The effect of the interlayer element on the exfoliation of layered Mo$_2$AC (A = Al, Si, P, Ga, Ge, As or In) MAX phases into two-dimensional Mo$_2$C nanosheets

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2014 Sci. Technol. Adv. Mater. 15 014208
(http://iopscience.iop.org/1468-6996/15/1/014208)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 129.120.87.225
This content was downloaded on 07/02/2017 at 17:18

Please note that terms and conditions apply.

You may also be interested in:

Trends in electronic structures and structural properties of MAX phases: a first-principles study on M$_2$AlC (M = Sc, Ti, Cr, Zr, Nb, Mo, Hf, or Ta), M$_2$AlN, and hypothetical M$_2$AlB phases
Mohammad Khazaei, Masao Arai, Taizo Sasaki et al.

Vibrational and mechanical properties of single layer MXene structures: a first-principles investigation
Uur Yorulmaz, Ayberk Özden, Nihan K Perkgöz et al.

A comparative first-principles study of the electronic, mechanical, defect and acoustic properties of Ti$_2$AlC and Ti$_3$AlC
Jie Tan, Han Han, Darshana Wickramaratne et al.

Phase stability, electronic structure and mechanical properties of molybdenum disilicide: a first-principles investigation
Yingjie Qiao, Hexin Zhang, Changqing Hong et al.

First-principles study of electronic structure, mechanical and optical properties of V$_4$AlC$_3$
Chenliang Li, Biao Wang, Yuanshi Li et al.

A new layer compound Nb$_4$SiC$_3$ predicted from first-principles theory
Chenliang Li, Jeilai Kuo, Biao Wang et al.

Structure of the ternary carbide Ti$_3$SnC$_2$ from ab initio calculations
M B Kanoun and M Jaouen

The investigation of dependences of mechanical and electronic properties of TiB$_2$ on pressure using first-principles method
Mingliang Wang
The effect of the interlayer element on the exfoliation of layered Mo\(_2\)AC (A = Al, Si, P, Ga, Ge, As or In) MAX phases into two-dimensional Mo\(_2\)C nanosheets

Mohammad Khazaei\(^1\), Masao Arai\(^1\), Taizo Sasaki\(^2\), Mehdi Estili\(^3\) and Yoshio Sakka\(^4\)

\(^1\) Computational Materials Science Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Ibaraki, Japan
\(^2\) Computational Materials Science Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba 305-0047, Ibaraki, Japan
\(^3\) International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba 305-0047, Ibaraki, Japan
\(^4\) Materials Processing Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba 305-0047, Ibaraki, Japan

E-mail: khazaei.mohammad@nims.go.jp

Received 27 September 2013
Accepted for publication 19 January 2014
Published 10 February 2014

Abstract

The experimental exfoliation of layered, ternary transition-metal carbide and nitride compounds, known as MAX phases, into two-dimensional (2D) nanosheets, is a great development in the synthesis of novel low-dimensional inorganic systems. Among the MAX phases, Mo-containing ones might be considered as the source for obtaining Mo\(_2\)C nanosheets with potentially unique properties, if they could be exfoliated. Here, by using a set of first-principles calculations, we discuss the effect of the interlayer ‘A’ element on the exfoliation of Mo\(_2\)AC (A = Al, Si, P, Ga, Ge, As or In) MAX phases into the 2D Mo\(_2\)C nanosheets. Based on the calculated exfoliation energies and the elastic constants, we propose that Mo\(_2\)InC with the lowest exfoliation energy and the highest elastic constant anisotropy between \(C_{11}\) and \(C_{33}\) might be a suitable compound for exfoliation into 2D Mo\(_2\)C nanosheets.

