the Γ point of the 1D Brillouin zone. In fact, it can be seen from Figure 3d that, for zigzag nanotubes, within the zone-folding scheme, the line segments for band-structure mapping pass through both the Γ and K valleys of 2D Brillouin zone at the centers of the line segments. Hence, when plotting out the 1D band structure, the highest Γ-valley and K-valley derived valence-band energies, as well as the lowest K-valley derived conduction-band energies, will all be mapped to the Γ points of the 1D Brillouin zones of zigzag nanotubes (Figure 3c). As a result, zigzag nanotubes are expected to have both VBM and CBM located at Γ. If we consider effects beyond QCE as perturbations to the mapped 1D band structures, zigzag nanotubes are expected to be direct-bandgap semiconductors regardless of tube diameters, in consistent with DFT results.

Since the valence-band energies of TMDC monolayers at Γ and K are quite close ($E_{VB}^K - E_{VB}^\Gamma$ around 0.1 eV for MoS$_2$ monolayer [41] and 0.38 eV for MoSe$_2$ monolayer [42]), if effects beyond QCE are considered, the VBM of zigzag nanotubes may either derive from the valence-band electronic states of 2D monolayer at or near the K valley, which have mainly in-plane Mo $d_{x^2-r^2} + d_{xy}$ and S $p_x + p_y$ character, or derive from monolayer states at Γ, which mainly have Mo $d_{z^2}$ and S $p_z$ contributions (see also Figure S2) [43, 44]. The CBM of zigzag nanotubes are expected to derive from the conduction-band states in the K-valley electronic states of monolayer, which mainly have Mo $d_{z^2}$ character with a small S $p_x + p_y$ contribution.

On the other hand, in armchair nanotubes, we can see from Figure 3g that, after band-structure mapping, K-derived electronic states are separated from Γ-derived states in the new 1D Brillouin zone. The K-derived states will be located at 2/3 of the Γ-X path, while the Γ-derived states remain at the Γ of the 1D Brillouin zone of a nanotube. Hence, if only QCE effect is considered, armchair nanotubes of TMDCs are direct-bandgap semiconductors with both VBM and CBM located at 2/3 of the Γ-X path. However, effects beyond QCE may lead to the raising of the energy levels of Γ-derived electronic states with respect to K-derived states. In this case, the VBM of nanotubes will shift to Γ (or the vicinity of Γ), and the system may become an indirect-bandgap semiconductor. This is exactly what happens to armchair nanotubes with small tube diameter (Figure 3h).

Now that QCE has been excluded as a major contribution to diameter-dependent band-edge level in TMDC nanotubes, our study will focus on how the band-edges, which derive from the electronic states of monolayer at Γ or K/K' valleys, respond to the effects of flexoelectricity and strain in the nanotubes.

Curvature-Induced Flexoelectric and Electrostatic Potential Effect. When a sheet of 2D material is rolled to form a nanotube, the resulting curvature leads to the redistribution of charge inside and outside the nanotube, generating radial electric polarizations [35, 36, 45–50]. This phenomenon has essentially the same origin as flexoelectricity in bulk crystals, where a strain gradient breaks local inversion symmetry and generates macroscopic polarization [51]. In fact, in reference to a flat TMDC monolayer, the outer chalcogen layer of a TMDC nanotube is stretched, whereas the inner layer is compressed. As a result, in the neighborhood of the surface of a TMDC nanotube, an effective transverse strain gradient of 1/R exists in the layer normal direction [36], where R is the radius of the nanotube. The resulting radial flexoelectric polarization generates an electrostatic potential difference between the inner and outer sides of the nanotube, as illustrated for a MoSe$_2$ zigzag (14,0) nanotube in Figure 4a. The voltage difference is named flexovoltage and denoted by $\Delta V_{flexo}$, which can be computed as $\Delta V_{flexo} = V_{inner} - V_{outer}$. Here $V_{inner}$ and $V_{outer}$ represent the electrostatic potentials of the hollow region inside the tube and the vacuum region far away from the tube surface, respectively. At the leading order, $\Delta V_{flexo}$ is proportional to inverse diameter $1/D$ [36, 45].

The flexoelectric polarization and the corresponding redistribution of charge also change the average electrostatic potential experienced by the electronic states inside a nanotube. This effect will lead to a shift in the absolute energy levels of the electronic states with respect to the vacuum. For a given atomic arrangement and electron density distribution, the local electrostatic potential inside a nanotube is given by $V_{ion}(\mathbf{r}) = V_{ion}(\mathbf{r}) - \frac{|e|}{4\pi\varepsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$, where $V_{ion}(\mathbf{r})$ is the ionic potential from all atoms, and the second term is the Hartree
potential from electrons with density distribution \( n(\mathbf{r}) \). \( e \) is the elementary charge, and \( \varepsilon_0 \) is the vacuum permittivity. The \( V_{\text{elstat}}(\mathbf{r}) \) of a MoSe\(_2\) zigzag (14, 0) nanotube is visualized in Figure 4a.

The average electrostatic potential experienced by an electrostatic state inside a nanotube, whose normalized electron wavefunction given by \( \psi(\mathbf{r}) \), can be calculated as \( V_{\text{elstat}} = \int V_{\text{elstat}}(\mathbf{r})|\psi(\mathbf{r})|^2 d\mathbf{r} \). Since the band-edge states of TMDC monolayers and nanotubes predominantly derive from the \( d \) orbitals of the transition-metal atoms [43, 44, 52], the change in \( V_{\text{elstat}} \) of a band-edge state before and after forming a nanotube, denoted by \( \Delta V_{\text{elstat}} \), can be approximated by the average local electrostatic potential shift near the transition-metal site (\( \Delta V_{\text{core}} \)). \( \Delta V_{\text{core}} \) is calculated within a spherical region centered at the lattice site, with a radius of \( \sim 1.2 \) Å, which is roughly half of the nearest-neighbor distance between Mo and Se. The corresponding electrostatic potential energy shift, \( \Delta E_{\text{core}} = -|e|\Delta V_{\text{core}} \), is similar in magnitude to the energy level shift of the core electrons in the transition-metal atoms, as the core electrons are tightly bound to the nuclei and do not participate in chemical bonding. We have also calculated the average local electrostatic potential shifts of all atoms (including both Mo and Se) in the tube, and found that the difference between the two approaches is small (with a relative difference of less than 10%), indicating the validity of our approach. In other words, \( \Delta V_{\text{core}} \) calculated at the transition-metal site can be well approximate the \( V_{\text{elstat}} \) of band-edge states in TMDC nanotubes.

