Nanoscale

PAPER



Cite this: Nanoscale, 2015, 7, 14062

Received 12th June 2015, Accepted 17th July 2015 DOI: 10.1039/c5nr03895b

www.rsc.org/nanoscale

1 Introduction

In recent years, two-dimensional (2D) materials have been considered as emerging materials for applications in future nanoelectronics and optoelectronics due to their fascinating electronic, mechanical, optical or thermal properties.¹⁻³ As a typical example, graphene, a hexagonal lattice of carbon atoms, has attracted intensive research since its isolation and become one of the promising candidates for the future of nanoelectronics.4-6 Although massless Dirac-fermion behavior means graphene possesses extremely high mobility, the absence of a fundamental band gap severely limits its applications in field-effect transistors (FETs).^{5,7,8} Therefore, extensive efforts have been devoted to solving the problem of opening a gap in different graphene nanostructures.⁹ At the same time, some new types of 2D materials, such as few-layer transition metal dichalcogenides (TMDs),¹⁰⁻¹² have also been studied, and in particular monolayer MoS₂ possesses a direct

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Effects of stacking order, layer number and external electric field on electronic structures of few-layer C₂N-h2D

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Recently, a new type of two-dimensional layered material, *i.e.* a nitrogenated holey two-dimensional structure C_2N-h2D , has been synthesized using a simple wet-chemical reaction and used to fabricate a field-effect transistor device (*Nat. Commun.*, 2015, **6**, 6486). Here we have performed a first-principles study of the electronic properties of few-layer C_2N-h2D with different stacking orders and layer numbers. Because of the interlayer coupling mainly in terms of the orbital interaction, band structure of this system, especially splitting of the bands and band gap, depends on its stacking order between the layers, and the band gap exhibits monotonically decreasing behavior as the layer number increases. All the few-layer C_2N-h2D materials have characteristics of direct band gap, irrespective of the stacking order and layer number examined in our calculations. And bulk C_2N-h2D has an indirect or direct band gap, depending on the stacking order. Besides, when we apply an out-of-plane electric field on few-layer C_2N-h2D , its band gap will decrease as the electric field increases due to a giant Stark effect except for the monolayer case, and even a semiconductor-to-metal transition may occur for few-layer C_2N-h2D with more layers under an appropriate electric field. Owing to their tunable band gaps in a wide range, the layered C_2N-h2D materials will have tremendous opportunities to be applied in nanoscale electronic and opto-electronic devices.

band gap of ~1.9 eV.¹⁰ Although the monolayer MoS_2 has been used to fabricate a FET, the low carrier mobility¹³ of ~200 cm² V^{-1} s⁻¹ limits its wider application in electronics. Recently, few-layer black phosphorous (phosphorene), with a high mobility, high in-plane anisotropy and characteristics of a direct band gap semiconductor, was isolated from bulk black phosphorus,^{14–17} and has immediately received considerable research attention.^{18–22} Although phosphorene possesses both an appreciable band gap and a high carrier mobility, its puckered lattice is not able to strictly confine the movement of the carrier within the 2D surface.²³ So it is still necessary to seek 2D planar materials with a suitable band gap and potential in nanoelectronic applications.

Recently, a flat layered 2D crystal with evenly distributed holes and nitrogen atoms, named C_2N -h2D, has been simply synthesized *via* a bottom-up wet-chemical reaction. Furthermore, a FET based on C_2N -h2D multilayers with a high on/off ratio of 10^7 was fabricated and C_2N -h2D possesses an optical band gap of ~1.96 eV.²⁴ These results may make C_2N -h2D multilayers a very promising candidate material for future applications in electronics and optoelectronics at the nanoscale level. So examining the electronic structure, especially the band gap, of C_2N -h2D multilayers and exploring its possible modulations by interior (stacking order and layer number) and

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exterior (external electric field) factors will be helpful to further exploit the future applications of this new type of 2D material.

