Stable halogen 2D materials: the case of iodine and astatine

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Abstract
Two-dimensional (2D) materials have applications towards electronic devices, energy storages, and catalysis, et al. So far, most of elemental 2D materials are composed based on groups IIIA, IVA or VA. To expand the 2D material family, the orbital hybridization becomes a key factor to determine stability. Here we predict that sp²d³ hybridization of the outmost electrons in iodine and astatine can build up 2D triangle lattices, delta-iodiene and delta-astatiene, using first-principles calculations. Each atom is connected by σ bonds with nearest 6 atoms and the π bonds are thus introduced. The band gaps can approach zero because of interaction of unpaired single electron between each atom, if the identical bond length is reduced. By inducing compression strain, the Dirac points or topological nontrivial points can be created in the delta-iodiene and delta-astatiene. Our discovery paves a new way to construction of 2D materials.

Keywords: 2D materials, density functional calculations, band structures, Dirac point, iodine

(Some figures may appear in colour only in the online journal)

1. Introduction
The two-dimensional (2D) material has become a star in the areas of new energy [1,2] catalysis [3, 4], and electronic devices [5] etc. So far, single-elemental 2D materials have mainly been built up by the elements of main group IIIA, IVA, or VA [6]. Graphene and graphene-like structures have been found, such as borophene [7,8], indiene (group IIIA) [9], silicene [10–14], germanene [15–18], stanene (group IVA) [19–22], black phosphorene(BP) [23–26], bismuthene [27–29], and arsenene (group VA) [27,30,31]. In some of 2D materials, e.g. graphene, the unpaired p-wave electrons can form weak π bonds, inducing linear-energy dispersion to induce mass-less Dirac fermions [32]. Meanwhile, VA group elements, e.g. BP, can form 2D configurations sustained by sp³-hybridized orbitals, where their Dirac points arise from appearance of band inversion [33–36] and formation of π bonds [32]. Their linear-energy dispersion brings Dirac points, also implying the existence of massless Dirac fermions [37,38]. By far, the 2D materials from group IIIA–VA are generally recognized as possessing sp² or sp³ hybrid orbitals, exhibiting covalent σ bonds strong enough to sustain the 2D configurations [6]. However, construction of 2D materials by elements beyond IIIA, IVA and VA main group, e.g., VIIA sounds challenging. Atoms from VIIA are difficult to form a periodical configuration because of weak covalent bonding, and the constraints of the hybridization rule including d bands. It is not favourite because of the octet rule, either.

On the other hand, considering the low energy difference between p wave orbitals and d wave orbitals of I and At atoms, the s–p–d hybridization should be possible, despite the factor that the covalent bonding in elemental 2D materials is weaker than those in group IIIA–VA. Our previous work has verified the stability of such bonding [39]. Therefore, it is possible to
design 2D materials of I or At with stable structures. Here we present halogen 2D materials as halogenene, deriving from element iodine or astatine in group VIIA. The 2D structures arise from triangle configurations and named as delta-iodiene and delta-astatiene, demonstrating their difference from the square cells in the previous report [39]. The delta-halogenene is built up based on sp2d3 hybridized $\sigma$ bands, but $\pi$ band at the high symmetry points is difficult to come into being due to the relatively long bond length (LBL), although there is an unpaired electron in each atom [40–42]. Dirac points can be further introduced using band inversion [43], arising from bond length reduction to form $\pi$ bonds [41].

2. Computational methods

First-principles calculations were performed using the plane wave code Vienna $ab$ initio simulation package (VASP) [44]. Generalized-gradient approximation (GGA) with the Perdew–Burke–Ernzerh of functional (PBE) was used to describe the exchange–correlation effects [45] and the projector augmented wave method (PAW) was employed for the electron–ion interactions [46]. The cut-off energy of the plane-wave expansion was set to 400 eV. All configurations are fully relaxed, the remanent force threshold and energy tolerance per atom are 0.01 eV Å$^{-1}$ and $1 \times 10^{-8}$ eV, respectively. The accuracy 0.02 $2\pi$/Å was used for $K$ point sampling. Gamma algorithm was used for all $K$ points. A 30 Å vacuum layer was used to prevent the interaction between periodic structures. The phonon spectra were calculated based on DFPT algorithm with a $2 \times 1 \times 1$ supercell [47]. According to the formula:

$$E_b = E_{at} - E_{sheet}$$

the binding energies of materials ($E_b$) were calculated, where $E_{at}$ is the energy of an isolated spin polarized atom and $E_{sheet}$ is the energy of each atom in the 2D materials [48].

