Hexagonal $M_2C_3$ ($M = \text{As, Sb, and Bi}$) monolayers: new functional materials with desirable band gaps and ultrahigh carrier mobility

Peng-Fei Liu, Tao Bo, Zhifeng Liu, Olle Eriksson, Fangwei Wang, Jijun Zhao and Bao-Tian Wang

Based on first-principles calculations, we propose a new type of two-dimensional (2D) material $M_2C_3$ ($M = \text{As, Sb, and Bi}$) showing an infinite hexagonal lattice, in which C atoms adopt $sp^2$ hybridization and $M$ atoms prefer three-fold coordination with lone pair electrons. Such monolayers are calculated to be stable verified by their moderate cohesive energies, the absence of imaginary modes in their phonon spectra, and the high melting points predicted via molecular dynamics simulations. $Sb_2C_3$ and $Bi_2C_3$ monolayers possess intrinsic band gaps of 1.58 and 1.23 eV (based on HSE06 calculations), values suitable for photovoltaic applications. The intrinsic acoustic-phonon-limited carrier mobility of the $As_2C_3$ sheet can reach up to $4.45 \times 10^5$ cm$^2$ V$^{-1}$ s$^{-1}$ for electrons at room temperature, higher than that of $(60-200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ MoS$_2$ and $(\sim 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ few-layer phosphorene, approaching the figure of merit in graphene (3 $\times$ $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The well-located band edge and visible light absorption make stretched $Sb_2C_3$ a potentially promising optoelectronic material for photocatalytic water splitting. Besides, $Sb_2C_3/As_2C_3$ excitonic solar cells have been proposed, and their power conversion efficiencies are estimated to exceed 23%. First-principles calculations have demonstrated that $Sb_2C_3/Bi_2C_3$ heterojunctions are indeed 2D node-line semimetals in the absence of spin–orbit coupling.

1 Introduction

Since the mechanical cleavage method for exfoliating graphene from graphite in 2004, materials with ultrathin two-dimensional (2D) structures have attracted much attention.\textsuperscript{2-6} With one atom thickness but a very large lateral area, graphene shows novel structure-related properties, \textit{e.g.}, massless Dirac fermions,\textsuperscript{1} high electron/hole mobility,\textsuperscript{7} superconductivity with proper doping,\textsuperscript{8} ballistic electronic propagation,\textsuperscript{9} and the quantum Hall effect.\textsuperscript{10} However, the trait of zero band gap in pristine graphene greatly hampers its potential applications in modern electronics although its mobility is ultra-high. Beyond graphene, MoS$_2$ is another important 2D material with a finite band gap,\textsuperscript{11,12} but its carrier mobility is relatively low (60–200 cm$^2$ V$^{-1}$ s$^{-1}$).\textsuperscript{13} In this context, phosphorene, atomically thin phosphorus exfoliated from black phosphorus, seems to be an ideal candidate due to its inherent direct band gap (2.0 eV) and high hole mobility (of the order $10^5$ cm$^2$ V$^{-1}$ s$^{-1}$).\textsuperscript{14,15} However, few-layer phosphorene-based devices are environmentally-vulnerable when exposed to air and can only be used in an inert atmosphere.\textsuperscript{16,17} Thus, it is necessary to explore new potential 2D materials, which have not only controlled finite band gaps but also high carrier mobility.

Among the well-known 2D materials, elemental carbon and phosphorus have been studied extensively as both can experimentally and theoretically form stable 2D allotropes.\textsuperscript{1,4,15,18-20} Recently, theoretical studies have beautifully provided evidence of the existence of monolayer PC allotropes,\textsuperscript{21-26} which can show metallic properties with superconductivity,\textsuperscript{26} semimetalllic properties with an anisotropic Dirac cone, or semiconducting properties with superior carrier mobility depending on the configuration and ratio. Subsequently, few-layer black PC has
been successfully synthesized$^{27-29}$ and its field-effect transistor exhibits a high hole mobility of 1995 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature.$^{21}$ Black PC could also be a tunable anisotropic plasmonic metamaterial which provides a viable platform for hyperbolic metamaterials, bringing widespread application in biosensors, single-photon sources, nanoantennae, and subwavelength resolution imaging.$^{29}$ These results have shown that good semiconducting behavior can be induced in 2D phosphorus carbide nanomaterials.