Figure 4b shows the calculated values of \( \Delta V_{\text{core}} \), together with the values of \( \Delta V_{\text{flexo}} \), for MoSe\(_2\) zigzag nanotubes as a function of inverse diameter \( 1/D \). The calculated \( \Delta V_{\text{flexo}} \) and \( \Delta V_{\text{core}} \) for MoSe\(_2\), WS\(_2\), WSe\(_2\), and MoTeV\(_2\) nanotubes are of similar values, as shown in Figure S3. For TMDC tubes with diameters between 50 Å to 15 Å, \( \Delta V_{\text{flexo}} \) are in the range from 0.2 V to 0.4 V, which are three to four times larger than those of SWCNTs at similar diameters [36], indicating quite strong flexoelectric effects in TMDC nanotubes.

Our result in Figure 4b also indicates that, in the large-diameter limit, \( \Delta V_{\text{core}} \) is around one half of \( \Delta V_{\text{flexo}} \) at the corresponding diameter. This is understandable given that flexoelectricity-induced electrostatic potential change decreases from the inner to outer side of a tube, eventually becoming zero far outside the tube.

With the calculated electrostatic potential change, we can determine the contribution of curvature-induced flexoelectricity on the band-edge levels of TMDC nanotubes. To this end we compute the hypothetical VBM and CBM levels of TMDC nanotubes by adding the calculated electrostatic potential energy shift \( \Delta E_{\text{core}} = -|e|\Delta V_{\text{core}} \) to the CBM and VBM energies of the monolayer, and then compare these model-derived band-edge levels to the DFT-computed VBM and CBM levels of nanotubes. The results for MoSe\(_2\) zigzag nanotubes are shown in Figure 4c.

It can be concluded from Figure 4c that, when tube diameters are around or larger than 50 Å, the shifts in the energy levels of the CBM and VBM of MoSe\(_2\) nanotubes with respect to that of the monolayer can be explained by the curvature-induced flexoelectric effect. At smaller
diameters \((D < 30 \text{ Å for VBM and below 50 Å for the CBM of MoSe}_2\text{ nanotubes})\), however, additional contributions beyond flexoelectricity must be taken into account to explain the evolution of band-edge levels. In particular, the transition from downward to upward shifting in the VBM levels, when \(D\) is below 30 Å, cannot be rationalized within the framework of flexoelectric effect.

**Circumferential Tensile Strain Effect.** Given that flexoelectricity-induced electrostatic effect alone cannot explain the evolution of VBM and CBM in small-diameter tubes, we next investigate the effect of strain on the band-edge levels. As mentioned earlier, when a TMDC monolayer is rolled into a nanotube, the inner layer of chalcogen atoms are compressed while the outer-layer atoms are stretched. This causes a distortion to the trigonal prismatic coordination between the transition-metal and chalcogen atoms. The distortion becomes increasingly severe as the tube diameter decreases, resulting in a rapid increase of bending energy \([53]\). The bending energy in the system, however, can be partially reduced if the tube diameter is slightly enlarged, albeit at the cost of adding circumferential tensile strain energy into the system. That is, enlarging the circumference of a nanotube through bond stretching leads to a decrease in the curvature and thus the bending energy, at the cost of adding tensile strain energy along the circumferential direction of the tube.

The competition between bending energy (which favors a larger tube diameter) and circumferential tensile strain energy (which favors a smaller deviation from the original tube diameter) results in an optimized diameter that is slightly larger than the original value of \(D_0 = |C_h|/\pi\), where \(C_h\) is the chiral vector defined in a pristine monolayer before rolling. In Figure 5a we illustrate the enlargement of the diameter of a MoSe\(_2\) nanotube after structural relaxation in DFT, and present the circumferential tensile strains in MoSe\(_2\) nanotubes as a function of relaxed tube diameters \(D\). The circumferential tensile strain \(\varepsilon\) is defined as the relative change in the circumference of a tube before and after structural relaxation: \(\varepsilon = (\pi D - \pi D_0)/\pi D_0\), that is, \(\varepsilon = D/D_0 - 1\). Both \(D\) and \(D_0\) are measured from the transition-metal atoms. A rapid increase in \(\varepsilon\) when \(D\) is below 50 Å can be observed. The strain versus diameter curve in Figure 5a can be well fitted by \(\varepsilon = \alpha(d/D)^2 + \beta(d/D)^3\), where \(d = 6.5 \text{ Å is the interlayer distance in bulk MoSe}_2\) \([54]\), and \(\alpha = 0.39, \beta = 3.0\) are best-fit numerical coefficients.

The above scaling of circumferential tensile strain \(\varepsilon\) with respect to tube diameter \(D\) can be rationalized within the framework of continuum mechanics. For a rectangular sheet of solid with thickness \(d\), after rolling into a tube, its bending energy per unit volume \(E_{\text{bending}}\) scales with \(1/D\) as \(E_{\text{bending}} = \frac{1}{2}Y(d/D)^2\) at the leading order, where \(Y\) is the in-plane Young’s modulus \([55]\). For better connection to the continuum limit, we take the thickness \(d\) of TMDC monolayers as the interlayer distance of the corresponding bulk. On the other hand, the circumferential tensile strain energy per unit volume \(E_{\text{tensile}}\), at the leading order, is given by \(E_{\text{tensile}} = \frac{1}{2}Y\varepsilon^2\). The total strain energy per unit volume \(E_{\text{total}}\) is then the sum of \(E_{\text{bending}}\) and \(E_{\text{tensile}}\): \(E_{\text{total}} = \frac{1}{2}Y(d/D)^2 + \frac{1}{2}Y\varepsilon^2\).

Since \(\varepsilon = D/D_0 - 1, \varepsilon = 0\) if \(D = D_0\). However, \(\varepsilon = 0\) is not the lowest-energy state: \(E_{\text{total}}\) can be reduced if \(D\) is slightly larger than \(D_0\). Minimizing \(E_{\text{total}}\) with respect to \(D\), we obtain \(\varepsilon = \frac{d^2 D_0}{2Y} \approx \left(\frac{d}{D_0}\right)^2\). The coefficient of the second-order term in \(d/D\) of the \(\varepsilon\) versus \(D\) scaling from this simple analysis is \(1/3\), which is in close agreement with our earlier DFT numerical result of \(\alpha = 0.39\).

The above analysis establishes that both circumferential tensile strain and bending strain exist in TMDC nanotubes. Both types of strain are expected to affect the band-edge levels through strain-induced changes in the electron-orbital interaction and hybridization. This “chemical bonding contribution” adds to the electrostatic contribution from the flexoelectric effect discussed earlier. While the flexoelectric potential shift from curvature-induced flexoelectricity in general causes a lowering of the energy levels of both VBM and CBM with respect to vacuum energy, strain-induced band-edge energy shift can be either positive or negative, depending on the nature of orbital interaction involved in a specific band-edge state.