Here, we perform first-principles calculations to investigate the electronic structure of few-layer C2N-h2D and obtain several important findings. Monolayer C2N-h2D has a direct band gap of ~2.47 eV at the Γ point. Few-layer C₂N-h2D still exhibits a sizable direct band gap, which decreases as the laver number increases monotonically. Possible stacking orders with high symmetries along with their relative stabilities are also studied, and it is revealed that the stacking order can also alter the band gap of few-layer C₂N-h2D. These properties are ascribed mainly to orbital interactions between conduction bands of different layers. Different from the few-layer case, the characteristics of the indirect or direct band gap of bulk C2Nh2D are related to its stacking order. The smaller interlayer binding energies show feasible exfoliation of the C2N-h2D materials. What is more, we have explored how the band structure of few-layer C₂N-h2D responds to a vertical electric field, and found that a giant Stark effect induces the decrease of the band gap and even the semiconductor-to-metal transition, with the decreasing rate of the band gap being determined by the layer number. All in all, the band gap of few-layer C₂N-h2D can be modulated in a relatively wide range by changing the stacking order, controlling the layer number and applying an external electric field, which will bring fine tunability of their potential applications in nanoelectronics and nanophotonics.

2 Methods

In this study, our first-principles calculations are based on density functional theory (DFT) and implemented in the VASP package.^{25,26} The atomic structure of every C₂N-h2D layer is constructed in the xy-plane. A large value (15 Å) of the vacuum region along the z-direction is used to avoid interaction between two adjacent periodic images. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)²⁷ and projector augmented wave (PAW) potentials are used. In all computations, the kinetic energy cutoff is set to be 520 eV in the plane-wave expansion. For the geometry optimization, $5 \times 5 \times 1$ and $5 \times 5 \times 4$ Monkhorst-Pack k-meshes are adopted for few-layer and bulk C₂N-h2D, respectively. All of the geometry structures are fully relaxed until energy and forces are converged to 10⁻⁵ eV and 0.01 eV Å⁻¹, respectively. The effect of the van der Waals (vdW) interactions is accounted for by using the empirical correction method proposed by Grimme (DFT-D2),²⁸ which is a good description of long-range vdW interactions.^{22,29,30} As a benchmark, the DFT-D2 calculation gives an interlayer distance of 3.25 Å and a binding energy of -25 meV per carbon atom for bilayer graphene, consistent with previous experimental measurements and theoretical studies.^{31,32} We have also performed tests of hybrid functional calculations using the HSE06 33-35 functional for some cases in this study, which give qualitatively consistent results compared with the PBE results, such as similar relative

stabilities of different stacking orders and modulations of the band gap by various factors, although the HSE06-derived band gaps are larger than those calculated by PBE.

3 Results and discussion

To obtain a thorough knowledge of few-layer C_2N-h2D , we first studied the geometric and electronic properties of monolayer C₂N-h2D. The ball-stick models of monolayer C₂N-h2D are illustrated in Fig. 1(a). Calculations show that the equivalent lattice parameter of monolayer C2N-h2D is 8.330 Å, with inplane covalent bond lengths of 1.429/1.470 Å for the C-C bond and 1.336 Å for the C–N bond. There are 12 C atoms and 6 N atoms in a unit cell and uniform holes in the C₂N-h2D layer. Monolayer C_2N -h2D is a semiconductor with a direct band gap of 1.66 eV at the Γ point, as depicted in Fig. 1(b). This band gap value is smaller than 2.47 eV as obtained by our HSE06 calculation due to underestimation of the Kohn-Sham treatment in DFT.36 At the same time, we plot the isosurfaces of the band decomposed charge density corresponding to the valence band maximum (VBM) and the conduction band minimum (CBM), which is shown in Fig. 1(c) and (d), respectively. It is found that the CBM and VBM have distinct spatial distributions and origins of orbitals: the former is a π state with a strong contribution by the p_z orbital of the N atom (Fig. 1(c)), and the latter consists of two degenerate σ states distributed in the C₂N-h2D plane (Fig. 1(d)). The spatial properties of the VBM and CBM result in the existence of nearly flat bands near two band edges. These calculation results are consistent with those in a previous study.²⁴