Antimonene$^{30}$ and bismuthene,$^{31}$ belonging to the same group V family as phosphorene, have been successfully synthesized experimentally and show tremendous electro-optical properties. Besides, several theoretical predictions have successfully guided the syntheses of some 2D materials, such as silicene,$^{32,33}$ Janus TMDs,$^{34,35}$ Cu$_2$Si sheets,$^{36,37}$ borophene,$^{38-40}$ and blue phosphorene.$^{41-43}$ It is intriguing to find out whether the binary compounds of C and M (M = As, Sb, and Bi) also form stable 2D monolayers and possess superior properties. Based on ab initio calculations, we propose a novel family of 2D carbides M$_2$C$_3$ with hexagonal lattices containing C and M atoms. Phonon spectra and ab initio molecular dynamics (AIMD) simulations provide compelling evidence for the thermal and dynamical stabilities of M$_2$C$_3$ monolayers. Remarkably, we find that M$_2$C$_3$ monolayers are intrinsic semiconductors with band gaps of 2.27, 1.53, and 1.28 eV for As$_2$C$_3$, Sb$_2$C$_3$, and Bi$_2$C$_3$, respectively, using state-of-the art hybrid density functional calculations. The As$_2$C$_3$ monolayer possesses a relatively high work function of strained Sb$_2$C$_3$ can be induced in 2D phosphorus carbide nanomaterials.

The phonon calculations were carried out within the harmonic approximation via the force-constant method$^{52}$ as implemented in the PHONOPY code.$^{53}$ The orbital-resolved phonon spectra were calculated by postprocessing phonon eigenvalues on the basis of the phononic kp theorem$^{54,55}$

$$
\sum_{\mathbf{k}} e_{\mathbf{k},\mathbf{\sigma}}(\mathbf{r}) \cdot e_{\mathbf{k}+\mathbf{\Delta},\mathbf{\sigma}}(\mathbf{r}) = |\delta_{\mathbf{\sigma},\mathbf{\Delta}} - 0(\mathbf{\Delta})|, 
$$

where $e_{\mathbf{k},\mathbf{\sigma}}(\mathbf{r})$ was the displacement of the atom $j$ in the eigenvector of the ($k,\sigma$) vibrational mode, and $\Delta$ was a small wave vector.

The positions of the valence-band maximum (VBM) and conduction band minimum (CBM) were defined as

$$
E_{\text{CBM/VBM}} = E_{\text{GEC}} \pm \frac{1}{2} \epsilon_{\text{HSE06}},
$$

where $E_{\text{GEC}}$ was the band gap center energy calibrated with respect to the vacuum level.$^{56}$

To obtain the optical absorption spectra of M$_2$C$_3$ monolayers, the imaginary part of the frequency-dependent dielectric function was calculated from the interband transition in the independent-particle picture without including the local field effects using the following equation:$^{57}$

$$
\epsilon_2(\omega) = \frac{2\pi}{\Omega_0} \sum_{\mathbf{k},\mathbf{\sigma}} |\langle \Psi_{\mathbf{k}} | \mathbf{a}_{\mathbf{\sigma}}^T | \Psi_{\mathbf{k}}^{\text{c}} \rangle|^2 \delta(E_{\mathbf{k}}^{\text{c}} - E_{\mathbf{k}} - E). 
$$

The real part of the dielectric function $\epsilon_1$ was obtained by the Kramers–Kronig transformation. Then the optical absorption coefficients $\alpha(\omega)$ were evaluated according to the following equation (where $c$ is the speed of light in a vacuum)$^{58,59}$

$$
\alpha(\omega) = \sqrt{\frac{\omega}{c}} \left[ \sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega) \right]^{1/2}.
$$

The carrier mobility was obtained in the framework of deformation potential (DP) theory on the basis of the effective mass approximation.$^{60}$ The analytical expression of acoustic-phonon-limited carrier mobility in 2D materials can be defined as follows:$^{61-64}$

$$
\mu_{2D} = \frac{e^2 h}{k_B T m^* |v(E)|},
$$

where $m^*$ was the effective mass in the transport direction, $e$ was the electron charge, $T$ was the temperature (300 K), $v$ was the DP constant, and $v(E)$ was the 2D elastic modulus.