We first investigate the effect of circumferential tensile strain on the band-edge levels of TMDC nanotubes (the effect of bending strain will be discussed later). This effect can be studied by first looking at the evolution of the band-edge levels of TMDC monolayers under uniaxial tensile strain, and then employing the zone-folding framework developed earlier to deduce the corresponding circumferential strain-induced changes in the band-edge levels of nanotubes.

We again use MoSe\(_2\) monolayers and nanotubes as model systems to illustrate the effect of circumferential tensile strain on the evolution of band-edge states. The strain-dependent electronic structures of TMDC monolayers have been investigated before \([56-59]\), but its connection to the band-edge evolution of TMDC nanotubes has not been carefully studied. Figure 5b,c show that, as uniaxial tensile strain is imposed along the zigzag direction of monolayer, both the absolute energy levels of VBM and CBM at the \(K\) point of 2D Brillouin zone exhibit a downward shift. In contrast, the VBM at \(\Gamma\) point exhibits an upward shift.

The different strain-dependent behavior among the three band-edge states of TMDC monolayers can be rationalized within the tight-binding picture of solid-state electronic structure, in terms of the competition between on-site orbital energy and inter-site orbital hopping energy. The on-site orbital energy is affected by the local electrostatic potential, while the inter-site orbital hopping is sensitive to the distance between neighboring atoms and influences the splitting between bonding and anti-bonding orbitals. The band-edge states of TMDC monolayers are predominantly derived from the \(d\) orbitals of transition-metal atoms \([52, 60]\). As tensile strain causes the increase of the distance between
orbs on neighboring atomic sites, the hopping integrals are in general reduced, leading to a smaller bonding-antibonding splitting. This contributes to a raise in the absolute energy of a bonding orbital and a lowering in the energy of an antibonding orbital.

On the other hand, tensile strain also changes the local electrostatic environment of electron orbitals on each atom, which affects their on-site energies. This effect is akin to the crystal-field effect in chemistry. As in-plane tensile strain is imposed on a TMDC monolayer, the increased interatomic distance causes an overall decrease in the electron density surrounding the core region of each atom (since the contribution to electron density from other atoms is reduced). This leads to an increase in the local electrostatic potential at atomic sites and hence a decrease in the electrostatic potential energies of electron orbitals residing on the atoms. The strain-induced local electrostatic potential change is indeed found in DFT calculations: Figure S4 shows that in a strained MoSe$_2$ monolayer, the electrostatic potential energy of an electron residing at the Mo site decreases almost linearly with uniaxial tensile strain at a rate of $\sim$30 meV per one percent of tensile strain.

Therefore, whether a band-edge state in a monolayer raises or lowers in energy after imposing a tensile strain depends on its bonding/antibonding nature, as well as the competition between bonding effect (inter-site hopping integral) and electrostatic effect (on-site energy). An antibonding orbital will decrease in energy as the two effects add up together, whereas a bonding orbital may either exhibit upward or downward shifting in the absolute energy, depending on which of the two effects is
more dominant. In many semiconductors (but not all), the VBM is a bonding orbital while the CBM is an antibonding orbital. Hence, the absolute band-edge shifts under strain is typically larger in CBM than in VBM, as illustrated schematically in Figure S5.

In a TMDC monolayer, the CBM at $K$ is an antibonding orbital that mainly derives from the transition-metal $d_{z^2}$ orbitals and, to a lesser extent, the chalcogen $p_x + p_y$ orbitals [43]. Hence, when a tensile strain is applied, this antibonding orbital (CBM at $K$) rapidly lowers in energy. In contrast, the top valence-band (VB) states at $K$ and $\Gamma$ are bonding orbitals. The former (VB at $K$) has an in-plane orbital character that mainly derives from the transition-metal $d_{x^2-y^2} + d_{xy}$ and chalcogen $p_x + p_y$ orbitals, whereas the latter (VB at $\Gamma$) has an out-of-plane transition-metal $d_z$ and chalcogen $p_z$ character [43, 44].

DFT results in Figure 5b show that, under uniaxial tensile strain, the energy of the VBM at $K$ exhibits a downward shift (negative deformation potential [59]), whereas the VBM at $\Gamma$ exhibits an upward shift (positive deformation potential). Nevertheless, the absolute values of VB energy shifts at $K$ and $\Gamma$ are both smaller than that of CBM at $K$, in consistent with the competition between bonding/antibonding effect and electrostatic effect in the strain-induced variation of bonding orbitals.

When the uniaxial tensile strain imposed on a MoSe$_2$ monolayer is beyond a critical value ($\sim 4.9\%$), the energy of VBM at $K$ becomes higher than that of VBM at $\Gamma$, resulting in a direct-to-indirect bandgap transition in MoSe$_2$ monolayer (Figure 5c). Similar strain-induced band-edge evolution also occurs in other TMDCs monolayers, and the critical strain of direct-to-indirect bandgap transition increases in the order of MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$, and MoTe$_2$ [58, 59]. This order is mainly due to the larger $K-\Gamma$ energy separations in the valence bands of selenide monolayers than those in the sulfide counterparts [41, 42, 44], as the slopes of strain-dependent VBM energies are quite similar among different TMDC monolayers [59]. Besides, although the results presented here are for TMDC monolayers uniaxially stretched along the zigzag direction, previous studies have shown that, due to the in-plane isotropy of TMDC monolayers, uniaxial strain along other directions (such as the armchair direction) leads to almost identical results of absolute band-edge shifts in TMDC monolayers [58, 59].

On the basis of tensile-strain induced band-edge evolution in TMDC monolayers, we can invoke the zone-folding scheme of monolayer-to-tube electronic-structure mapping as discussed earlier, and expect that the circumferential tensile strain in TMDC nanotubes would induce alterations in the corresponding mapped band-edge state. With respect to armchair nanotubes, since both the VBM and CBM at $K$ in monolayer are mapped to 2/3 of the $\Gamma$-$X$ path in the 1D Brillouin zone of nanotube ($k = 2\pi/3T$), whereas the VB state at $\Gamma$ in monolayer is mapped to the $\Gamma$ of nanotube, it is expected that in armchair TMDC nanotubes, as diameter decreases, circumferential tensile strain will cause downward shifts of both CBM and VBM at $k = 2\pi/3T$, but an upward shift of the VBM at $\Gamma$. When the diameter of a tube is sufficiently small, circumferential tensile strain will eventually cause the energy level of VBM at $\Gamma$ to become higher than that of the VBM at $k = 2\pi/3T$, rendering small-diameter armchair nanotubes indirect bandgap semiconductors. This direct-to-indirect bandgap transition of armchair nanotubes was indeed observed in earlier [22, 32, 34] and our DFT calculations (Figure S1). Accompanying this direct-to-indirect bandgap transition is a change in the VBM from $K$ valley-derived to $\Gamma$ valley-derived.