Keywords: MAX phase, MXene, exfoliation, carbide and nitride, nanosheet

1. Introduction

Two-dimensional (2D) nanosheets are expected to have a significant impact on a large variety of applications, ranging from electronic and thermoelectronic to gas storage, catalysis, high-performance sensors, support membranes and coatings [1–3]. These important applications have stimulated tremendous research into the synthesis and characterization of new complex 2D systems. So as to obtain new 2D nanosheets, as a top-down approach, experimentalists have focused on the exfoliation of layered organic and inorganic materials with weak van der Waals interlayer interactions. For instance, monolayers and flakes of 2D graphene were obtained mechanically by rubbing graphite against other surfaces or by the sonication of graphite powder in various aqueous or organic solvents [4]. Similar mechanical techniques were also applied to some of the inorganic layered materials, such as boron nitrides and metal chalcogenides [5, 6]. Recently, a selective chemical etching method with hydrofluoric acid (HF) was proposed to exfoliate some members of a family...
of highly conductive, tough layered ceramics with strong interlayer interactions, known as the MAX phases, into 2D carbide nanosheets [7–14]. The MAX phases are compounds with the chemical formula of $\text{MX}_n$ ($n = 1, 2$ or $3$) where ‘M’, ‘A’ and ‘X’ are an early transition metal, an element from groups 13–16 in the periodic table, and carbon and/or nitrogen, respectively [15]. After the removal of the interlayer ‘A’ element by HF treatment, the 2D carbide and nitride nanosheets created are called MXenes [7, 8]. By using the above method, three-dimensional particles of $\text{Ti}_2\text{AlC}_3$, $\text{Ti}_2\text{AlC}_2$ and $\text{Ta}_2\text{AlC}_2$ were successfully exfoliated into 2D-$\text{Ti}_2\text{C}$, $\text{-Ti}_3\text{C}_2$ and $\text{-Ta}_3\text{C}_3$ nanosheets [7, 8].

Owing to the large compositional possibilities of the MAX phases, a large number of new 2D $\text{MX}_n$ systems is also expected to be synthesized. The first-principles calculations have shown that the 2D MXenes possess a variety of electronic structures depending on their composition and surface functionalization [16–24]. In addition, some MXenes were predicted to have peculiar properties such as large Seebeck coefficients [21]. Hence, the experimental synthesis and characterization of some of the MXenes are a priority because of their expected remarkable properties for energy-related applications. In this regard, 2D $\text{Mo}_2\text{C}$ is one of the target systems, since it has been predicted to have unique electronic and thermoelectric properties [25]. In addition the nanostructured $\text{Mo}_2\text{C}$ thin films are considered as an active catalyst in a wide variety of reactions: for methane aromatization, hydrodesulfurization, hydrodenitrogenation and so on [26–33].

It is expected that 2D $\text{Mo}_2\text{C}$ nanosheets could be synthesized from the exfoliation of layered $\text{Mo}_2\text{AC}$ powders, using an appropriate selective etchant. The models of bulk $\text{Mo}_2\text{AC}$ and 2D $\text{Mo}_2\text{C}$ nanosheets are presented in figure 1. At least seven possible compositions could be considered for $\text{Mo}_2\text{AC}$ (where $\text{A} = \text{Al, Si, P, Ga, Ge, As or In}$) MAX phases. Among them, $\text{Mo}_2\text{GaC}$ has already been experimentally synthesized [34, 35] and was shown to be a superconductor with the transition temperature of $3.7–4.1$ K [36]. $\text{Mo}_2\text{AlC}$ has also already been synthesized as a solid solution, $(\text{Ti}_1-\text{Mo}_1)\text{AlC}$, and used for the fabrication of a $\text{Ti}(\text{Ti}_1-\text{Mo}_1)\text{AlC}/10$ wt% $\text{Al}_2\text{O}_3$ composite [37]. There is no reason that the other Mo-containing MAX phases cannot be synthesized in the near future.

Here, using a set of first-principles calculations, we investigate the exfoliation possibility of seven possible layered $\text{Mo}_2\text{AC}$ ($\text{A} = \text{Al, Si, P, Ga, Ge, As or In}$) MAX phases into 2D $\text{Mo}_2\text{C}$ nanosheets. First, by calculating the elastic constants, it is shown that the above $\text{Mo}_2\text{AC}$ systems are mechanically stable. Then, considering the elastic constant results and by calculating the exfoliation energies, it is concluded that $\text{Mo}_2\text{InC}$ is the best source to realize a perfect 2D $\text{Mo}_2\text{C}$ nanosheet.