For bilayer C₂N-h2D, we consider three kinds of high symmetry stacking structures, namely, AA-, AB-, and AB'-stacking. As shown in Fig. 2(a), in AA-stacking, the top layer is directly stacked on the bottom layer and they are matched perfectly in the xy-plane, whereas in AB- and AB'-stacking, the hole centers of the top layer are positioned at the center of the hexatomic rings composed of C atoms (Fig. 2(b)) and hexatomic rings composed of C and N atoms (Fig. 2(c)) of the bottom layer, respectively. In fact, AB- and AB'-stacking can be viewed as shifting the top layer of AA-stacking by vectors of a/3-b/3 and a/2 where a and b are basis vectors of the unit cell, respectively. Our total energy calculations indicate that AB-stacking is the most favorable configuration for bilayer C2N-h2D, being 16 and 3 meV per atom lower than that of AA- and AB'-stacking, respectively. Besides, we also note that the calculated lattice constants of these three stackings differ slightly. Band structures of the AA-, AB- and AB'-stacked bilayer C2N-h2D are shown in Fig. 2(d)-(f). Clearly, the direct band gap feature is retained regardless of the stacking orders, and both the VBM and CBM are still located at the Γ point for these three bilayer C₂N-h2D materials. The AB-stacked bilayer C₂N-h2D has the widest band gap of 1.49 eV, while the band gap of the AA- and AB'-stacked bilayer C2N-h2D is 1.34 eV and 1.21 eV, respectively, and they are all smaller than the band gap of 1.66 eV for the monolayer case. It is noted that the energy difference





Fig. 1 (a) Top view and side view of the atomic structure of monolayer C_2N-h2D in the unit cell. The directions of two basis vectors **a** and **b** of the unit cell are indicated. (b) Band structures of monolayer C_2N-h2D . Γ (0.0, 0.0, 0.0), M (0.5, 0.5, 0.0), and K (1/3, 1/3, 0.0) refer to special points in the first Brillouin zone. (c) and (d) are the charge density corresponding to the CBM and VBM for monolayer C_2N-h2D , respectively. The isovalue is 0.003 e Bohr⁻³. The grey and silvery balls represent C atoms and N atoms, respectively. All of the side views are along the direction of the basis vector **a**.

between AB-stacking with the largest band gap and AB'-stacking with the smallest band gap is only 3 meV per atom.

As shown above, different stacking orders result in different interaction strengths and band gaps of bilayer C₂N-h2D. It is understandable that AB-stacking is the most stable, mainly determined by long-range weak interactions and related to the repulsion between charge centers, similar to the case of graphite, if we consider the hexatomic rings composed of C atoms as the charge centers. However, different from graphite, bilayer C_2N-h2D has a metastable configuration, *i.e.* AB'-stacking, of which the total energy is close to that of AB-stacking as revealed above. In fact, here the N atoms connecting the adjacent hexatomic carbon rings should also be considered as the charge centers, resulting in metastable AB'-stacking. On the other hand, the decreased band gap of bilayer C2N-h2D compared with the one for monolayer C2N-h2D should be ascribed to splitting of the conduction band (CB) and valence band (VB) induced by interlayer coupling, especially orbital interactions between two layers. Since the VBM of monolayer C2Nh2D is σ states distributed in the C₂N-h2D plane, orbital hybridization between the VBMs of two layers and the splitting of the VB are weak. In contrast, the CBM is a π -conjugated state distributed out of the plane so it has a stronger orbital hybridization between two layers and then larger splitting of the CB (see Fig. 2(d) and (e)). Of course, this interlayer orbital

hybridization depends on detailed spatial matching between the CB of two layers, so the stacking order of bilayer C_2N-h2D has a non-negligible influence on its band structure, especially its band gap, as shown in Fig. 2(d) and (e).

For trilayer C₂N-h2D, we consider four kinds of high symmetry stacking structures based on the three stacking orders for bilayer C2N-h2D: AAA-stacking, ABA-stacking, ABC-stacking, and AB'A-stacking. Here the symbol C means a C2N-h2D layer with a shift relative to layer A by a vector of $2\mathbf{a}/3-2\mathbf{b}/3$. The atomic structures of these trilayer C2N-h2D materials are shown in Fig. 3(a)-(d), respectively. According to our total energy calculations, ABC-stacking is the most stable configuration, which is only 0.5 meV per atom lower than that of ABAstacking because of sufficient weak interactions between the next nearest layers, and AB'A- and AAA-stacking are 4 meV per atom and 19 meV per atom higher than ABC-stacking, respectively. It is obvious that the energy relationship between the three stacking orders of bilayer C_2N-h2D is preserved in trilayer C_2 N-h2D. Then, their band structures are depicted in Fig. 3(e)-(h), respectively. Obviously, various stacking orders of trilayer C₂N-h2D are all semiconductors with a direct band gap, and all their CBMs and VBMs are still located at the Γ point. The splitting of the CB and VB is further enhanced compared with those in bilayer C₂N-h2D. And the band gaps of these four stacked configurations have similar characteristics with those