By multiplying the two crystal axes of $a$-axis and $b$-axis with the same scaling coefficient, the biaxial strain of the crystal was employed. Since the lattice constants $a$ and $b$ of P6/mmm space group are equivalent to each other, uniaxial strain was introduced by further multiplying one of the crystal axes with a scaling factor.

3. Results and discussion

3.1. Introducing VII A group into the 2D elemental materials: delta-halogenene

3.1.1. Structure and phonon spectrum. The halogenene structures with planar configurations are shown in figures 1(a) and (b). They are named as delta-iodiene and delta-astatiene because of triangular cell configurations. The configurations can be more stable than those of hexagonal ones (see section 3.2 more elaboration of delta-halogenene for more details). Planar delta-halogenene structures can be stable, because of absence of imaginary frequency in phonon spectra (figures 1(c) and (d)). There is only one atom in each of their primitive cells, so there are only acoustic branches visible in the phonon spectra. The schematic diagram of the primary cell with a P6/mmm spatial point group and the first Brillouin zone (BZ) can refer to figures 1(e) and (f).

Moreover, the delta-halogenene is different from any previously reported hexagonal structures, and even different from borophene with the delta structure. The $\sigma$ bonds in the delta-halogenene come from s–p–d hybridization, whereas those in previous literatures are from s–p hybridization (see details in section 5 hybrid orbital analysis).
3.1.3. Band structure and density of states. The lattice constants of delta-halogenene structures are much larger than those of graphene or boron nitride [52]. Meanwhile, both band structures and density of states (DOS) confirm that delta-iodiene and delta-astatiene are with wide band gaps of 2.85 eV and 2.25 eV, respectively (figure 2), similar to wide bandgap 2D materials, arsenene (2.49 eV) and antimonene (2.28 eV), respectively (figure 2), similar to wide bandgap 2D materials, arsenene (2.49 eV) and antimonene (2.28 eV) [30]. Due to the LBLs of delta-astatiene and delta-iodiene, it can be understood as that the unpaired single electrons become localized and thus p$_z$ orbitals cannot overlap in spatial to form π bonds.

3.2. More elaboration of halogenene

In this section, three configurations are taken into account, planar, buckling and puckered structures, which shows that only the planar triangle configuration is stable.

3.2.1. Hexagonal halogenene structures. Hexagon-halogenene (figures 3(a) and (b)) shows imaginary frequencies in the phonon spectra (figures 3(c) and (d)), implying such 2D configuration is unstable. Moreover, the electron localization function (ELF) value can be evaluated referring to the colour of legend (figure 4). From blue through green to red, the higher the ELF value is, the higher the localization degree of electrons is. The ELF section diagram shows there is a strong anti-localized region [53] in the centre of a hexagon structure (figures 4(a) and (c)), which could explain why the hexagon-halogenene is unstable. In a unit cell, if the other hexagon lattice is introduced to locate the centre of the hexagon (figure 4(b)), a triangular periodic structure can be created removing imaginary frequency completely (figure 1(c)). Although the additional atoms cannot increase the binding energy for a single bond (figures 4(a) and (b)), the increasing bond density enhances the bonding level substantially (figure 4(b)).

Although most of the elemental 2D materials have hexagonal structures, the halogenene hexagon configuration cannot be sustained by the sp$^2$ hybridized σ bonds. The ELF around a halogenene atom is between 0.2 and 0.4, which shows a weaker covalent bonding state than that of other 2D materials [53].

In addition, the ELF can be illustrated in three dimensional (3D) images (figure 4(e)). The bond length is 3.37 Å for iodiene, and 3.51 Å for astatiene, which is much shorter than the van der Waals diameter [53], suggesting a covalent bond is formed. Each atom has six nearest neighbours (figure 4(e)). Because each atom with an unpaired single electron is connected by σ bonds with surrounding 6 atoms, it is possible to form π bonds (see section 3.3 for more details).

3.2.2. Buckled halogenene structures. Triangular and hexagonal buckled configurations are both considered to be halogenene candidates (figures 5(a) and (c)). According to the lattice constants of planer delta-iodiene and delta-astatiene (table 1), the bond lengths of buckled iodiene and astatiene
Figure 4. Electronic local functions (ELF) of delta-iodiene and delta-astatiene. (a) Hexagon-iodiene. (b) Delta-iodiene. (c) Hexagon-astatiene. (d) Delta-astatiene. Obviously unstable hexagon structures have larger electron vacuum regions than triangular structures. (e) Top and side view of delta-iodiene electronic local functions of 7 × 7 super-cell.