**2. Method of calculations**

The first-principles calculations were performed within the framework of the density functional theory with the Perdew–Burke–Ernzerhof version of the generalized gradient approximation (GGA) as the exchange-correlation functional [38]. The projector augmented wave method was used for the basis. In the calculations, a plane-wave cutoff energy of $520$ eV was used. The positions of atoms, cell parameters and angles were fully optimized by using the conjugate gradient method and applying the Methfessel–Paxton smearing scheme [39] with a smearing width of $0.1$ eV. In the optimized structures, the magnitude of the force acting on each atom became less than $0.005$ eV Å$^{-1}$. The total energies of the optimized structures were well converged within $10^{-6}$ eV cell$^{-1}$. In the structural optimizations of bulks, the Brillouin zone was sampled using a set of $12 \times 12 \times 4$ k points [40]. The densities of states were obtained using $42 \times 42 \times 18$ k points and using a tetrahedron technique. All of the calculations were done by VASP code [41]. We have also performed a set of spin-polarized calculations within GGA. However, all the compounds were found to be non-magnetic. The current GGA approach obtains the equilibrium lattice parameters for $\text{Mo}_2\text{GaC}$ in good agreement with the experimental results within $2\%$ [34, 35].

$\text{Mo}_2\text{AC}$ ($\text{A} = \text{Al, Si, P, Ga, Ge, As or In}$) with hexagonal structures adopt $P6_3/mmc$ space group symmetry. The elastic constants are obtained by means of a Taylor expansion of the total energy of the strained crystal with respect to a small distortion parameter ($\alpha$), as described in [42]. In this study, the elastic constants are derived from the total energy calculations of nine different distortions $\alpha = \pm0.02$, $\pm0.015$, $\pm0.01$, $\pm0.005$ and $0$. The bulk modulus is estimated by fitting the curve of total energies to the third-order Birch–Murnaghan equation of state [43].
Table 1. Structural parameters and bond distances in bulk Mo₂AC (A = Al, Si, P, Ga, Ge, As or In) with P6₃/mmc symmetry.

| Mo₂AC | a (Å) | c (Å) | c/a | Mo–A (Å) | Mo–C (Å) |
|-------|-------|-------|-----|----------|----------|
| Mo₂AlC | 3.029, 3.038⁺ | 13.448, 13.48⁺ | 4.440, 4.437⁺ | 2.779 | 2.122 |
| Mo₂SiC | 3.103, 3.119⁺ | 12.401, 12.39⁺ | 3.996, 3.972⁺ | 2.643 | 2.133 |
| Mo₂PC | 3.185, 3.200⁺ | 11.603, 11.62⁺ | 3.643, 3.612⁺ | 2.565 | 2.150 |
| Mo₂GaC⁺ | 3.071, 3.01⁺⁻, 3.084⁺ | 13.147, 13.18⁺⁻, 13.16⁺ | 4.281, 4.369⁺, 4.267⁺ | 2.766 | 2.121 |
| Mo₂GeC⁺ | 3.135, 3.149⁺ | 12.636, 12.64⁺ | 4.030, 4.040⁺ | 2.718 | 2.134 |
| Mo₂AsC⁺ | 3.200, 3.225⁺ | 12.210, 12.17⁺ | 3.816, 3.774⁺ | 2.695 | 2.145 |
| Mo₂InC⁺ | 3.132, 3.140⁺ | 13.980, 14.01⁺ | 4.463, 4.462⁺ | 2.985 | 2.127 |

⁺ Barsoum [34].
⁻ Jetschko et al [35].
⁻⁻ Cover et al [44].

Table 2. Calculated elastic constants and bulk moduli of Mo₂AC (in GPa; A = Al, Si, P, Ga, Ge, As or In) systems.

| Structure | C₁₁ | C₁₂ | C₁₃ | C₃₃ | C₄₄ | B |
|-----------|-----|-----|-----|-----|-----|---|
| Ti₃AlC | 304.4, 302⁺, 305⁺ | 65.4, 62⁺ | 64.0, 61⁺ | 269.9, 269⁺ | 105.7, 109⁺ | 139.3, 138⁺ |
| Mo₂AlC | 354.4, 333⁺ | 98.0, 97⁺ | 146.7, 144⁺ | 358.9, 327⁺ | 110⁺, 114⁺ | 139⁺, 168⁺ |
| Mo₂SiC | 326.2, 311⁺ | 151.4, 149⁺ | 197.9, 192⁺ | 359.1, 338⁺ | 130.3, 124⁺ | 229.1, 225⁺ |
| Mo₂PC | 266.4, 262⁺ | 139.2, 148⁺ | 228.9, 218⁺ | 331.0, 292⁺ | 106.4, 105⁺ | 190.1, 225⁺ |
| Mo₂GaC⁺ | 312.0, 294⁺ | 94.05, 98⁺ | 163.7, 160⁺ | 313.9, 289⁺ | 128.4, 127⁺ | 191.5, 190⁺ |
| Mo₂GeC+++ | 306.4⁺⁺ | 101.4⁺⁺ | 169.0⁺⁺ | 311.2⁺⁺ | 102.1⁺⁺ | 248.6⁺⁺ |
| Mo₂AsC⁺ | 307.1, 299⁺ | 152.7, 151⁺ | 180.5, 170⁺ | 311.9, 325⁺ | 100.9, 97⁺ | 214.4, 212⁺ |
| Mo₂InC⁺ | 286.2, 247⁺ | 139.7, 140⁺ | 206.1, 200⁺ | 325.5, 306⁺ | 56.3, 60⁺ | 220.6, 209⁺ |
| Mo₂InC+++ | 300.1, 270⁺ | 101.1, 94⁺ | 120.6, 124⁺ | 290.2, 286⁺ | 86.2, 85⁺ | 173.3, 169⁺ |