On the other hand, when it comes to zigzag TMDC nanotubes, since the monolayer VBM and CBM states at (or near) $K$, as well as the monolayer VBM state at $\Gamma$, are all mapped to the $\Gamma$ point of 1D Brillouin zone of the corresponding nanotube, zigzag nanotubes are expected to remain direct-bandgap semiconductors regardless of the tube diameter. Nevertheless, the VBM of large-diameter zigzag nanotubes are expected to derive from the monolayer VBM at $K$ and have similar orbital characters, whereas the VBM of small-diameter zigzag nanotubes are expected to derive from monolayer VBM at $\Gamma$, since in a uniaxially strained monolayer, the energy level of VBM at $\Gamma$ eventually becomes higher than that of VBM at $K$. Hence, a change in the orbital character of VBM will also occur in small-diameter zigzag nanotubes. Before the occurrence of this change in band-edge orbital character, the absolute energy level of VBM in zigzag nanotubes is expected to exhibit a downward shift as the tube diameter decreases, whereas after the transition in orbital character, decreasing tube diameter will raise the VBM energy. Thus, despite the chirality difference, the diameter dependence of the band-edge levels of armchair and zigzag nanotubes exhibit the same trend, as indeed observed in our DFT calculations (Figure 1c,d and Figure 2a–c).

The change in the orbital character of VBM in MoSe$_2$ zigzag nanotubes from large-diameter to small-diameter ones is shown in Figure 5d. We can see from the figure that, when the diameter of a MoSe$_2$ zigzag nanotube is $\sim 41 \, \text{Å}$, the VBM has an in-plane orbital character with mostly Mo $d_{z^2-y^2} + d_{xy}$ contribution. In contrast, in a smaller-diameter tube with $D = 20 \, \text{Å}$, the VBM has an out-of-plane character with Mo $d_z$ and Se $p_z$ character. This is in consistent with the zone-folding of zigzag nanotubes from a strained monolayer. In Figure 5e, we further track the energies of topmost in-plane and out-of-plane VB orbitals as a function of tube diameter, and find that the transition of VBM character from in-plane $d_{z^2-y^2} + d_{xy}$ to out-of-plane $d_z$ orbitals occurs at a diameter of $\sim 30 \, \text{Å}$. This is in line with the fact that, at this diameter, the VBM energy levels of MoSe$_2$ nanotubes start to increase with the decrease of tube diameters.

The above results allow us to quantitatively model the diameter-dependent band-edge shifts of TMDC nanotubes by taking into account both flexoelectric effect
and circumferential tensile strain effect. To this end, we first revisit Figure 4b, where we calculate the shift of average electrostatic potential near the Mo site in MoSe$_2$ nanotubes with respect to that of MoSe$_2$ monolayer, and we show in Figure 4c that the electrostatic potential shifts cause a lowering of both VBM and CBM in MoSe$_2$ nanotubes. These results, however, were calculated from relaxed TMDC nanotubes, which possess circumferential tensile strain after structural optimization. However, as concluded from our earlier discussion of strained monolayer, in addition to curvature-induced flexoelectric potential effect, the bond-distance change induced by circumferential tensile strain can also cause an electrostatic potential energy shift in TMDC nanotubes (Figure S4). Hence, if we want to account for the effects of flexoelectric potential and circumferential tensile strain together, directly adding the total band-edge energy shifts caused by circumferential tensile strain (as modeled using uniaxially tensile strained monolayers) on top of the total electrostatic potential energy shifts of nanotubes in Figure 4c may cause a double counting of electrostatic contribution. Instead, the correct approach would be adding only the bonding part of the contribution $\Delta E^{\text{bonding}}$ from circumferential tensile strain. $\Delta E^{\text{strain}}$ can be obtained by subtracting the tensile strain-induced electrostatic-potential energy shift $\Delta E^{\text{strain}}$ from the total energy-level shift of VBM or CBM in monolayers, as illustrated in Figure S5. The results of $\Delta E^{\text{strain}}$ for uniaxially strained MoSe$_2$ monolayers are presented in Figure S6.

To compare the flexoelectricity-induced and circumferential tensile strain-induced electrostatic potential energy shifts, we carried out the following computational experiment: when relaxing the structure of a MoSe$_2$ nanotube rolled from a 2D monolayer, the positions of transition-metal atoms are fixed in space, while chalcogen atoms are allowed to relax in DFT. This fixes the diameter of the tube during structural relaxation. The nanotube after the restricted relaxation will thus not possess circumferential tensile strain. We then compute the electrostatic potential energy shifts near the Mo site in such restrictedly relaxed nanotubes (zero circumferential tensile strain), using the same methodology as in fully relaxed nanotubes. The result, shown in Figure S7, indicates that for tube diameter above 50 Å, the flexoelectric effect dominates the electrostatic potential energy shifts, as circumferential tensile strain is small in this diameter regime (Figure 5a). However, for tube diameter below 40 Å, the circumferential tensile strain-induced electrostatic potential energy shift is comparable or even larger than the flexoelectric contribution.

Having obtained the bonding part of the circumferential tensile strain-induced band-edge shifting $\Delta E^{\text{strain}}_{\text{bonding}}$, we then model the VB energies of nanotubes as $V_{\text{BM tube}} = V_{\text{BM mono}} + \Delta E^{\text{strain}}_{\text{core}} + \Delta E^{\text{strain}}_{\text{bonding}}$, where $V_{\text{BM tube}}$ and $V_{\text{BM mono}}$ represent the VB energies of nanotube and monolayer, respectively. The model for CBM is analogous. We then calculate and plot the modeled VB and CBM of MoSe$_2$ zigzag nanotubes and compare the results to actual DFT-computed values, as shown in Figure 5f (see also Figure 5e for a more specific comparison between model and DFT for topmost in-plane and out-of-plane VB orbitals). The results demonstrate that for tube diameter above 30 Å, combining flexoelectric effect and circumferential tensile strain effect can well explain the evolution of the energy levels of both VBM and CBM in MoSe$_2$ nanotubes. In particular, the rapid upward shifts in VBM energies at small tube diameter are correctly captured.