### 3 Results and analysis

#### 3.1 Structures of M$_2$C$_3$

The geometric configuration of monolayers of M$_2$C$_3$ is shown in Fig. 1a. They all share a honeycomb 2D form with a high group symmetry of $P6_3/mmm$ (No. 191). In the structures, the lattice parameter ($l_0$) obtained from ab initio calculations was 5.86, 6.39, and 6.70 Å for As$_2$C$_3$, Sb$_2$C$_3$, and Bi$_2$C$_3$, respectively (Table 1). There was one unique M (M = As, Sb, and Bi) atom (site symmetry 4h) and one independent C atom (site symmetry 6i) in the primitive cell. The 2D structure contained the planar...
ECoH bonding characteristic of graphene and the significantly different nonplanar sp^3 bonding feature found in 2D monoelemental arsenene,\textsuperscript{65} antimonene,\textsuperscript{30} and bismuthene.\textsuperscript{31} The C–C bond length was 1.33 Å for the three monolayers, which lies close to the value (1.42 Å) in sp^3 bonded graphite (or graphene).\textsuperscript{1} All M atoms were trigonally coordinated to ambient C atoms via quasi sp^3-hybridization bonding. As shown in Table 1, due to the atom effective radii of M atoms, the M–C bond lengths display an increasing trend with the following order: As\textsubscript{2}C\textsubscript{3} (2.00 Å) < Sb\textsubscript{2}C\textsubscript{3} (2.20 Å) < Bi\textsubscript{2}C\textsubscript{3} (2.31 Å). From the top view of the lattices, the M\textsubscript{2}C\textsubscript{3} sheets can be viewed as an enlarging of arsenene,\textsuperscript{65} antimonene,\textsuperscript{30} and bismuthene\textsuperscript{31} with the inserting of C atoms into the 2D networks.\textsuperscript{64} Thus, the M\textsubscript{2}C\textsubscript{3} sheets had periodically distributed pores of 5.86, 6.39, and 6.70 Å diameter, for As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3}, respectively, which were equal to their corresponding lattice constants, suggesting potential applications in gas separation and storage.

### 3.2 Stabilities of M\textsubscript{2}C\textsubscript{3}

To confirm the stability of M\textsubscript{2}C\textsubscript{3}, we have computed the cohesive energy (E\textsubscript{coh}) with respect to the isolated atoms, defined as

\[
E_{\text{coh}} = E_{\text{M}_2\text{C}_3} - n_M E_M - n_C E_C,
\]

where \(E_{\text{M}_2\text{C}_3}\), \(E_M\), and \(E_C\) are the total energy of a M\textsubscript{2}C\textsubscript{3} sheet, single M atom, and single C atom, respectively; \(n_M\) and \(n_C\) are the numbers of M or C atoms per unit cell. The calculated cohesive energies of M\textsubscript{2}C\textsubscript{3} sheets are \(-5.16\), \(-4.89\), and \(-4.66\) eV per atom for As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3}, respectively (Table 1). For comparison, the cohesive energies we calculated, for graphene,\textsuperscript{14,15} silicene,\textsuperscript{33} black phosphorene,\textsuperscript{14,15} arsenene,\textsuperscript{65} antimonene,\textsuperscript{30} and bismuthene,\textsuperscript{31} at the same theoretical level, were \(-7.85\), \(-3.83\), \(-3.48\), \(-2.97\), \(-2.64\), and \(-2.46\) eV per atom, respectively. It is obvious that the cohesive energies of M\textsubscript{2}C\textsubscript{3} are lower than the majority of the well-known 2D materials, which means that the experimental synthesis may be achieved with appropriate substrates.

The orbital-resolved phonon spectra and projected phonon density of states (PhDOS) for As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3} are shown in Fig. 1. The orbital-resolved phonon spectra and projected phonon density of states (PhDOS) for As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3} are shown in Fig. 1b and Fig. S1 (ESI†). 

The calculated linear elastic constants based on Hooke's law helps to stabilize the 2D geometry.