⁺⁺/+ Cover et al [44].
⁻⁻⁻ Rosen et al [45].
⁻⁻⁻⁻ Sun et al [46].
⁻⁻⁻⁻⁻ Shein and Ivanovskii [47].

3. Results and discussion

The optimized structures for all Mo₂AC (A = Al, Si, P, Ga, Ge, As or In) were obtained. Table 1 presents the optimization results for the lattice parameters of bulk Mo₂AC (A = Al, Si, P, Ga, Ge, As or In), and the corresponding Mo–A and Mo–C bond distances. Table 2 indicates the calculation results of the elastic constants and the bulk modulus for the studied Mo₂AC systems. Our results in tables 1 and 2 are in excellent agreement with the previous experimental and theoretical studies [34, 35, 44–47]. From table 2, it can be seen that the current results for all Mo₂AC systems satisfy the elastic stability criteria: C₁₁ > |C₁₂|, C₄₄ > 0, (C₁₁ + C₁₂)C₃₃ − 2C₁₁C₁₂ > 0 [48]. Thereby, it is predicted that all above Mo₂AC systems are mechanically stable and can probably be formed in particular experimental conditions. However, it should be noted that there might be some other competing phases, which might be thermodynamically more favorable than the Mo₂AC systems [49].

From table 1, it is found that in Mo₂AC systems, the lattice constant a and Mo–C distances are not affected significantly by different A elements. In contrast, the lattice constant c and Mo–A bond distances are strongly affected by different A elements. These trends may indicate that Mo–C bonds are rather stronger than A–A bonds. Indeed, the A–A bond length is larger than twice the corresponding covalent radius of A element. Therefore the lattice constant is basically determined by the chemical bonds in the Mo₂C layers. The strength of Mo–C and Mo–A bonds will be discussed on the basis of the electronic structure below.

Figure 2 shows the calculated band structures of the various Mo₂AC systems. It is observed that all Mo₂AC structures are metallic, similar to many other MAX phases [50–57]. Figures 3(a)–(g) show the local density of states (LDOS) for each atom. In order to investigate the contribution of each atomic orbital in the LDOS, the projected densities of states (PDOSs), decompositions into each angular momentum channel, are also calculated. As an example, the PDOSs of Mo₂GeC are shown in figures 3(h)–(j). In general, the obtained band structure and LDOS features of Mo₂AC (A = Al, Si, P, Ga, Ge, As or In) are similar.

Metal atoms usually take part in bonding via their partially filled valence shells. Thereby, in Mo₂AC systems, C, Al, Si, P, Ga, Ge, As or In atoms are involved in the bonding states through their outmost s and p orbitals, and Mo is mainly involved through its d orbitals. Accordingly, the hybridizations of Mo–d, C–s, C–p, A–s and A–p orbitals contribute to the LDOS of Mo₂AC. As an example, let us discuss the LDOS and PDOS of Mo₂GeC in figures 3(g)–(j). In the lowest energy region, the states near −12.0 eV can be clearly assigned as bonding states between C 2s and Mo 4d orbitals. Above these bands, the Ge 4s orbitals form wider bands at energies between −12.0 and −8.0 eV from the hybridization with Mo 4d. The PDOSs of C–p and Ge–p are
Figure 2. Band structures of Mo$_2$AC ($A =$ Al, Si, P, Ga, Ge, As or In). $\Gamma(0,0,0)$, $M(1/2,0,0)$, $K(1/3,1/3,0)$, $A(0,0,1/2)$, $\Lambda(1/2,0,1/2)$ and $H(1/3,1/3,1/2)$ symmetry points of the Brillouin zone of a Mo$_2$AC. The Fermi energy is at zero.

mainly distributed between $-8.0$ and $-4.0$ eV and between $-5.0$ and $-2.0$ eV, respectively. These states can be regarded as bonding states between the C 2p/Ge 4p and the Mo 4d orbitals. The states near the Fermi energy are mainly derived from the Mo 4d orbitals.