Figure 5. Structural changes of buckled iodiene as typical halogenene before and after geometric optimization. Buckled delta-halogenene. (a) Before geometric optimization. (b) After geometric optimization. Buckled hexagonal halogenene. (c) Before geometric optimization. (d) After geometric optimization.

Figure 6. Phonon spectra of buckled structures. (a) Delta-astatiene, (b) hexagon-astatiene, (c) delta-iodiene, and (d) hexagon-iodiene.

Figure 7. Phonon spectra of delta-iodiene for different values of the buckling Δ. (a) Δ = 0.2 Å (b) Δ = 0.8 Å. (c) Δ = 1.4 Å.

Figure 8. Phonon spectrum of hexagon-iodiene for different values of the buckling Δ. (a) Δ = 0.2 Å (b) Δ = 0.8 Å. (c) Δ = 1.2 Å.

were set as 3.37 angstroms and 3.51 angstroms. However, the geometric optimization makes the single-layer buckled delta-halogenene into a planar bilayer structure, and the buckled hexagon-halogenene into a planar structure.

Figure 6 shows the phonon spectra of buckled structures. It is found out that all the four structures have imaginary frequencies, indicating that the buckled structures of iodiene and astatiene cannot be stable, which is consistent with the result of the geometric optimization.

When buckled delta-iodiene have the same bond length with planer delta-iodiene, the buckling Δ is 1.4 Å (figure 7(c)). In figure 7, it can be seen that the structure remains unstable with different Δ.

When buckled hexagonal iodiene have the same bond length with planer delta-iodiene, the buckling Δ is 1.2 Å (figure 8(c)). When buckling Δ decreases, there are imaginary
3.2.3. Puckered halogenene structures. According to the bond length of planer delta-iodiene (3.37 Å) and delta-astatiene (3.51 Å), the structure model of puckered iodiene and puckered astatiene (figure 9(c)) were built. The phonon spectra of these two structures show that both of them have virtual frequencies (figures 9(a) and (b)), indicating that puckered iodiene and astatiene cannot be stable.

3.3. From wide band gap semiconductors to Dirac semimetals

3.3.1. Biaxial strain. The band structure of delta-iodiene and delta-astatiene can be further tuned by strain. When biaxial tensile strain is applied to delta-halogenene, its band gap increases (figures 10(a2) and (b2)). When applying biaxial compression strain, the band gap of delta-halogenene became smaller with the strain increasing (figure 10). When the strain reaches the critical values, 10.2% for delta-iodiene (figure 10(a3)) and 9% for delta-astatiene (figure 10(b3)), the band gap of delta-halogenene became zero. Further increase of strain can induce the band inversion, leading to the formation of topological nontrivial points [54], suggesting the delta-halogenene is a topological semimetal system [55] or a quantum spin hall (QSH) system [56]. When the strain increases to 12.5%, the contact bands are converted into inversion bands (figures 10(a4) and (b4)). Dirac points surrounding the gamma point in BZ form Dirac arc near the Fermi level. More bands are involved into band inversion if strain is...
Figure 12. Band structures of uniaxial strained delta-iodiene and delta-astatiene. Band structure under 12.5% of (a) delta-iodiene, (b) delta-astatiene, and under 15% of (c) delta-iodiene, (d) delta-astatiene. (e) 3D HOMO and LUMO band structure of delta-iodiene under 15% uniaxial strains. (f) 3D HOMO and LUMO band structure of delta-astatiene under 15% uniaxial strain. The LUMO structure is turned $180^\circ$ for a better vision.

Figure 13. Band structure of delta-iodiene with and without SOC. (a1–d1) band structure of iodiene without SOC under different compression strain. (a2–d2) band structure of iodiene with SOC effect under different compression strain.

Figure 14. Band structure of delta-astatiene with and without SOC. (a1–d1) band structure of astatiene without SOC under different compression strain. (a2–d2) band structure of astatiene with SOC effect under different compression strain.

Figure 11 illustrates the 3D band structure of delta-iodiene under biaxial strain. Beyond the critical strain (10.2% for iodiene, figure 10(a3)), the Dirac arcs (strain $= 12.5\%$ or $15\%$) or topological nontrivial lines (figures 11(c) and (d)) increased to 15% (figures 10(a5) and (b5)). When biaxial strain is applied in delta-halogenene, the bond length can be shortened to less than 3.0 Å, and then the $\pi$ bands come into being because of the electron cloud overlap of suspended electron bonds between adjacent atoms.