Fig. 2 Three stacking structures of bilayer C_2N-h2D . (a, b, c) Top views (upper panel) and side views (lower panel) of AA-, AB-, and AB'-stacking, respectively. A 2 x 2 supercell is adopted for the top view. (d, e, f) The band structures of AA-, AB-, and AB'-stacking, respectively. The C atoms in different layers are represented by grey and green balls. And the N atoms in different layers are represented by blue and orange balls. Γ (0.0, 0.0, 0.0), M (0.5, 0.5, 0.0), and K (1/3, 1/3, 0.0) refer to special points in the first Brillouin zone.

of their corresponding bilayer C_2N -h2D: ABA- and ABC-stacking (corresponding to AB-stacking) have larger band gaps of 1.40 eV and 1.35 eV respectively, and AAA- (corresponding to AA-stacking) and AB'A-stacking (corresponding to AB'-stacking) have smaller band gaps of 1.15 eV and 0.94 eV respectively. Here ABA stacking with the largest band gap only has an energy difference of 3.5 meV per atom from AB'A-stacking with the smallest band gap.

Since AB- and ABC-stacking are the most stable configurations for bilayer and trilayer C_2N -h2D respectively, we built two types of bulk C_2N -h2D structures according to them. The calculations show that bulk C_2N -h2D with rhombohedral ABCstacking possesses an indirect band gap of 1.07 eV, and its atomic structure and band structure are shown in Fig. 4(a) and (d) respectively. Clearly, its CBM is located at point A although its VBM is still at the Γ point. We have also calculated the band structure of bulk C_2N -h2D with hexagonal AB-stacking (see Fig. 4(b) and (e)) which is only 1.6 meV per atom higher than that with rhombohedral ABC-stacking, and it has a direct band gap at the Γ point of 1.26 eV. This difference can be interpreted by employing band-folding analysis as follows: for the simplest bulk case with only a monolayer in the unit cell, the CB should have the dispersion characteristic that the state at point A is the CBM, because the CB is a p_z -derived π -conjugated state with mirror anti-symmetry with respect to the layer plane as discussed above, then the state at point A is of a bonding nature between the adjacent layers. For bulk C_2N-h2D with ABC-stacking, the CB is deduced approximately by folding the CB of the simplest bulk case, and the three layers in one unit cell results in that the CBM is folded to new A point; but for the case with AB-stacking, the folded CBM is at the Γ point because of the two layers in one unit cell. So the indirect or direct band gap property of bulk C_2N-h2D is related to the parity (odd or even) of the layer number in the unit cell.

We also built four-layer and five-layer C_2N-h2D structures according to ABC-stacking which is the most stable in trilayer and bulk C_2N-h2D as shown above. The calculated lattice constants ($a = |\mathbf{a}| = |\mathbf{b}|$), interlayer distances (Δc), layer-averaged maximal differences (Δz) of the intra-layer atomic *z*-coordinates, and interlayer binding energies of the various few-layer (with layer number *n*) and bulk C_2N-h2D structures with ABCstacking are listed in Table 1. The lattice constant *a* undergoes



Fig. 3 (a)–(d) The atomic structures of the AAA-, ABA-, ABC-, and AB'A-stacked trilayer C_2N-h2D , respectively; (e)–(h) the electronic band structures of the AAA-, ABA-, ABC-, and AB'A-stacked trilayer C_2N-h2D , respectively. The grey and silvery balls represent C atoms and N atoms, respectively. Γ (0.0, 0.0, 0.0), *M* (0.5, 0.5, 0.0), and *K* (1/3, 1/3, 0.0) refer to special points in the first Brillouin zone.