To check the mechanical stability of M\textsubscript{2}C\textsubscript{3} sheets, we have calculated the linear elastic constants based on Hooke's law through the energy–stress relationship.\textsuperscript{70} The calculated 2D elastic constants are \(C_{11} = 97.12\), \(C_{12} = 28.77\), \(C_{44} = 18.92\) N m\textsuperscript{-1}, and \(C_{66} = 34.15\), \(24.78\), \(19.41\) N m\textsuperscript{-1} for As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3}, respectively. These values meet the requirements of the stability criteria for 2D structures in the hexagonal class,\textsuperscript{64,71} e.g. \(C_{11} > |C_{12}|\) and \(C_{66} > 0\). The in-plane axial Young's moduli \((E = (C_{11} - C_{12})/C_{11})\) were 88.56, 65.68, and 51.81 N m\textsuperscript{-1}, which are much lower than that of graphene (340 N m\textsuperscript{-1})\textsuperscript{72} and MoS\textsubscript{2} (123 N m\textsuperscript{-1})\textsuperscript{73} but in the same order of magnitude as silicene (62.31 N m\textsuperscript{-1}).\textsuperscript{74} The calculated Poisson's ratios for M\textsubscript{2}C\textsubscript{3} are 0.296, 0.327, and 0.340 for As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3}, respectively, which are similar to those (0.16–0.59) of monolayer honeycomb structures of group-IV elements and III–V binary compounds.\textsuperscript{75}

The thermal stability of M\textsubscript{2}C\textsubscript{3} sheets has been examined by carrying out AIMD simulations\textsuperscript{31} at 1000 and 2000 K for 5 ps. As shown in Fig. S2 (ESI†), the structural integrity of M\textsubscript{2}C\textsubscript{3}
well retained and can be optimized back to their initial structures via ab initio relaxation calculations after the simulation at 1000 K. The compounds thoroughly degrade and the atomic configurations show serious distortion at 2000 K. Thus the three monolayers can maintain a stable 2D form at least up to 1000 K, which suggests good thermal stability at high temperature.

3.3 Chemical bonding and electronic structure

The electron localization function (ELF)\textsuperscript{76} can provide a good description of electron localization and chemical bonding character in solids. To highlight the bonds of C–C and M–C, the isosurfaces of ELF maps visualized by different colours were calculated and are plotted in Fig. 2 using VESTA software.\textsuperscript{77}

![Fig. 2 ELF maps sliced perpendicular to the (001) direction for (a) As\textsubscript{2}C\textsubscript{3}, (b) Sb\textsubscript{2}C\textsubscript{3}, and (c) Bi\textsubscript{2}C\textsubscript{3}. In the ELF maps, red and blue refer to the highest (1.0) and lowest (0.0) values of ELF, indicating a fully localized electron region and a low electron density area, respectively.](image)

For M\textsubscript{2}C\textsubscript{3} sheets, the electrons are well localized around the M atoms and the bonds of C–C, implying that C atoms adopt the favoured planar sp\textsuperscript{2}-hybridization and M atoms prefer the nonplanar sp\textsuperscript{3}-hybridization with lone pair electrons, which is common in graphene and arsenene/antimonene/bismuthene monolayers.\textsuperscript{30,31,65}

The orbital-resolved band structures and projected density of states (PDOS) of As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3} monolayers are shown in Fig. 3. Obviously, As\textsubscript{2}C\textsubscript{3} and Sb\textsubscript{2}C\textsubscript{3} are indirect band gap semiconductors since the VBM is located at the $\Gamma$ point whereas the CBM lies at the $K$ point. Monolayer Bi\textsubscript{2}C\textsubscript{3} has a direct PBE band gap of 0.81 eV, which is lower than that of As\textsubscript{2}C\textsubscript{3} (1.42 eV) and Sb\textsubscript{2}C\textsubscript{3} (0.92 eV) at the same computing level. Refined calculations based on the HSE06 method\textsuperscript{49,50} give enlarged gaps of 2.27, 1.53, and 1.28 eV for As\textsubscript{2}C\textsubscript{3}, Sb\textsubscript{2}C\textsubscript{3}, and Bi\textsubscript{2}C\textsubscript{3} monolayers, respectively. From the orbital-resolved band structures, one can see that the bands in the vicinity of the Fermi level mainly originate from the hybridization of M and C atomic orbitals. The PDOS analysis further revealed that the edges of the valence bands are dominated by the p orbitals of M atoms hybridized with visible contributions from the C-p orbitals, while the conduction band edges are mainly coming from the C-p orbitals and partly from the M-p orbitals. The contributions from other orbitals could be almost negligible for M\textsubscript{2}C\textsubscript{3} sheets around the Fermi level. The corresponding real-space charge distributions of the VBM and CBM are shown in Fig. 3. The valence bands at the $\Gamma$ point are mainly contributed