Figure 11 illustrates the 3D band structure of delta-iodiene under biaxial strain. Beyond the critical strain (10.2% for iodiene, figure 10(a3)), the Dirac arcs (strain $= 12.5\%$ or $15\%$) or topological nontrivial lines (figures 11(c) and (d))
Figure 15. Orbital hybridization of iodine. (a–f) orbital projection band structure. s, p_x, p_y, d_{xy}, d_{x^2−y^2} and d_{z^2} orbitals participate in the hybridization. The projected density of the d orbital is magnified by 30 times. (g) Hybridization of iodine and astatine atomic orbitals. The orange boxes are the orbitals that are participating in the hybridization. (h) The orbital projection band structure of p_z is isolated from those orbitals that participate in the hybridization. The p_z orbital is occupied by an unpaired electron.

arise from the inversion of the valence bands and conduction bands. Here the strain is employed to promote the HOMO band level and the band gap will be reduced simultaneously. Once the HOMO becomes contacted with LUMO, the further compressive strain will lead to the bands, both conductance band and valance band, to reverse around the gamma points. The LUMO shows obvious band inversion under strain, but the HOMO not (figures 11(e) and (f)).

3.3.2. Uniaxial strain. Under uniaxial strain, the structure symmetry will be broken, and the band structure undergoes different evolution history from that under biaxial strain (figures 10 and 11). Since the high symmetry is lost, anisotropy arises in the properties. For delta-iodiene, even 12.5% strain cannot reduce the band gap to zero (figure 12(a)), and the band structure loses its symmetry near the gamma point. When uniaxial strain reaches 15%, the band inversion occurs in the band structure (figure 12(c)). The LUMO and HOMO bands contact and introduce Dirac arcs, suggesting a Dirac semi-metal state or topological semi-metal state appear in delta-iodiene (figure 12(e)).

The delta-astatiene is also studied under uniaxial compression (figures 12(b), (d) and (f)). The difference is that the band inversion in delta-astatiene occurs much earlier than that in delta-iodiene, that is, under 12.5% strain (figure 12(b)). Although the uniaxial strain reduced the symmetry of 2D configuration, the band inversion remains in LUMO centred around the gamma point. Therefore, the variation of the band structure in delta-astatiene is similar to that of iodiene under uniaxial strain.

4. Effect of SOC on Dirac point (topological nontrivial points)

As we all know, the spin-orbit coupling (SOC) can induce a very strong inner magnetic field in some specific materials, including some 2D materials, such as 2D-Bi sheet, 2D-Sb sheet, and 2D-Se3Bi2 sheet and so on. If the magnetic field is strong enough to induce the band inversion on the surface, the topological nontrivial point can be created. Here, the biaxial strain can induce the band inversion. Moreover, the inverted band structure can be further modified to the real situation with applying SOC, suggesting a topological structure should be possible.

Since delta-halogenene is wide band gap semiconductor, SOC can make the band gap reduction (figures 13(a1) and (a2), 14(a1) and (a2)). If applying strain effect only without considering SOC, the compressive strain 10.2% can only make the VB contact with CB, and the band gap become zero but no Dirac point can be observed. However, if considering SOC as well as strain simultaneously, the band inversion become very significant (figures 13(b1) and (b2), 14(b1) and (b2)). With the strain increasing, the SOC can tune the inverted band into more elaborate structures (figures 13(c1) and (c2), 14(c1) and (c2)).

5. Hybrid orbital analysis

The orbital projection band structures demonstrate the orbital hybridization in BZ (figures 15(a)–(f)). Based on the analysis, it is found out that s, p_x, and p_y, while the d_{xy}, d_{x^2−y^2}, and d_{z^2} are all important participants.
All the orbitals in halogen atoms have been demonstrated in figure 15(g), where all the possible hybrid orbitals are shown. Meanwhile the sp^2d^3 hybrid orbitals have been marked into yellow, suggesting the left orbitals and possible hybrid orbitals should be ignorable.

If the orbital has not participated the sp^2d^3 hybrid, its orbital projection band should not overlap with any hybrid branch (figure 15(h)), where the p Orbital projection band shows a completely different outline from hybrid one.

6. Conclusion
With first-principles calculations, we predict two stable 2D configurations, delta-iodiene and delta-astatiene. The existence of VIIA elemental 2D configuration is reasonable and might be realized in experiments. The sp^2d^3 orbital hybridization permits the covalent bonds to accommodate all the outermost electrons, and the high density of covalent bonds make the atoms tightly and steadily bounded into the planar 2D configurations with wide band gaps. Further applying strain can induce the Dirac semimetal or topological semimetal states. It is believed that, by selecting the appropriate substrate, the method of CVD can be used to prepare delta-iodiene or delta-astatiene in the experiment.

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