Fig. 4 (a, b) Crystal structures of bulk C₂N-h2D with rhombohedral ABC-stacking and hexagonal AB-stacking, respectively. (c) Schematic of the Brillouin zone with high-symmetry points and lines of bulk C₂N-h2D. Band structures of bulk C₂N-h2D with (d) rhombohedral ABC-stacking and (e) hexagonal AB-stacking.

a decrease by 0.025 Å on passing from monolayer to bulk C₂Nh2D for ABC-stacking, and the layer-averaged maximal difference Δz of the intra-layer atomic *z*-coordinates increases by 0.110 Å at the same time, whereas the interlayer distance Δc decreases by 0.076 Å from the bilayer to bulk phase. The

Table 1 Calculated lattice constants *a*, interlayer distances Δc , layeraveraged maximal differences Δz of the intra-layer atomic *z*-coordinates, and interlayer binding energies of *n*-layer C₂N-*h*2D with ABCstacking and two types of bulk C₂N-*h*2D

n	Stacking order	a (Å)	Δc (Å)	Δz (Å)	Interlayer binding energy (meV per atom)
1	А	8.330		0	
2	AB	8.321	3.183	0.047	23.9
3	ABC	8.317	3.161	0.069	33.1
4	ABCA	8.316	3.159	0.073	37.8
5	ABCAB	8.313	3.158	0.079	40.7
Bulk	ABC	8.305	3.107	0.110	53.3
Bulk	AB	8.310	3.162	0	51.6

decrease of the lattice constant *a* with the increased layer number *n* may be related to the increase of the layer-averaged maximal difference Δz of the intra-layer atomic *z*-coordinates since the bond lengths should be almost unchanged, similar to the case of few-layer black phosphorus.¹⁷ The interlayer binding energy increases by 29.4 meV per atom from the bilayer to the bulk case, since two surface layers of few-layer C_2N-h2D have smaller contributions to the interlayer binding energy compared with the inner layers. Even for the bulk case, the interlayer binding energy of 53.3 meV per atom, *i.e.* 0.26 J m⁻², is still smaller than the experimentally estimated cleavage energy in graphite of 0.36 J m⁻²,³² suggesting feasible exfoliation of bulk and few-layer C_2N-h2D .

We have also examined the layer number dependence of the band structure of few-layer C_2N-h2D with ABC-stacking. Similar to the cases of the bilayer and trilayer C_2N-h2D , the band structures of the four-layer and five-layer C2N-h2D have the characteristic of splitting of the CBs and VBs due to the interlayer coupling and the direct band gaps at the Γ point which further decrease (not shown). Since DFT calculations typically underestimate the fundamental band gap, we have also checked the band gap of the most stable few-layer C₂Nh2D with ABC-stacking using the HSE06 hybrid functional calculation.33-35 Comparison between the HSE06 and PBE results indicate that the PBE band gaps are underestimated by about 0.6-0.8 eV for the few-layer C2N-h2D materials examined in our calculations. As shown in Fig. 5, the band gap of fewlayer C2N-h2D calculated using HSE06 decreases monotonically as the layer number increases, tunable from 2.47 eV for the monolayer to 1.84 eV for the five-layer, and to 1.66 eV for the bulk case. The experimentally measured optical band gap of multilayer C₂N-*h*2D is 1.96 eV,³⁶ smaller than the calculated HSE06 band gaps of few-layer C2N-h2D with the layer number n < 3, which is reasonable due to the exciton binding energy. By combining the varying range of the band gap from the monolayer to the bulk case and the modulation of the band gap by the stacking order as shown in the bilayer and trilayer cases, we can judge that the few-layer C₂N-h2D materials have a tunable band gap from in the near-infrared to green visible wave band. It can also be deduced that few-layer C2N-h2D with the layer number in a broad range should possess a direct band gap and can then be predominantly used in optoelectronic applications compared with its bulk case, which is different from the case of MoS₂ where only the monolayer has a direct band gap.¹⁰ Only when the layered C₂N-*h*2D material is thick enough so that its long-range periodicity along the direction perpendicular to the C2N-h2D layers and dispersion characteristics of the CB along the Γ A line form, can the indirect band gap property of rhombohedral ABC-stacking be distinguished from the direct band gap property of hexagonal



Fig. 5 Evolution of the band gap (calculated using HSE06) $E_g(n)$ of fewlayer C₂N-h2D with ABC-stacking as a function of the layer number *n*. Inserts: $\ln[E_g(n) - E_{bulk}] \sim \ln(n)$ plot (upper-right) and $\ln[E_g(n) - E_{bulk}] \sim n$ plot (lower-left), with the red dash lines showing their linear fitting and the fitting formulae are also presented.