**Bending Strain Effect.** While our model combining flexoelectric and circumferential tensile strain effects can well explain the evolution of band-edge levels in TMDC nanotubes, it can be seen from Figure 5f that the model prediction becomes less quantitatively accurate as tube diameter becomes smaller, especially when the tube diameter is below the critical point of transition in VBM orbital character. This is because, as tube diameter decreases, bending strain will start to play a more important role in the band-edge evolution, whose effect has not been included in our model. Indeed, when the tube diameter is below the transition diameter, both the VBM and CBM of TMDC nanotubes have mainly transition-metal $d_{z^2}$ characters. At the leading order, curvature will reduce the hopping integral $t$ between $d_{z^2}$ orbitals on adjacent sites as $t = t_0 - \gamma (\frac{\alpha}{R})^2$, where $\gamma$ is a coefficient, $\alpha$ is the distance between two neighboring sites, and $R$ is the tube radius [61, 62]. A decrease in $R$ will contribute to a decrease in the hopping integral $t$. Hence, bending strain will contribute further to decreased bonding-antibonding splitting in small-diameter tubes, leading to additional upward shifts of VBM and downward shifts of CBM, which is consistent with the results in Figure 5f.

To sum up the preceding discussions, the diameter-dependent band-edge evolution of TMDC nanotubes can be well understood by taking into account the effects of flexoelectricity, circumferential tensile strain, and bending strain. Flexoelectric potential effect dominates in large-diameter (above 50 Å) nanotubes, lowering both the CBM and VBM of TMDC nanotubes with respect to the corresponding values in a monolayer, whereas circumferential tensile and bending strain effects are responsible for the rapid downward and upward shifts of the CBM and VBM in small-diameter tubes, respectively. In particular, circumferential tensile strain is responsible for the change of the VBM character from in-plane to out-of-plane orbitals, which causes the non-monotonic diameter-dependent variation of the VBM energy levels.

**Photoluminescence Quenching in Small-Diameter TMDC Nanotubes.** Our study of the diameter-dependent band-edge evolution in TMDC nanotubes also provides insight into the optical properties of these nanotubes. A TMDC monolayer can be considered as a tube with an infinitely large radius of curvature. The five Mo- and W-dichalcogenides discussed in this work are all direct-bandgap semiconductors in the monolayer form and exhibit interband photoluminescence [37, 38, 41, 42, 57, 63]. However, on the basis
of our analysis, neither armchair nor zigzag nanotubes of TMDC are expected to exhibit photoluminescence below a critical tube diameter. In armchair nanotubes, the disappearance of photoluminescence is due to a direct-to-indirect bandgap transition below the critical diameter. In zigzag nanotubes, however, it is caused by a change in the orbital character of VBM from mainly in-plane transition-metal \( d_{x^2−y^2} \) plus out-of-plane transition-metal \( d_z \) plus chalcogen \( p_z \). As the CBM orbital remains predominantly of the transition-metal \( d_z \) character regardless of the tube diameter, the dipole matrix elements between VBM and CBM will vanish after the transition in VBM character. This is because, for non-zero dipole matrix elements, the initial and final states of optical transition need to have different parity, which is no longer the case after the transition in VBM character. The symmetry-forbidden optical transition [26] thus results in the disappearance of photoluminescence in small-diameter zigzag nanotubes. Other chiral nanotubes are not expected to have photoluminescence below a critical diameter of a similar value either, as based on the 2D-to-1D zone folding discussed earlier, all small-diameter chiral TMDC nanotubes shall become indirect bandgap semiconductors below a critical diameter, due to circumferential tensile strain effect, as only in the special case of zigzag nanotubes would both the \( K \) and \( \Gamma \) points of the 2D Brillouin zone of a corresponding monolayer be mapped to the same \( \Gamma \) point in the 1D Brillouin zone of a nanotube (see Figure 3d and 3g).

On the basis of the above discussion of the relation between band-edge character and photoluminescence, it is clear that the diameter value at which the photoluminescence of TMDC nanotubes disappears is the same as when the diameter dependence of VBM energy levels changes sign. From Figures 1c,d and Figures 2a–c, we determine that the transition diameters in MoS\(_2\), WS\(_2\), MoSe\(_2\), WSe\(_2\), and MoTe\(_2\) nanotubes are about 55 Å, 50 Å, 30 Å, 28 Å, and 29 Å, respectively. Previous DFT studies have only discussed the direct-to-indirect bandgap transition in armchair nanotubes of TMDCs, where the transition diameters of MoS\(_2\) and MoSe\(_2\) armchair nanotubes were separately determined to be 52 Å and 33 Å [32, 34]. Experimentally, Liu et al. carried out optical measurements of single-walled MoS\(_2\) grown on BN nanotubes and determined that photoluminescence is still present in MoS\(_2\) nanotubes with a diameter around 60–70 Å, with which our DFT results are consistent [64]. Our results indicate that MoSe\(_2\), WSe\(_2\), and MoTe\(_2\) nanotubes have smaller critical diameters of photoluminescence quenching than MoS\(_2\) and WS\(_2\) nanotubes, making them (Se- or Te-based TMDC nanotubes) more attractive for certain optoelectronic applications.

**Band Alignment in 1D vdW Heterostructures of TMDC Nanotubes.** Having understood the diameter-dependent evolution of the band-edge levels and orbital characters of individual TMDC nanotubes, we next investigate the band alignment of coaxial TMDC nanotubes in 1D vdW heterostructures. An example of such 1D vdW heterostructure was introduced in Figure 1a, where a WS\(_2\)@MoS\(_2\) heterostructure that consists of a single-walled WS\(_2\) nanotube nested in a larger-diameter MoS\(_2\) nanotube is illustrated.

It has been known that in the case of 2D vdW heterostructures formed between semiconducting Mo- and W-dichalcogenide monolayers, with the only exception of the stacking between WSe\(_2\) and MoTe\(_2\) (which forms Type I band alignment), all the other nine 2D vdW heterostructures exhibit Type II band alignment [4, 5, 65, 66]. However, for 1D vdW heterostructures of TMDC nanotubes, we have demonstrated that tube diameter strongly affects the band-edge levels of individual nanotubes. Hence, when two TMDC nanotubes of different materials types and tube diameters are brought together, the band-edge alignment between the nanotubes will depend on the specifics of tube diameters. Furthermore, as a smaller-diameter TMDC nanotube is nested inside a larger-diameter one, the flexovoltage generated by the outer tube will cause an additional shift of the band energy levels in the inner tube [35]. The diameter-dependent band-edge levels of individual nanotubes, in combination with the flexovoltage effect (and possibly other intertube coupling effects, which will be discussed later), are expected to cause a significant difference between the band alignment of TMDC nanotubes in a 1D vdW heterostructure versus its 2D counterpart, and possibly induce transitions between different types of band alignment. This intriguing possibility is investigated below.

We first present our results on the band alignment in 1D vdW heterostructures formed between zigzag nanotubes of MoS\(_2\) and WS\(_2\) (the results for heterostructures of armchair nanotubes are found to be similar). The diameter dependence of the VBM and CBM levels of individual MoS\(_2\) and WS\(_2\) nanotubes have been shown in Figure 1c,d, and the flexovoltages \( \Delta V_{\text{flexo}} \) of TMDC nanotubes are shown in Figure S3.

