Two-dimensional square ternary Cu_2MX_4 ($M = \text{Mo}, \text{W}$; $X = \text{S}, \text{Se}$) monolayers and nanoribbons predicted from density functional theory

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Two-dimensional (2D) materials often adopt a hexagonal lattice. We report on a class of 2D materials, Cu_2MX_4 ($M = \text{Mo}, \text{W}$; $X = \text{S}, \text{Se}$), that has a square lattice. Up to three monolayers, the systems are kinetically stable. All of them are semiconductors with band gaps from 2.03 to 2.48 eV. Specifically, the states giving rise to the valence band maximum are confined to the Cu and X atoms, while those giving rise to the conduction band minimum are confined to the M atoms, suggesting that spontaneous charge separation occurs. The semiconductive nature makes the materials promising for transistors, optoelectronics, and solar energy conversion. Moreover, the ferromagnetism on the edges of square Cu_2MX_4 nanoribbons opens applications in spintronics.

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I. INTRODUCTION

Two-dimensional (2D) materials exhibit unique and fantastic properties, which are distinctly different from their bulk counterparts and thus have created tremendous interest in synthesis, properties, and applications [1–3]. By mechanical [4,5] and chemical [6–8] exfoliation materials with one or few atomic layers, such as BN, MoS_2 , and WSe_2 , can be obtained from weakly bonded layered compounds. The electronic properties range from zero gap semimetallic graphene over semiconductors with considerable band gaps (e.g., MoS_2) to the wideband gap insulator BN. It turns out that these free-standing 2D systems commonly adopt a hexagonal structure; thus, all display a similar edge morphology and symmetry-dependent band gap [9]. While a monoatomic framework may hamper applications, more complex 2D materials with more than one element incorporated in the structure are expected to yield new properties due to more tunable degrees of freedom.

Monoatomic tetragonal networks are unlikely to be formed due to the valence pair repulsion rule [10]. Based on density functional theory calculations, Zhang *et al.* [11] have proposed a tetragonal TiC monolayer with a rectangular lattice formed by strong in-plane p - d bonding in conjunction with out-of-plane electron delocalization. The material is a semiconductor with a narrow indirect band gap of ~ 0.2 eV, which limits widespread applications. It is thus highly desirable to explore new materials with sizable band gaps. In this paper, density functional theory is employed to demonstrate a novel class of square 2D materials based on Cu_2MX_4 ($M = \text{Mo}, \text{W}$; $X = \text{S}, \text{Se}$), which shows kinetic stability. The monolayers have a thickness of 2.60 to 2.90 Å and consist of two nested square lattices of Cu and M atoms, both of which are tetrahedrally coordinated to bridging X atoms, forming a square packed layer of metal atoms sandwiched between layers of X atoms. The Cu-X and M-X bonds are predominately ionic with some covalency features. In the bulk, these layers are coupled by weak van der Waals (vdW) forces, thus allowing exfoliation into atomically thin sheets, similar to MoS_2 [4]. The exfoliated monolayers are semiconductors with indirect band gaps

(2.03–2.48 eV) in the visible light range, making them suitable for photocatalysis.

II. COMPUTATIONAL METHODS

This paper is based on the Vienna *Ab initio* Simulation Package [12–14] and the frozen-core projector-augmented wave method [15,16]. The spin-polarized Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation is employed for the exchange-correlation potential [17], and a cutoff energy of 500 eV is used. For the monolayers and nanoribbons (NRs), 15 and 5 special k points, respectively, are found to be sufficient to sample the Brillouin zone. A vacuum thickness of 15 Å is introduced to obtain well-separated monolayers and NRs. Geometry optimization is continued until the residual forces are less than 0.01 eV/Å. Due to the absence of strong bonding between the layers, a damped vdW correction is adopted [18]. A comprehensive test has been performed with a range of empirical parameters to calculate the lattice constants of the bulk phases [19]. The hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional [20,21] is used to calculate the band structures of the bulk and monolayers. *Ab initio* molecular dynamics simulations are performed using the Nosé-Hoover thermostat [22], where the equations of motion are integrated by the Verlet algorithm [23] with a time step of 2 fs. Phonon dispersion curves are obtained using the finite-displacement method implemented in the CASTEP software.