A strong heteropolar covalent bond is formed when the atomic levels of the paired atoms are close in energy. When the hybridizations are stronger, the bonding states will be created in the lower energies. In the LDOSs of Mo$_2$AC systems in figure 3, it can be seen that the centers of C-s and C-p bands do not vary significantly in the different system. This fact indicates that the strengths of Mo–C bonds in different Mo$_2$AC systems are relatively similar. This is the reason why the Mo–C bond distances of Mo$_2$AC are very similar to $\sim 2.1$ Å. In contrast, the centers of the A-s and A-p bands of Mo$_2$AC systems differ significantly, which might imply the different strength of the Mo–A bonds in the different Mo$_2$AC systems. But since the atomic energy levels of A elements (Al, Si, P, Ga, As or In) are different from each other, it is not easy to compare the strength of Mo–A bonds in Mo$_2$AC systems from the LDOSs. However, such information might be inferred indirectly from the calculations of the elastic constants and the exfoliation energy.

Here, we discuss the calculated $C_{11}$ and $C_{33}$ elastic constants, which are listed in table 2. Basically, $C_{11}$ and $C_{33}$ elastic constants are kinds of quantities that imply the stiffness of overall chemical bonds along the $ab$ and $c$ directions, respectively. It is observed that in the case of Ti$_2$AlC, which was successfully exfoliated into 2D Ti$_2$C nanosheets in the experiments, $C_{11}$ is larger than $C_{33}$. Therefore, if $C_{33}$ is smaller than $C_{11}$, it might be more feasible to break the Mo–A–Mo bonds under appropriate mechanical and chemical tensions without significantly damaging the Mo–C–Mo bonds. By considering the elastic constants of Mo$_2$AC systems in table 2, it is seen that the $C_{33}$s of Mo$_2$PC and Mo$_2$AsC are larger than their $C_{11}$s, while for other compounds, $C_{33}$ and $C_{11}$ are similar or $C_{11}$ is larger than $C_{33}$. This indicates that in Mo$_2$PC and Mo$_2$AsC, the strength of the chemical bonds along the $c$ lattice is stronger than that of the overall chemical bonds in the $ab$ lattices. Therefore
it is suggested that the chance for the exfoliation of Mo$_2$PC and Mo$_2$AsC into 2D Mo$_2$C layers is very little. In contrast, the $C_{11}$ of Mo$_2$InC is smaller than its $C_{11}$. This implies more chances for obtaining 2D Mo$_2$C nanosheets from the Mo$_2$InC MAX phase. In addition, from the bulk modulus calculations, it appears that Mo$_2$InC/Mo$_2$SiC is the softest/hardest among the considered Mo$_2$AC systems. It should be noted that the bulk modulus $B$ in hexagonal systems is directly related to $C_{11}$, $C_{12}$, $C_{13}$ and $C_{33}$ elastic constants: $B = (2C_{11} + 2C_{12} + 4C_{13} + C_{33})/9$ [42].

In addition to the elastic constants, the strength of the chemical bonds between Mo and A atoms can be measured in another way by calculating the exfoliation energy of a bulk Mo$_2$AC system into 2D Mo$_2$C. In experiments, the exfoliation occurs dynamically; there are a lot of affecting parameters such as an acidic solution type, the concentration of the acid and the temperature. However, it is impossible or very difficult to simulate the details of this process using the current computational facilities. At present, static calculations are considered as the only way that we can provide some useful information on the exfoliation process. In such calculations, the exfoliation energy is defined as $\Delta H_f = \frac{1}{2}(E_{\text{tot}}(\text{Mo}_2\text{AC}) - E_{\text{tot}}(\text{Mo}_2\text{C}) - E_{\text{tot}}(\text{A}))$, where $E_{\text{tot}}(\text{Mo}_2\text{AC})$, $E_{\text{tot}}(\text{Mo}_2\text{C})$ and $E_{\text{tot}}(\text{A})$ stand for the total energies of bulk Mo$_2$AC, 2D Mo$_2$C and the ‘A’ element, respectively. The total energy of an ‘A’ element is estimated from its most stable bulk structure, as indicated in table 3 [58–64]. The results of the exfoliation energies are presented in table 4. For comparison, we have also calculated the exfoliation energy of a 2D Ti$_2$C nanosheet from Ti$_2$AlC, which was experimentally obtained. Thus, the Mo$_2$AC

---

**Figure 3.** (a)–(f) LDOS for Mo$_2$AC ($A = \text{Al, Si, P, Ga, Ge, As or In}$). (g)–(j) Local projected densities of states of Mo$_2$GeC on different atoms and different atomic orbitals. The Fermi energy is at zero.