In a coaxial 1D vdW heterostructure, the diameter of the inner nanotube is, by definition, smaller than the outer one. As such 1D vdW heterostructures are expected to form through templated growth of an outer tube on an inner one [7], or else via elemental substitution [67] in double-walled nanotubes, we consider the difference in radii between the outer and inner tubes in a 1D vdW heterostructure to be the same as the interlayer distance \( d \) of a corresponding 2D vdW heterostructure, which in the case of 2D MoS\(_2\)/WS\(_2\) heterostructure has a value \( d \approx 6.2 \) Å [68]. For a zigzag nanotube with a chiral index \((n,0)\), the tube diameter \( D \) is related to the chiral index \( n \) as \( D = n a_0(1 + \varepsilon)/\pi \), where \( a_0 = |a| \) is the in-plane lattice constant of the corresponding TMDC monolayer (see Figure 3a), and \( \varepsilon \) is the circumferential tensile strain discussed earlier. Based on \( D_{\text{outer}} - D_{\text{inner}} \approx 2d \), we determine that the difference in chiral index between the outer and inner nanotubes of a 1D vdW heterostructure is \( \eta_{\text{outer}} - \eta_{\text{inner}} \approx 12 \). Hence, we investigate the
FIG. 6. Band alignment in 1D vdW heterostructures consist of WS$_2$ nanotubes nested in MoS$_2$ nanotubes. (a) CBM and VBM levels of individually separated MoS$_2$(n$_{outer}$, 0) nanotubes and smaller-diameter WS$_2$(n$_{outer}$ − 12, 0). D$_{outer}$ denote the diameters of MoS$_2$ nanotubes in the heterostructures. Since the tubes are separated in this case, the effect of flexoelectric potential $\Delta V_{\text{flexo}}$ on the band alignment is not considered. (b) Alignment of CBM and VBM after the nanotubes form coaxial WS$_2$@MoS$_2$ 1D vdW heterostructures. The positive flexovoltage of an outer MoS$_2$ nanotube leads to a downward shifting of the energy levels of the inner WS$_2$ nanotube by an amount of $-|e|\Delta V_{\text{flexo}}$. (c) Calculated electronic band structure of a WS$_2$(10, 0)@MoS$_2$(22, 0) heterostructure. Projection of electronic states to the inner WS$_2$ nanotube is denoted by blue filled circles and to the outer MoS$_2$ nanotube by red open circles, with the relative weight represented by the size of the markers. (d) The CBM and VBM wavefunctions (probability density isosurfaces) of the WS$_2$(10, 0)@MoS$_2$(22, 0) heterostructure, viewed along the tube-axis direction.

The band alignment in 1D vdW heterostructures formed between (n$_{outer}$, 0) and (n$_{outer}$ − 12, 0) nanotubes of MoS$_2$ and WS$_2$.

Figure 6a shows the alignment between the VBM and CBM of larger-diameter MoS$_2$(n$_{outer}$, 0) nanotubes and smaller-diameter WS$_2$(n$_{outer}$ − 12, 0) nanotubes as a function of n$_{outer}$ and D$_{outer}$, before coaxial 1D vdW heterostructures are formed. Between such individually separated nanotubes of MoS$_2$ and WS$_2$, at large tube diameter D$_{outer}$, the band alignment belongs to the Type II category, which is in consistent with MoS$_2$/WS$_2$ 2D vdW heterostructures formed by stacking of monolayers. As the diameters of the nanotubes (determined by n$_{outer}$) decrease, because the CBM energy level of the smaller-diameter WS$_2$(n$_{outer}$ − 12, 0) nanotube decreases faster with n$_{outer}$ than that of the larger-diameter MoS$_2$(n$_{outer}$, 0) nanotube, the band alignment eventually becomes Type I, albeit at a small tube diameter of D$_{outer}$ ≈ 28 Å.

However, when the WS$_2$ and MoS$_2$ nanotubes form coaxial 1D vdW heterostructures, the positive flexovoltage $\Delta V_{\text{flexo}}$ of the outer MoS$_2$ nanotube, generated in the region where the smaller-diameter WS$_2$ nanotube is nested, will cause an additional lowering of the energy levels of the inner tube, thus accelerating the transition of band alignment from Type II to Type I. This can be clearly seen from Figure 6b, where we have added the additional electrostatic potential energy shifts $-|e|\Delta V_{\text{flexo}}$, caused by the flexovoltage of the outer MoS$_2$ nanotube, to the VBM/CBM levels of the inner WS$_2$ nanotube. The band alignment between the coaxial nanotubes is then replotted. It can be seen that the combined effects of diameter-dependent band-edge levels and flexovoltage-induced electrostatic potential shift lead to a transition from Type II to Type I band alignment in the WS$_2$@MoS$_2$ 1D vdW heterostructure at a larger
critical diameter of $D_{\text{outer}} \approx 35\,\text{Å}$. The critical transition point corresponds to a WS$_2$(22,0)@MoS$_2$(34,0) heterostructure.

To confirm the predicted existence of transition in band alignment from Type II to Type I in WS$_2$@MoS$_2$ 1D vdW heterostructures, we have explicitly calculated the electronic band structure of a WS$_2$(10,0)@MoS$_2$(22,0) coaxial heterostructure. The almost identical lattice constants of MoS$_2$ and WS$_2$ nanotubes along the tube-axis direction ($T = \sqrt{3}a_0$, with $a_0 \approx 3.18\,\text{Å}$), as well as the relatively small values of $n_{\text{outer}}$ and $D_{\text{outer}}$ in this model system, allow us to build an explicit atomistic representation of the 1D vdW heterostructure and carry out DFT calculations of its electronic structure. Note that such calculations would be extremely challenging if a 1D vdW heterostructure is built from TMDC nanotubes with incommensurate lattice constants along the tube-axis direction (which is the case for heterostructures formed between all other Mo- or W-dichalcogenide nanotubes), as a much larger supercell would be needed to model a heterostructure in which both the inner and outer nanotubes are in strain-free state along the translational symmetric direction. The challenges of direct first-principles calculation of the electronic structures of 1D vdW heterostructures represent a key reason that, after using the present small-size model system to demonstrate the reliability of our approach, we will determine the band alignment in all other 1D vdW heterostructures using the same approach, that is by combining the diameter-dependent band energy evolution of individual TMDC nanotubes with the inter-tube coupling effect coming from flexovoltage.

The calculated electronic band structure of the WS$_2$(10,0)@MoS$_2$(22,0) heterostructure is shown in Figure 6c. Projection of the electronic states near the fundamental gap onto the inner and outer MoS$_2$ nanotubes demonstrates that the predominant contributions to both the VBM and CBM of the heterostructural system stem from the inner WS$_2$(10,0) nanotube. This is also explicitly shown in Figure 6d, where it can be seen that both the VBM and CBM wavefunctions are localized on the inner tube. The results thus confirm that the WS$_2$(10,0)@MoS$_2$(22,0) heterostructure has a Type I band alignment, in consistent with the prediction in Figure 6b.