III. RESULTS AND DISCUSSION

Cu_2MX_4 has two phases: the primitive phase with space group $P\bar{4}2m$ and the body-centered phase with space group $I\bar{4}2m$. In the $P\bar{4}2m$ phase, the M atoms in adjacent layers are located directly above one another, whereas in the $I\bar{4}2m$ phase, they are offset by a vector $(1/2, 1/2, 0)$, presumably for minimizing the electrostatic repulsion between the X atoms of adjacent layers. Experimental data [19,24,25] indicate that $|c|$ is shorter than $|a|$ ($=|b|$) in the $P\bar{4}2m$ phase, whereas it is shorter than $2|a|$ ($=2|b|$) in the $I\bar{4}2m$ phase, as shown in Table I. The PBE functional excluding vdW corrections largely overestimates $|c|$ and gives wrong trends in all compounds. In contrast, inclusion of vdW corrections gives qualitatively consistent results. The band gaps of the layered compounds

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TABLE I. Structural parameters and band gaps of various compounds obtained using the PBE and PBE + vdW functionals. Band gaps in brackets are calculated by the HSE06 + vdW functional. For comparison, experimental values are also included (Ref. [19,25]).

Cu_2MX_4	Space group	Functional	$ a = b $ (Å)	$ c $ (Å)	Interlayer separation (Å)	Band gap (eV)
Cu_2MoS_4	$P\bar{4}2m$	PBE	5.44	5.58	3.25	1.13
		PBE + vdW	5.38	5.11	2.50	0.95 [1.71]
		Experiment	5.38	5.28		
	$I\bar{4}2m$	PBE	5.43	11.32	3.06	1.16
		PBE + vdW	5.38	9.89	2.36	0.99 [1.82]
		Experiment	5.41	10.35		1.76
Cu_2MoSe_4	$P\bar{4}2m$	PBE	5.59	6.11	3.27	0.80
		PBE + vdW	5.51	5.40	2.56	0.60 [1.26]
		Experiment	5.51	5.55		
	$I\bar{4}2m$	PBE	5.59	11.58	2.95	0.90
		PBE + vdW	5.52	10.60	2.46	0.78 [1.47]
		Experiment				
Cu_2WS_4	$P\bar{4}2m$	PBE	5.47	5.69	3.09	1.43
		PBE + vdW	5.40	5.08	2.49	1.24 [2.15]
		Experiment	5.42	5.26		
	$I\bar{4}2m$	PBE	5.46	11.22	3.00	1.56
		PBE + vdW	5.40	9.82	2.32	1.35 [2.26]
		Experiment	5.44	10.07		
Cu_2WSe_4	$P\bar{4}2m$	PBE	5.61	6.05	3.20	1.02
		PBE + vdW	5.52	5.37	2.75	0.83 [1.53]
		Experiment	5.54	5.51		
	$I\bar{4}2m$	PBE	5.61	11.78	3.04	1.23
		PBE + vdW	5.52	10.53	2.43	1.11 [1.87]
		Experiment	5.56	10.69		

obtained by the HSE06 functional with vdW corrections range from 1.26 to 2.26 eV for both phases. Specifically, the HSE06 + vdW band gap of the Cu_2MoS_4 $I\bar{4}2m$ phase agrees well with the experimental value (1.76 eV) [26]. Figure 1(a) and 1(b) shows the HSE06 + vdW band structures of the two phases of Cu_2MoS_4 . Both are indirect semiconductors with the valence band maximum (VBM) due to hybridized S p and Cu d orbitals and the conduction band minimum (CBM) due to the M e_g states. Regardless of the employed method (PBE + vdW or HSE06 + vdW; see Table I), the results display a similar behavior: (1) For each compound, the $I\bar{4}2m$ phase has a larger band gap, and (2) the band gap increases from Mo to W for common X and decreases from S to Se for common M .