![Fig. 3 Calculated orbital-resolved band structures and projected density of states for (a) As\textsubscript{2}C\textsubscript{3}, (b) Sb\textsubscript{2}C\textsubscript{3}, and (c) Bi\textsubscript{2}C\textsubscript{3}. The colors of band structures are weighted by the contribution from M (blue) and C (red) atoms. The green, magenta, and dark yellow lines in the projected density of states highlight the s, p, and d orbitals. The high-symmetry points of $\Gamma$, $K$, and $M$ represent (0, 0, 0), (−1/3, 2/3, 0), and (0, 1/2, 0), respectively. Real-space charge distribution of the VBM and CBM for (d) As\textsubscript{2}C\textsubscript{3}, (e) Sb\textsubscript{2}C\textsubscript{3}, and (f) Bi\textsubscript{2}C\textsubscript{3}.](image)
to by M-p\(_x\) orbitals with indispensable components from C-p\(_{x,y}\) orbitals for As\(_2\)C\(_3\) and Sb\(_2\)C\(_3\) while the VBM of Bi\(_2\)C\(_3\) is mainly from M-p\(_x\) and C-p\(_{x,y}\) orbitals. The distributions of the CBM for the three monolayers are mainly characterized by the hybridized bonding and antibonding bands of C-p\(_z\) and M-p\(_{x,y}\) orbitals. Meanwhile, the C-p\(_z\) orbital characteristic of the CBM weakens on going from As\(_2\)C\(_3\) and Sb\(_2\)C\(_3\) to Bi\(_2\)C\(_3\) with the increasing mass of the M atoms.

3.4 Band edges and optical properties

The calculations with an HSE06 function revealed that the band gaps of M\(_2\)C\(_3\) all exceeded the free energy of water splitting of 1.23 eV. Additionally, for a 2D semiconductor to facilitate photocatalytic water-splitting, the CBM energy must be higher than the oxidation potential of O\(_2\)/H\(_2\)O (−5.67 eV).\(^78\) In recent years, intensive efforts have been devoted to addressing this issue via first-principles frameworks, including in a series of work by the Hybertson group\(^79\) and Galli group.\(^80\) They promise to be more accurate for the electronic screening based on quasiparticle correction and explicit modeling of interface heterostructures. Herein, on the basis of the HSE06 method,\(^49,50\) we have calculated the band edges of M\(_2\)C\(_3\) with respect to the vacuum level (Fig. 4 and Fig. S3, ESI\(^\dagger\)).\(^56\) Comparing the band edge positions of single-layer M\(_2\)C\(_3\) with the redox potentials of hydrogen evolution (H\(^+/\)H\(_2\)) and oxygen evolution (O\(_2\)/H\(_2\)O) at pH = 0, we find that the pristine M\(_2\)C\(_3\) monolayers are not suitable for photocatalytic water splitting.

Since a 2D film must eventually be deposited or grown on a substrate for device application, it is quite crucial to check the effects of strain on the band gaps and band edge positions for M\(_2\)C\(_3\). Using the HSE06 method,\(^49,50\) we applied biaxial strains in the range from −6% to +6% to relax atomic positions and obtain the corresponding CBM and VBM from the relaxed configurations (Fig. 4).\(^59\) Over large regions of strain, the CBM and VBM levels depend linearly on strain. However, for the three materials we observed that the slope changes abruptly at certain strains due to the change of band edge positions, which induce a transition between an indirect and a direct band gap phase for M\(_2\)C\(_3\). When stretching M\(_2\)C\(_3\), we can see that only the band edges of Sb\(_2\)C\(_3\) are appropriate for initializing photocatalytic redox reactions of water.