So far, we have neglected the electronic coupling between the inner and outer nanotubes in a 1D vdW heterostructure beyond the flexovoltage effect. We show below that this approximation is sufficient to determine the band alignment in 1D vdW heterostructures under most circumstances. With respect to the alignment of CBM, since the CBM of TMDC nanotubes are all predominantly derived from the $d$ orbitals of the transition-metal (Mo or W) atoms, with only a minor contribution from the $p_x/p_y$ orbitals of chalcogen (S, Se, or Te) atoms, the CBM wavefunctions of TMDC nanotubes are well confined within respective nanotubes. Thus, the electronic wavefunctions of CBM in inner and outer nanotubes have little overlap, resulting in negligible effect of hybridization on the CBM energy levels. This rather weak hybridization of CBM in TMDC heterostructures has been shown in the case of 2D vdW heterostructures of TMDC monolayers [68], and it is also clearly shown for the WS$_2$@MoS$_2$ 1D vdW heterostructure in Figure 6c. Therefore, the CBM band alignment determined using our approach is rather robust in practice, which is corroborated by comparing the calculated CBM energy level of the WS$_2$(10,0) nanotube in the 1D vdW heterostructure in Figure 6b and Figure 6c, where we find that the difference in CBM energy between our approach and explicit DFT calculation is as small as 0.035 eV.

The effect of intertube hybridization on the VBM alignment of inner and outer nanotubes in 1D vdW heterostructures is more subtle than that of CBM. In a 2D vdW heterostructure of TMDC monolayers, ref. [68] shows that the hybridization between the monolayer VBM states at the $K$ point of 2D Brillouin zone, which mainly derive from the $d_{xy}+d_{xz}+d_{yz}$ orbitals of transition-metal atoms, is also negligible. On the other hand, the hybridization between the VBM states at $\Gamma$, which have out-of-plane characters and mainly derive from the transition-metal $d_z^2$ and chalcogen $p_z$ orbitals, depends on the relative energy levels of the VBM states prior to the formation of the 2D vdW heterostructure. If the VBM at $\Gamma$ of the two monolayers are close in energy, then hybridization effect can be strong, even pushing the energy of interlayer “antibonding” state above that of the highest VBM at $K$, as in the case of MoS$_2$/WS$_2$ 2D vdW heterostructure [68]. However, in our case of 1D vdW heterostructures of TMDC nanotubes, the strong internal flexoelectric electric field pointing from the inner side to the outer side of a nanotube, whose magnitude is estimated to be on the order of $\Delta V_{\text{flexo}}$ divided by the thickness of the tube wall (up to 1 V/nm in small-diameter nanotubes), will suppress the delocalization of VBM wavefunctions between inner and outer nanotube. Such electric field induced localization of electronic states has been shown for TMDC bilayers under a vertical electrical field, as well as in double-walled nanotubes [30, 69]. Hence, the effect of hybridization on the energy levels of VBM in 1D vdW heterostructure is limited. This is again corroborated by the explicitly calculated band-energy levels of the WS$_2$(10,0)@MoS$_2$(22,0) heterostructure in Figure 6c, where by comparison with Figure 6b (obtained by considering only the flexovoltage effect), we determine that the VBM energy-level difference between the two approaches is also small (within 0.15 eV).

The computationally proven existence of band-alignment transition from Type II to Type I in WS$_2$@MoS$_2$ 1D vdW heterostructures motivates us to investigate all 20 possible types of 1D vdW heterostructures formed between MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, and WSe$_2$ nanotubes. In Figure S8 to Figure S17, we present the calculated band alignment between $(n_{\text{outer}}, 0)$ and $(n_{\text{outer}}−12, 0)$ nanotubes of these TMDCs before and after forming 1D vdW heterostructures. The most important finding from these calculations, as shown in Figure 7,
FIG. 7. 1D vdW heterostructures that exhibit Type I band alignment at large tube diameters. (a) Calculated band alignment between semiconducting Mo- and W-dichalcogenide monolayers. Blue and red represent valence and conduction band, respectively. (b) Band alignment between inner MoSe₂ and outer WS₂ nanotubes in MoSe₂@WS₂ 1D vdW heterostructures, constructed from calculated VBM and CBM energy levels of individual WS₂(outer, 0) and MoSe₂(outer - 12, 0) nanotubes, and accounting for the additional effect of the flexoelectric potential ΔVflexo generated by the outer WS₂ nanotube on the inner MoSe₂ nanotube. (c,d) Similar to (b), but for MoTe₂@MoSe₂ and MoTe₂@WS₂ 1D vdW heterostructures, respectively.

The reason that these three 1D vdW heterostructural systems can undergo Type II to Type I band alignment transition at large tube diameters can be understood by considering the band alignment of their corresponding 2D monolayers, which are shown in Figure 7a. Between any two of MoSe₂, MoTe₂, and WS₂ monolayers, the difference in their CBM energy levels is small – less than 0.2 eV, while the difference in their VBM energy levels is relatively large (on the order of 0.5 eV or higher). The small difference in the CBM level of the three TMDCs has been found to be quite robust with respect to the computational methodologies employed [66]. Although the three TMDCs form Type II band alignment in 2D vdW heterostructures, in 1D vdW heterostructures, if the inner tube belongs to a TMDC that has higher CBM level than the outer TMDC in the monolayer form, due to the combined effect of the inner tube experiencing more diameter-induced lowering of the CBM, as well as the additional lowering of band energies due to the flexovoltage generated by the outer tube, the CBM level of the inner
tube can be pulled down to such a level that it becomes lower than the CBM of the outer tube. Meanwhile, because the VBM energy difference between the monolayers of inner and outer TMDCs is relatively large, the VBM level of the inner tube remains higher than that of the outer tube. Consequently, a transition from Type II to Type I band alignment is readily induced in these three 1D vdW heterostructural systems.

The flexovoltages $\Delta V_{\text{flexo}}$ in TMDC nanotubes, which are on the order of 0.15–0.2 eV when the tube diameter is around 50 Å (Figure S3), is by no means a small number. Even when the tube diameter increases to 100 Å, $\Delta V_{\text{flexo}}$ is still on the order of 0.1 eV. Such large values of flexovoltages alone are enough to shift the relative order of CBM levels in certain 1D vdW heterostructures with close CBM energies between individual nanotubes.