The contrasting results on the lattice constants obtained by the PBE and PBE + vdW functionals reflect that the

vdW interaction plays a vital role in layered materials, thus suggesting the possibility of exfoliating Cu_2MX_4 into monolayers. Figure 2 shows the phonon dispersion curves of the four monolayer systems. In each case, the acoustic branches determine the stability of the system. We observe no imaginary phonon mode in square Cu_2MoS_4 and Cu_2WS_4 , confirming the kinetic stability. Analogous features of the two plots indicate a similar bonding in these systems. In contrast, imaginary modes are observed around the M point in square Cu_2MoSe_4 . The imaginary part is small in square Cu_2WSe_4 , which may introduce a tiny distortion along the corresponding mode but is not enough to destabilize the structure. Table II summarizes the structural parameters and band gaps of the stable systems. For $X = \text{S}$ from Mo to W, the in-plane lattice constant increases and the layer thickness shrinks, leading to

FIG. 1. HSE06 band structures of Cu_2MoS_4 in the (a) $P\bar{4}2m$ and (b) $I\bar{4}2m$ phases.

FIG. 2. Phonon band structures of square (a) Cu_2MoS_4 , (b) Cu_2MoSe_4 , (c) Cu_2WS_4 , and (d) Cu_2WSe_4 monolayers calculated by the finite displacement method.

longer Cu-S and Cu-M bonds (unchanged M-S bond length). For $M = \text{W}$ from S to Se, both the in-plane lattice constant and the layer thickness grow, thus weakening the bonds in square CuWSe_4 . The further expansion in square CuMoSe_4 makes this system unstable. In the following, square Cu_2MoS_4 is chosen as a representative example for further analysis.

We have calculated the total energies of square Cu_2MoS_4 as a function of $|\mathbf{a}|$ and $|\mathbf{b}|$ and show the results as a color map in Fig. 3(a). A single minimum is found at $|\mathbf{a}| = |\mathbf{b}| = 5.37 \text{ \AA}$, which is slightly less than the bulk value. For clarity, the square unit cell is illustrated in Fig. 3(c). Solution-based exfoliation of graphite and inorganic layered compounds has been demonstrated to be a viable approach to mass production of 2D sheets [6,27–29]. We thus simulate the exfoliation of Cu_2MoS_4 for the $P\bar{4}2m$ and $I\bar{4}2m$ stackings by lifting the top layer. Figure 3(b) shows the energy cost of this process as a function of the number of layers. The energy required to exfoliate a monolayer in the $P\bar{4}2m$ phase is smaller than that in the $I\bar{4}2m$ phase. This behavior originates from the smaller electrostatic repulsion between neighboring layers, as the interlayer separation is found to be $0.14 \text{ \AA}$ smaller than in the $P\bar{4}2m$ phase. As the number of layers increases, the energy cost in both cases increases because the topmost layer interacts

not only with the adjacent layer but also with more distant layers. The exfoliation energies in the two stackings lie in the range of 13 to $21 \text{ meV/\AA}^2$, as found in many layered materials, e.g., graphite and MoS_2 [30]. This reflects weak vdW interlayer interaction, thus confirming the feasibility of exfoliation.

Plots of the electron localization function [31] are shown in Fig. 3(d). High and low values around the anions and cations, respectively, reveal an ionic nature of the S-Cu and S-Mo bonds. Some covalency is also present; see the nonspherical shape around S. By Bader charge analysis [32], we find that square Cu_2MoS_4 largely preserves the charge distribution of the bulk. Each Cu atom donates 0.50 electrons to S, which is the same as the amount Cu donates in Cu_2O , indicating a Cu +1 oxidation state. The charge depletion from Mo amounts to 2.34 electrons, which is 1.32 electrons larger than in monolayer MoS_2 , suggesting a Mo +6 oxidation state [25]. The ionic bonding and tetrahedral coordination of Cu and Mo play crucial roles for stabilizing the square framework. The strong Mo-S bonds with Mo located at the center of S tetrahedrons are analogous to the highly stable tetragonal sp^3 structure [33]. The $[\text{MoS}_4]^{2-}$ units are connected by Cu^+ ions to form a square packed layer, where the absence of dangling bonds on the S-terminated surfaces is similar to the

TABLE II. Structural parameters and band gaps of the three stable square Cu_2MX_4 monolayers. HSE06 band gaps are given in brackets.