AB-stacking. The relationship between the band gap $E_{\alpha}(n)$ and layer number n of the few-layer 2D material deserves further investigation. We have tried to fit this relationship for few-layer C_2 N-h2D with ABC-stacking ($n \rightarrow \infty$ for bulk) using two formulae: $E_g(n) = E_{bulk} + \alpha/n^{37}$ and $E_g(n) = E_{bulk} + \alpha e^{-\beta n} \cdot 1^7$ It is found that both the $\ln[E_g(n) - E_{bulk}] \sim \ln(n)$ plot (see upperright insert in Fig. 5) and the $\ln[E_g(n) - E_{bulk}] \sim n$ plot (see lower-left insert in Fig. 5) are linear to a great extent, with some small departures. The fitting results using the two formulae are $E_{g}(n) = 1.66 + 0.86/n$ and $E_{g}(n) = 1.66 + 1.23e^{-0.43n}$, respectively. The $E_g(n) \sim n$ relationship should correlate with the specific interlayer dispersion of the CB in the band structure of bulk C2N-h2D. Further examination of our fitting in the two inserts in Fig. 5 find that for C_2N-h2D with a smaller layer number, the formula $E_g(n) = E_{bulk} + \alpha e^{-\beta n}$ is more appropriate to represent this relationship, while the formula $E_o(n) = E_{\text{bulk}} +$ α/n may also become appropriate as the layer number increases.

Previous theoretical and experiment studies have showed that the external electric field may effectively modulate the band structure, especially the band gap, of various 2D fewlayer materials.³⁸⁻⁴³ So it is interesting to study how the electronic structure of few-layer C2N-h2D responds to a vertical electric field. Here we chose the monolayer to five-layer C2Nh2D materials as models to test. The electric field is applied perpendicular to the few-layer C2N-h2D surface and its positive direction is defined as the one from the top layer to the bottom layer (*i.e.* the first layer), with a strength ranging from 0.1 to 0.5 V Å⁻¹. For monolayer C₂N-h2D, its band gap is almost unchanged as the external electric field increases due to its planar structure. In contrast, the band gaps of few-layer C₂N-h2D with layer numbers from 2 to 5 exhibit a monotonically decreasing relationship with the increased electric field, and the decreasing rate of the band gap of C₂N-h2D with more layers is more rapid (Fig. 6(a)). For five-layer C₂N-h2D, the band gap even closes up and a semiconductor-to-metal transition occurs as an electric field of 0.5 V $Å^{-1}$ is applied, which is illustrated in Fig. 6(a) and (b). It is noted that the direct band gap characteristic of five-layer C2N-h2D is kept with the increasing electric field until it turns to a metal under the electric field of 0.5 V Å⁻¹. In order to understand these phenomena, we have calculated the band structures of these few-layer C₂N-h2D under different electric fields and analyzed contributions of each layer to all bands near the $E_{\rm F}$. The CBs and VBs of few-layer C2N-h2D without an electric field have already been split due to the interlayer coupling as discussed before. Under the electric field, this splitting is further enhanced with the splitting number remaining unchanged, and at the same time the splitting bands are redistributed to every layer (see Fig. 6(b)), *i.e.* spatial charge separation. The enhanced splitting of the CBs and VBs with the increased electric field results in the energy difference between the CBM and VBM, i.e. the band gap, decreasing and even turning to zero (Fig. 5(b)). Fig. 6(c)shows isosurfaces of the charge density corresponding to the CBMs and VBMs of five-layer C2N-h2D without the electric field and under an electric field of 0.2 V $Å^{-1}$, showing that the