Hitherto, we have established a complete framework for band alignment in 1D vdW heterostructure, by not only fully understanding the diameter-dependent evolution of the band-edge levels in individual nanotubes, but also unraveling the crucial effect of flexovoltage in inducing the transition from Type II to Type I band alignment in certain 1D vdW heterostructures. Although these results are built on a solid foundation, we would like to comment on a key technical aspect of our study. A question that a prospective reader may ask is whether DFT can accurately predict the band alignment of these 1D vdW heterostructures. Our answer to this question is solidly positive. First of all, a critical influencing factor of band alignment in 1D vdW heterostructures, that is the flexoelectricity and flexovoltage effect, is the ground-state property of a TMDC nanotube, for which DFT has excellent predictive accuracy. Second, although DFT is known to underestimate the bandgap of semiconductors, a previous study of band-edge levels in TMDC monolayers using more sophisticated GW calculations indicates that the underestimates of bandgap in DFT are relatively uniform across different TMDCs [66]. In particular, the relative energy differences of CBM levels among different TMDC monolayers are changed very little when switching the calculation method from DFT to GW. Thus, the results of this work are expected to be robust even if more sophisticated (but computationally extremely demanding) methodologies are adopted.

CONCLUSIONS

In conclusion, through comprehensive first-principles calculations and theoretical analysis, we have established a complete framework for understanding the band alignment in 1D vdW heterostructures of coaxial TMDC nanotubes. We have shown that the CBM levels of individual TMDC nanotubes exhibit a rapid and monotonic lowering when the tube diameter is reduced below 50–60 Å, whereas the VBM of TMDC nanotubes display an initial lowering before rising, with the transition diameter varies from ∼50 Å in MoS$_2$ and WS$_2$ nanotubes to ∼30 Å in MoSe$_2$, WSe$_2$, and MoTe$_2$ nanotubes. These properties can be fully explained in terms of curvature-induced flexoelectricity and the associated electrostatic potential effect, as well as the intrinsic circumferential tensile strain and bending strain within the TMDC nanotubes. Quantum confinement effect is found to play a negligible role on the band-edge evolution.

When the diameter of a TMDC nanotube is above 50 Å, the band-edge level evolution of both VBM and CBM in the nanotube is predominantly determined by the flexoelectricity-induced electrostatic potential effect, which lowers both the CBM and VBM levels of TMDC nanotubes by 50–100 meV in the diameter range of 50–100 Å. When the tube diameter is below 50 Å, the effect of circumferential tensile strain, which can reach ∼2% in a TMDC nanotube with a diameter of ∼30 Å, is the main source responsible for the rapid lowering of the CBM and the non-monotonic change of the VBM. We have shown that, the transition of the VBM of TMDC nanotube from downward to upward shifting as diameter reduces is caused by a change of the VBM orbital character from predominantly in-plane transition-metals $d_{xz}$-$d_{yz}$-$d_{xy}$ orbitals to out-of-plane transition-metals $d_{z^2}$ plus the chalcogen $p_z$ orbitals. The transition in the VBM orbital character of small-diameter TMDC nanotubes can be readily understood using the scheme of Brillouin-zone folding from the 2D band structures of uniaxially strained monolayer to the 1D band structures of nanotubes. We also show that the transition in the orbital character of VBM leads to direct-to-indirect bandgap transition in small-diameter armchair or chiral nanotubes, as well as photoluminescence quenching in zigzag nanotubes.

Building on the comprehensive understanding of the diameter-dependent evolution of the band-edge levels in individual TMDC nanotubes, we have investigated the band alignment in all 20 possible types of 1D vdW heterostructures formed between Mo- and W-dichalcogenide nanotubes. We show that the large flexoelectric voltages generated by outer nanotubes on the inner nested nanotubes play a crucial role in determining the band alignment of TMDC nanotubes in 1D vdW heterostructures. The combination of diameter-dependent band-edge levels, as well as the flexovoltage effect, leads to a transition from Type II to Type I band alignment in multiple 1D vdW heterostructural systems. In particular, we identify three 1D vdW heterostructural systems, namely MoSe$_2$@WS$_2$, MoTe$_2$@MoSe$_2$, and MoTe$_2$@WS$_2$, that already exhibit Type II to Type I transition when the outer-tube diameter is around or above 50 Å. These large-diameter 1D vdW heterostructural systems should still exhibit photoluminescence, and it is expected that they could be fabricated experimentally with relative ease, making these 1D heterostructural systems attractive for nanoscale optoelectronic applications.

Altogether, our work lays down a key foundation for understanding band alignment in 1D vdW heterostructures and paves the way for rational design of TMDC-
based 1D vdW heterostructures.

METHOD

First-principles calculations of the structural and electronic properties of TMDC nanotubes, monolayers, and 1D vdW heterostructures are carried out using DFT within the generalized gradient approximation (GGA) and Perdew-Burke-Enzerhof (PBE) exchange-correlation functional [70], as implemented in the Vienna Ab initio Simulation Package (VASP) [71]. The electron-ion interaction is described using the projector augmented-wave method [72, 73]. Electron wavefunctions are expanded in a plane-wave basis set with a consistent cut-off energy of 350 eV, which is sufficient to converge total energy calculations within 3 meV per atom. Atomistic models of TMDC nanotubes are built from TMDC monolayers with fully relaxed lattice constants. To avoid the spurious interaction between periodic image cells in plane-wave DFT calculations, a vacuum space of at least 15 Å perpendicular to the tube-axis direction is added in the supercell. The atomic positions of nanotubes are fully relaxed until the maximum force on each atom is less than 0.01 eV/Å. For TMDC monolayers, the 2D Brillouin zones are sampled using a \(1 \times 12\) \(\times\) \(\text{k-point mesh, with the non-unity dimension corresponding to the axial direction of nanotubes or heterostructures. Spin-orbit coupling (SOC) is not included as spin splitting is symmetry forbidden in both zigzag and armchair (non-chiral) nanotubes [28]. We have also compared the electronic band structures of a MoS\(_2\)(14,0) nanotube calculated with and without SOC, as shown in Figure S18. The result confirms the absence of spin-splitting in the zigzag nanotube and that the energy difference between the band-edge levels calculated with and without SOC is negligible.}

The vacuum energy level corresponding to each nanotube, monolayer, or 1D vdW heterostructural system is obtained by calculating the converged Hartree potential energy in the vacuum region far away from the modeled subject. For band alignment study, the energies of all band-edge states are aligned with respect to vacuum level.

ACKNOWLEDGEMENTS

We gratefully acknowledge the support by NSFC under Project No. 62004172. The work of W.L. is partially supported by Research Center for Industries of the Future at Westlake University under Award No. WU2022C041. The authors thank Drs. C.-M. Dai, J.-Q. Wang, and C. Hu for helpful discussions and the HPC Center of Westlake University for technical assistance.

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