Besides the above criteria, a photocatalyst must have excellent optical absorption mainly in the visible region with wavelengths of 380–780 nm.\(^56\) The calculated optical spectra with polarization vectors parallel to the layer plane for M\(_2\)C\(_3\) as a function of photon energy are shown in Fig. 4. It is seen that As\(_2\)C\(_3\) shows significant ultraviolet light absorption, while Sb\(_2\)C\(_3\) and Bi\(_2\)C\(_3\) show substantial absorption for both visible light and ultraviolet light, suggesting highly efficient utilization of solar radiation. Moreover, the average absorption intensities in the visible light region of Sb\(_2\)C\(_3\) are very strong with values of more than 10\(^4\) cm\(^−1\), which are superior to that of the famous 2D g-C\(_3\)N\(_4\) photocatalyst.\(^81\) For the effects of biaxial strain on the optical properties of M\(_2\)C\(_3\), the calculated results indicate that the negative strain will significantly affect the absorption coefficients of Sb\(_2\)C\(_3\) and Bi\(_2\)C\(_3\) in the form of red shift while the

Fig. 4 Schematic illustration of band edge positions of M\(_2\)C\(_3\) monolayers relative to the vacuum level, which is set to 0 eV. The reduction potential of H\(^+/\)H\(_2\)) and the oxidation potential of O\(_2\)/H\(_2\)O are marked by the red and blue dashed lines, respectively. The CBM and VBM band edge positions are marked by the solid black lines. (a, b and c) are for the pristine and strained (a) As\(_2\)C\(_3\), (b) Sb\(_2\)C\(_3\), and (c) Bi\(_2\)C\(_3\) within a strain range from −6% to 6% based on HSE06 level. The energy gaps of semiconductor photocatalysts are marked by the black arrows (solid: direct band gap; dotted: indirect band gap). Strain-dependent optical absorption coefficients s(\(\omega\)) for (d) As\(_2\)C\(_3\), (e) Sb\(_2\)C\(_3\), and (f) Bi\(_2\)C\(_3\) based on HSE06 level. The seven-colour light area between the dashed lines represents the visible light range (380–780 nm).
positive strain has little influence on these. Within a strain range of −6% to 6%, monolayer Sb₂C₃ exhibits strong absorption in the visible-light range.

3.5 Carrier mobilities of M₂C₃

The carrier mobility of M₂C₃ has been calculated on the basis of the DP theory proposed by Bardeen and Shockley, which has been widely used for investigating the electronic transport properties of 2D atomic layered structures.61-64 The effective mass and relaxation time are summarized in Table 2. The effective mass m* of holes was 1.037, 0.706, and 0.549 mₑ for As₂C₃, Sb₂C₃, and Bi₂C₃, respectively. On the other hand, the effective mass m* of electrons was 0.581, 0.477, and 0.464 mₑ for As₂C₃, Sb₂C₃, and Bi₂C₃, respectively. These values are much larger than those of phosphorene (0.15 and 0.17 mₑ for holes and electrons along the Γ–X direction),83 2D SnSe (0.13 and 0.16 mₑ for holes and electrons),84 h-BX (X = P, As, and Sb) (0.04–0.18 mₑ),85 x-PC (0.12 and 0.10 mₑ for holes and electrons along the X direction),22 and β-PC (0.05 mₑ along the X direction),22 but in the same order of magnitude as MoS₂ (0.46–0.60 mₑ)83 and GeP₃ (0.55–0.80 mₑ).86 The obtained deformation potentials (Eₓ) for electrons were 0.096, 0.339, and 0.714 eV for As₂C₃, Sb₂C₃, and Bi₂C₃ monolayers, respectively, which are much smaller than the corresponding Eₓ of holes (0.888, 1.708, and 3.850 eV). They are much smaller than those of other 2D materials which have values in the range 3.7–5.0 eV.22,61,83,84,86 These small values can be unrolled by the real-space charge distribution of the VBM and CBM shown in Fig. 3d–f, where the wavefunctions from p orbitals are extremely robust due to the bonding of sp²-hybridization from the C atoms and the isolation of lone pair electrons from M atoms.