Cu_2MX_4	$ \mathbf{a} = \mathbf{b} \text{ (\AA)}$	$d_{M-X} \text{ (\AA)}$	$d_{\text{Cu}-M} \text{ (\AA)}$	$d_{\text{Cu}-X} \text{ (\AA)}$	Layer thickness $\text{(\AA)}$	Band gap (eV)
Cu_2MoS_4	5.37	2.25	2.69	2.31	2.61	1.20 [2.03]
Cu_2WS_4	5.48	2.25	2.74	2.34	2.60	1.58 [2.48]
Cu_2WSe_4	5.52	2.38	2.76	2.47	2.88	1.25 [2.06]

FIG. 3. (Color online) (a) Total energy of square Cu_2MoS_4 as a function of the lattice parameters. (b) Energy required to exfoliate a single layer from a multilayer structure. Insets: Top and side views demonstrating the exfoliation. (c) Top (left) and side (right) views of single-layer Cu_2MoS_4 . (d) Electron localization function in the (110) plane along Mo-S (upper) and Cu-S (lower) bonds.

2D transition metal dichalcogenides [34–36]. In addition to the kinetic stability of square Cu_2MoS_4 , *ab initio* molecular dynamics simulations have been carried out for a 4×4 supercell at temperatures of 500, 750, and 1000 K, as shown in Fig. 4. We find no destabilization up to 750 K throughout a 4-ps simulation, whereas the Mo-S bond starts breaking at 1000 K.

The HSE06 functional cannot predict excitonic effects (~ 1 eV binding energy in monolayer MoS_2) [37,38], but it provides an obvious improvement for the band gaps of the bulk phases (Table I). Therefore, we focus on this choice in Fig. 5(a). Square Cu_2MoS_4 is a semiconductor with an indirect

band gap of 2.03 eV, slightly more than in the bulk due to quantum confinement [34]. The VBM and CBM are located at the M and Γ points, respectively, which is also found for square Cu_2WS_4 . The projected density of states is addressed in Fig. 5(b), showing two main peaks for the Mo d orbitals around 2 and 3 eV. They correspond to the e_g ($d_{x^2}, d_{x^2-y^2}$) and t_{2g} (d_{zx}, d_{xy}, d_{yz}) states in the tetrahedral crystal field. The CBM is predominantly due to the e_g states, while the VBM originates from hybridized S p and Cu d_{xy} and d_{xz} orbitals. Based on the charge density distribution of the states contributing to the VBM and CBM in Fig. 5(c), the electrons are confined at the Mo atoms, while the holes are confined at the Cu and S atoms.

FIG. 4. (Color online) Snapshots of square Cu_2MoS_4 at (a) 500 K, (b) 750 K, and (c) 1000 K.

FIG. 5. (Color online) (a) HSE06 band structure of square Cu_2MoS_4 . The inset shows the Brillouin zone. (b) Projected density of states. (c) Charge density ($0.03 |e|/\text{\AA}^3$) of states giving rise to the VBM (left) and the CBM (right). (d) Band alignment. Black solid and red dashed lines represent the PBE and HSE06 functionals, respectively. The water reduction (H^+/H_2) and oxidation ($\text{H}_2\text{O}/\text{O}_2$) potentials are shown by blue dotted lines.

Consequently, a spontaneous charge separation in the water photolysis reaction is expected to occur.

The band alignment in square Cu_2MX_4 is illustrated in Fig. 5(d) to understand the trends in this class of monolayers, which are found to be similar regardless of the methods (PBE or HSE06): For $X = \text{S}$ the VBM is almost unchanged, while the CBM appears at higher energy for $M = \text{W}$. However, when the atomic number of X increases, the energies of both the CBM and the VBM increase. The increment for the VBM is much larger, 0.69 versus 0.27 eV, using the HSE06 functional. The band alignment between square Cu_2WS_4 and Cu_2WSe_4 demonstrates a staggered heterojunction, in which free electrons and holes will be spontaneously separated, suitable for optoelectronics and solar energy conversion [39,40]. The physical origin of these trends is understood by the bonding characters. In square Cu_2MX_4 , the M - X bonds are primarily ionic and the M d states are split into e_g and t_{2g} manifolds. The Cu atoms just donate delocalized s electrons, providing a minimum contribution to the band gap formation. Therefore, the positions of the VBM and CBM are primarily determined by the anion X p and M e_g states, respectively, according to Fig. 5(b). The VBM of square Cu_2WS_4 is almost the same as that of square Cu_2MoS_4 (same X element). However, the energy of the W $5d$ states is higher than that of the Mo $4d$ states. Thus, the CBM of square Cu_2WS_4 is higher and a larger band gap is observed. For square Cu_2WS_4