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Fig. 6 (a) Variations of the band gaps of few-layer C_2N-h2D under the external field. (b) Calculated band structures of five-layer C_2N-h2D under the electric field of 0.5 V Å⁻¹, the bands localized in different layers are represented by different colored plots. (c) The charge density corresponding to the CBM and VBM of five-layer C_2N-h2D without and under the electric field of 0.2 V Å⁻¹, respectively. The isovalue is 0.003 e Bohr⁻³. (d) A schematic view of the bands shifting for five-layer C_2N-h2D under the electric field of 0.5 V Å⁻¹, with the green dash line representing the Fermi level and the light blue arrow representing the direction of the electric field.

electric field induced redistribution of the CBM and VBM to the top and bottom layers respectively. Here the electrostatic potential difference along the direction perpendicular to the C₂N-h2D surface plays a vital role, and it results in the shifting of bands for different layers with an almost linear response, which is shown in Fig. 6(d). The above-discussed band gap modulation of few-layer C2N-h2D under the external electric field can be ascribed to a giant Stark effect. Similar phenomena have been observed in single-walled boron nitride nanotubes,^{44,45} boron nitride nanoribbons^{46,47} and a MoS₂ bilayer.48 Since the CBM and VBM under the electric field are localized in the top and bottom layers respectively, their energy difference is determined by the electrostatic potential difference between the top and bottom layers. Therefore fewlayer C₂N-h2D with more layers has a more sensitive response of the band gap to the external electric field, meaning that five-layer C₂N-h2D can turn to metal under the usually accessible field. So increasing the layer number may be a feasible alternative scheme to the high electric field for realizing the semiconductor-to-metal transition of the layered 2D materials. It is also noted that for the thicker cases, such as five-layer C_2N-h2D , the response of the band gap to the electric field is not linear under the lower (close to zero) and higher fields (close to 0.5 V $Å^{-1}$) (Fig. 6(a)). The nonlinear behavior under the lower field should be ascribed to the spatial charge separation as discussed above, and is more obvious for the thicker cases because they have more hybrid states derived from the CB (VB) with larger splitting energies. Under the higher field, the CB begins to be close to the VB, and then the material is close to being a metal with an enhanced charge screening effect, which shows another nonlinear behavior for the relationship between the band gap and field applied.

4 Summary

In conclusion, on the basis of DFT calculations, we have performed theoretical research on the structural and electronic properties of few-layer C2N-h2D. AB-stacking is the most stable configuration for bilayer C2N-h2D, and ABC-stacking is favored in energy for few-layer C₂N-h2D with the layer number $n \ge 3$ up to the case of bulk C₂N-h2D. It is shown that few-layer C₂Nh2D is a novel category of 2D direct band gap semiconductor, independent of the stacking order and layer number. Variations of the stacking order and layer number may influence the splitting of bands in term of the orbital interaction between the bands of different layers, and then the band gap can also be modulated by these two factors in the range of the near-infrared to green visible wave band. Specifically, the band gap decreases as the number of layers increased with a decay relationship being fitted using an exponential or reciprocal formula. Bulk C₂N-h2D is also investigated, and the stacking order determines its characteristic of a direct or indirect band gap. The interlayer binding energy calculation shows its feasible exfoliation. At last, when an external electric field perpendicular to the few-layer C_2N-h2D surface is applied, the band gap of few-layer C_2N-h2D with the layer number $n \ge 2$ also decreases with an increase of the vertical electric field, which is governed by a giant Stark effect. This property can be also used to induce the semiconductor-to-metal transition by adopting a usually accessible combination of the layer number and electric field. For example, under an electric field of 0.5 V Å⁻¹, five-layer C_2N-h2D will turn to a metal. Thus, our theoretical predictions suggest that the layered C_2N-h2D material is very promising for use in optoelectronic applications, due to its tunable band gaps modified by the layer number, stacking order and external electric field.

Acknowledgements

This work is partially supported by the National Key Basic Research Program (2011CB921404), by NSFC (21421063, 91021004, 21233007, 21203099, 21273210), by CAS (XDB01020300), by Fundamental Research Funds for the Central Universities, and by USTCSCC, SCCAS, Tianjin, and Shanghai Supercomputer Centers.

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