The 2D in-plane stiffness (C²D) of As₂C₃, Sb₂C₃, and Bi₂C₃ monolayers was calculated to be 97.04, 73.57, and 58.45 N m⁻¹ (Fig. S5, ESIf), respectively, which was larger than that of phosphorene (28.94 N m⁻¹ along the Γ–X direction)83 and smaller than that of MoS₂ (127.44 N m⁻¹) and phosphorene (101.60 N m⁻¹ along the Γ–Y direction).83 The decrease of C²D for M₂C₃ shows that the interaction of M and C atoms becomes weak from As to Sb to Bi. The obtained acoustic-phonon-limited carrier mobility for electrons was 4.45 × 10⁵, 4.01 × 10⁴, and 7.57 × 10³ cm² V⁻¹ s⁻¹ for As₂C₃, Sb₂C₃, and Bi₂C₃, respectively. The hole mobility was found to be much smaller than that for electrons with values of 1.63 × 10³, 7.20 × 10², and 1.86 × 10² cm² V⁻¹ s⁻¹. The differences between electron and hole mobility can be mainly ascribed to the different deformation potentials and effective masses in M₂C₃. It can be seen that the obtained electron mobility of 4.45 × 10⁵ cm² V⁻¹ s⁻¹ for As₂C₃ is larger than that of the MoS₂ monolayer (60–200 cm² V⁻¹ s⁻¹)⁶¹ and few-layer black phosphorus (0.10–10⁷ cm² V⁻¹ s⁻¹)⁸⁷ and graphene (3.38 × 10⁵ cm² V⁻¹ s⁻¹).⁸⁷ Meanwhile, the ratio of electron and hole mobility was 273.0, 55.7, and 40.7 for As₂C₃, Sb₂C₃, and Bi₂C₃, respectively. Such large disparity can be used to separate electrons and holes,⁹⁸ thus further reducing carrier recombination rates.

3.6 vdW heterojunctions of M₂C₃

Deduced from the above analysis, the band gaps of Sb₂C₃ and Bi₂C₃ were 1.53 and 1.28 eV, respectively, which makes these monolayers promising solar-cell absorption materials.⁹⁸ For the Sb₂C₃ monolayer, we find theoretically that n-As₂C₃/p-Sb₂C₃ vdW heterojunctions (Fig. S6 and Table S1, ESIf) are direct-band-gap semiconductors characterized with typical type-II band alignment (Fig. 5, and Fig. S7–S10, ESIf) with high thermal stability (Fig. S11, ESIf), which could facilitate the effective separation of photogenerated electron and hole pairs and therefore become good candidates for next-generation solar cells.⁹⁰,⁹¹ The practical upper limit of the power conversion efficiency (η) for studying solar cells can be estimated in the limit of 100% external quantum efficiency as below:⁹²,⁹³

$$\eta = \frac{J_{sc}I_{sc}\beta_{FF}}{P_{solar}} = 0.65 \left( \frac{E_{g}^2 - \Delta E_{g} - 0.31 \int_{E_g}^\infty P(h\omega) d(h\omega)}{\int_{0}^\infty P(h\omega) d(h\omega)} \right),$$

where 0.65 is the fill factor (β_{FF}), P(h\omega) is the AM1.5 solar energy flux at the photo energy (h\ω), ΔE_{g} is the conduction band offset, J_{sc} is the maximum open circuit voltage, and J_{oc} is an integration in the limit external quantum efficiency of 100%. The efficient n-As₂C₃/p-Sb₂C₃ heterojunctions could have a power conversion efficiency (η) exceeding ~23%, which is comparable with g-SiC₂ based systems,⁹⁄₄ Al₂C based heterobilayers,⁹⁵ and phosphorene/MoS₂ systems.⁹⁶

For the Sb₂C₃/Bi₂C₃ heterojunctions (Fig. S6 and Table S1, ESIf), first-principles calculations show that they are indeed 2D node-line semimetals⁹⁷ in the absence of spin–orbit coupling (Fig. 5, Fig. S7 and S12, ESIf). It can be clearly seen that the Sb₂C₃ and Bi₂C₃ orbitals overlap around the K point and the orbital characters exchange after passing through the band crossing points, indicating an intrinsic band inversion from the formation of a heterojunction. To clearly show the node-line natures of the Sb₂C₃/Bi₂C₃ heterojunctions, we have calculated 3D band structures in the whole BZ using a two-dimension wave vector mesh. It is obvious that the conduction band and valence band meet at a circle centered at the K point rather than isolated points, exhibiting features of node-line semimetals similar to other 2D monolayers, such as MX (M = Pd and Pt; X = S, Se, and Te) monolayers,⁹⁷ honeycomb-kagome Hg₃As₂,⁹⁸ and line-centered square Be₂C.⁹⁹