and Cu_2WSe_4 , the Se p orbital is higher in energy, leading to a higher VBM and a narrow gap between the Se p and the W e_g states. Simultaneously, the higher Se p orbital pushes the cation d states farther upward than the deeper S p states, thus giving rise to a higher CBM. Since the upshift is larger for the VBM, the band gap is narrowed.

FIG. 6. (Color online) VBM, CBM, and band gap variations of square Cu_2MoS_4 as a function of the number of layers calculated by PBE in the (a) $P4_2m$ and (b) $I4_2m$ stackings.

FIG. 7. (Color online) Top and side views of the (a) 5-zCu, (b) 5-zS, (c) 5-zCuS, and (d) 5-ICuS NRs.

There are two requirements for a highly efficient photocatalyst: a gap of ~ 2.0 eV to cover a large portion of the solar spectrum and band edges that straddle the oxidation-reduction potentials of the reduction (H^+/H_2) and the oxidation ($\text{H}_2\text{O}/\text{O}_2$) [41]. According to our results, only square Cu_2MoS_4 satisfies the two requirements, making a promising candidate for spontaneous photosplitting of water. The band gap of square Cu_2WS_4 (2.48 eV) is larger than the ideal value. Also, the VBM of square Cu_2WSe_4 is higher than the water oxidation potential, implying that it is only suitable for water reduction. It is well known that the thickness affects the nature and size of the band gap [42]. However, the CBM originates from the sandwiched M atoms and the VBM is

primarily due to the $X p_x (p_y)$ states, with a small portion of Cu d states. Consequently, a minimal interlayer coupling is expected, suggesting that the VBM and CBM are not sensitive to the number of layers, as shown in Fig. 6.

NRs of 2D materials are particularly interesting for nanoscale electronic devices [43–47]. Subsequently, the electronic structures of square Cu_2MoS_4 NRs are investigated at the PBE level (due to the high computational cost of the HSE06 functional). Four types of NRs are considered (Fig. 7). The first three are oriented along the $\mathbf{a}$ lattice vector and are zigzag shaped: zCu (Cu edges), zS (S edges), and zCuS (Cu and S edges). For the latter case, there are in principle three possible configurations: centrosymmetric edges on both sides, mirror-symmetric edges, and Cu on one side and S on the other. Since the latter two cases are 0.05 and 0.85 eV, respectively, higher in energy, the first configuration is adopted in the following. The fourth type is oriented along the $\mathbf{a} + \mathbf{b}$ vector and is terminated by S and Cu (ICuS NRs). The previous analysis indicates that the Mo-S bonding is much stronger than the Cu-S bonding. Therefore, the dangling bonds along the S-Mo-S edge in the $\mathbf{a} + \mathbf{b}$ direction are not stable and thus are not taken into account. Our supercell model contains two unit cells, where there are N Mo atoms across the NRs.

Both spin-degenerate and spin-polarized structure optimizations have been performed to determine the ground states of the NRs. The zS and zCuS NRs turn out to be spin degenerate, while the zCu and ICuS NRs show spin polarization (110 and 310 meV of energy lower than the spin-degenerate state), independent of the NR width [Fig. 8(b)]. All four types of NRs are direct band gap semiconductors, and due to quantum confinement, all band gaps decrease with increasing width, as shown in Fig. 8(a). The total density of states shows that in the zS NR, the states giving rise to the VBM are located on the two edges and are unoccupied because of