### Table 2

<table>
<thead>
<tr>
<th>Comp. Carrier</th>
<th>Type</th>
<th>E₁ (eV)</th>
<th>C²D (N m⁻¹)</th>
<th>m* (mₑ)</th>
<th>μ (cm² V⁻¹ s⁻¹)</th>
<th>τ (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₂C₃</td>
<td>Electrons</td>
<td>0.096</td>
<td>97.04</td>
<td>0.581</td>
<td>4.45 × 10⁵</td>
<td>1.47 × 10⁴</td>
</tr>
<tr>
<td></td>
<td>Holes</td>
<td>0.888</td>
<td>73.57</td>
<td>1.037</td>
<td>1.63 × 10⁴</td>
<td>9.62 × 10³</td>
</tr>
<tr>
<td>Sb₂C₃</td>
<td>Electrons</td>
<td>0.339</td>
<td>73.57</td>
<td>0.477</td>
<td>4.01 × 10⁴</td>
<td>1.09 × 10⁴</td>
</tr>
<tr>
<td></td>
<td>Holes</td>
<td>1.708</td>
<td>73.57</td>
<td>0.706</td>
<td>2.60 × 10⁴</td>
<td>2.14 × 10⁴</td>
</tr>
<tr>
<td>Bi₂C₃</td>
<td>Electrons</td>
<td>0.714</td>
<td>58.45</td>
<td>0.464</td>
<td>7.57 × 10⁴</td>
<td>2.00 × 10³</td>
</tr>
<tr>
<td></td>
<td>Holes</td>
<td>3.850</td>
<td>58.45</td>
<td>0.549</td>
<td>1.86 × 10⁵</td>
<td>5.82 × 10⁴</td>
</tr>
</tbody>
</table>
junction solar cells have power conversion efficiencies exceeding higher that of graphene (3/C2 band edge and visible light absorption make strained Sb2C3/ Bi2C3 are intrinsic semiconductors with band gaps of 2.27, 1.58 eV). The room-temperature electron mobility of the 2D monolayer a potentially promising optoelectronic material for photocatalytic water splitting. Besides, Sb2C3/As2C3 heterostructures are weighted by the contribution from the Sb2C3 (blue) and Bi2C3 (red) monolayers.

**4 Conclusions**

In summary, we theoretically identify the existence of two-dimensional (2D) materials M2C3 (M = As, Sb, and Bi) with an infinite hexagonal lattice. In the structure, each C atom adopts sp2 hybridization with one C atom and two M atoms, while M atoms retain the sp3 hybridization character with lone pair electrons. Calculated results indicate that As2C3, Sb2C3 and Bi2C3 are intrinsic semiconductors with band gaps of 2.27, 1.58 and 1.23 eV. The room-temperature electron mobility of the M2C3 sheet is calculated to be 4.45 × 10^5 cm^2 V^{-1} s^{-1}, which is higher than that of graphene (3 × 10^5 cm^2 V^{-1} s^{-1}). The well-located band edge and visible light absorption make strained Sb2C3 monolayer a potentially promising optoelectronic material for photocatalytic water splitting. Besides, Sb2C3/As2C3 heterojunction solar cells have power conversion efficiencies exceeding ~23%, while Bi2C3/Sb2C3 heterojunctions possess features of 2D node-line band structures in momentum space in the absence of SOC. Our results highlight the unique electronic and structural properties of a new family of 2D materials and are expected to guide future studies toward experimental realization of efficient photoelectric applications based on these binary materials.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

Zhifeng Liu acknowledges financial support from the National Natural Science Foundation of China under Grant No. 11604165. We acknowledge the computational support from the Supercomputing Center of Dalian University of Technology (DUT) and the China Spallation Neutron Source (CSNS).

**References**