FIG. 8. (Color online) (a) Band gaps (as taken from the band structures) of four types of NRs as a function of the width. For the zCu and ICuS NRs, the band gaps of both nondegenerate spin channels are shown. The insets depict the charge density ($0.002 |e|/\text{\AA}^3$) of states, giving rise to the VBM and CBM for the 5-zS (bottom) and 5-zCuS (top) NRs. (b) Total magnetic moment (MM, or the difference between the spin majority and the spin minority charges) and energy difference (ΔE) between spin-polarized and spin-degenerate zCu and ICuS NRs as a function of the width. The insets show the charge difference between the spin majority and the spin minority densities ($0.002 |e|/\text{\AA}^3$) of the 5-zCu (bottom) and 5-ICuS (top) NRs.

FIG. 9. (Color online) Spin-polarized total density of states (left) and corresponding schematic diagrams (right) of the edge states for the (a) 5-zCu, (b) 5-zS, (c) 5-zCuS, and (d) 5-lCuS NRs.

Cu deficiency ($\text{Cu}_{2x-2}\text{Mo}_x\text{S}_{4x}$), displaying a shallow p -type doping, while the CBM is inherited from the 2D monolayer, as shown in Fig. 9(b). In the zCuS NR, the stoichiometry is the same as in the parent monolayer. The edge-induced states stem primarily from the Mo e_g orbitals of atoms near the Cu edge atoms, and they reflect deep n -type doping. The width-dependent band gaps open applications in transistors and optical devices with wide-range light emission.

In the zCu NR ($\text{Cu}_{2x+2}\text{Mo}_x\text{S}_{4x}$), two extra Cu atoms provide two extra s electrons to occupy the conduction bands, especially the Mo e_g states. The states are localized, confining a portion of charge at the four Mo atoms near the edges. We

obtain moments of $0.28 \mu_B$ per Mo, yielding a total magnetic moment of $2.0 \mu_B$, together with the edge Cu atoms. However, in the lCuS NRs ($\text{Cu}_{2x+4}\text{Mo}_x\text{S}_{4x+4}$), the four additional s electrons are confined along the two edges, mainly at the four S atoms (p_z states at the VBM), yielding a total magnetic moment of $4.0 \mu_B$. According to the two insets in Fig. 8(b), only the edge atoms contribute to the magnetism in zCu and lCuS NRs, while the inner atoms preserve the electronic properties of the 2D infinite systems. Consequently, the total magnetic moments and the energy difference between the spin-polarized and the spin-degenerate states hardly change when the width increases. A negligible energy difference between ferromagnetic and antiferromagnetic coupling of the two edges in the lCuS NR indicates a paramagnetic nature. In contrast, magnetism is preserved in the zCu NRs, because the magnetic moments mainly originate from the localized Mo d orbitals, which are not located at the edges. In addition, the two edges of the zCu NR are ferromagnetically coupled for $N = 5$ to 10 (width = 26.65 to 53.51 Å), and for $N = 15$ (width = 80.35 Å). The energy difference (~ 6 meV) between ferromagnetic and antiferromagnetic coupling does not depend on the NR width. Furthermore, antiferromagnetic ordering along an individual edge is not stable. The ferromagnetic behavior of the zCu NRs suggests the possibility of spin-polarized transport along the edges, and 2D dilute magnetic semiconductors are of great interest.

IV. CONCLUSIONS

We have performed first-principles calculations to demonstrate a novel class of 2D materials with a square lattice. Square Cu_2MoS_4 , Cu_2WS_4 , and Cu_2WSe_4 are found to be kinetically stable due to strong ionic bonding and the absence of dangling bonds at the X -terminated surfaces. The materials are semiconductors, with band gaps ranging from 2.03 to 2.48 eV. The states giving rise to the VBM are confined to the Cu and X atoms, while those giving rise to the CBM are confined to the M atoms. Spontaneous charge separation thus can be expected. NRs formed from the materials are highly interesting for applications in transistors, optoelectronics, and solar energy conversion. Besides size-dependent band gaps, the edge atoms of zCu and lCuS NRs are subject to spin polarization, which is found to be independent of the NR width. Particularly, ferromagnetic ordering is energetically favorable along the edges of zCu NRs, suggesting potential in spintronics.

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