**Table 3.** Structural properties of the ‘A’ metals. The lattice distances are in Å.

| ‘A’ Group | metals symmetry | $a$  | $b$  | $c$  |
|----------|----------------|-----|-----|-----|
| Al       | $Fm\overline{3}m$ | 4.039, 4.041$^a$ | 4.039, 4.041$^a$ | 4.039, 4.041$^a$ |
| Si       | $Fd\overline{3}m$ | 5.468, 5.431$^b$ | 5.468, 5.431$^b$ | 5.468, 5.431$^b$ |
| P        | $P1$           | 3.306, 3.313$^c$ | 11.260, 10.408$^d$ | 4.552, 4.374$^c$ |
| Ga       | $Cm\overline{ca}$ | 4.579, 4.523$^d$ | 7.774, 7.661$^d$ | 4.594, 4.524$^d$ |
| Ge       | $Fd\overline{3}m$ | 5.783, 5.657$^e$ | 5.783, 5.657$^e$ | 5.783, 5.657$^e$ |
| As       | $R\overline{3}m$ | 3.815, 3.759$^f$ | 3.815, 3.759$^f$ | 10.806, 10.457$^f$ |
| In       | $I\overline{4}/mmm$ | 3.328, 4.599$^g$ | 3.328, 4.599$^g$ | 4.977, 4.946$^g$ |

$^a$ Straumanis [58].
$^b$ Hom et al [59].
$^c$ Cartz et al [60].
$^d$ Sharma and Donohue [61].
$^e$ Smakula and Kalnajs [62].
$^f$ Schiferl and Barrett [63].
$^g$ Ridley [64].
Table 4. Calculated exfoliation energies of M\textsubscript{2}C from M\textsubscript{2}AC (A = Al, Si, P, Ga, Ge, As or In) systems.

| M\textsubscript{2}AC | Exfoliation energies (eV) |
|----------------------|--------------------------|
| Mo\textsubscript{2}AlC | −3.247                   |
| Mo\textsubscript{2}SiC  | −3.058                   |
| Mo\textsubscript{2}PC   | −3.247                   |
| Mo\textsubscript{2}GaC  | −3.104                   |
| Mo\textsubscript{2}GeC  | −2.901                   |
| Mo\textsubscript{2}AsC  | −2.818                   |
| Mo\textsubscript{2}InC  | −3.544                   |
| Ti\textsubscript{2}AlC  | −2.668                   |

systems with a lower exfoliation energy than Ti\textsubscript{2}AlC (−2.668 eV) might be exfoliated into 2D Mo\textsubscript{2}C nanosheets. Among the studied Mo\textsubscript{2}AC systems, the exfoliation energy of Mo\textsubscript{2}InC (−2.543 eV) is lower than that of Ti\textsubscript{2}AlC (−2.668 eV). Therefore, it can be the best candidate for the exfoliation into 2D Mo\textsubscript{2}C nanosheets.

In the experiment, during the exfoliation process, depending on the utilized etchant, various chemical groups terminate the surfaces of MXenes. In the above exfoliation energy calculations, we discussed the suitability of Mo-containing MAX phases for possible exfoliation, irrespective of the selective etchant. This is because, for example, HF has been observed to work only for the exfoliation of Al-containing MAX-phases, and does not affect/etch the other MAX-phases. Moreover, even if we wish to discuss such issues, in the static calculation approach, since the surface termination energy of 2D Mo\textsubscript{2}C does not depend on the ‘A’ element, it does not affect the ordering of the exfoliation energies in table 4. As examples of surface termination energies, here we report them for the Mo\textsubscript{2}C nanosheets functionalized with F, Cl, Br and OH groups (−7.81, −4.70, −3.90 and −6.86 eV, respectively) [25]. Such large negative energies indicate that Mo\textsubscript{2}C nanosheets make strong bonds with the F, Cl, Br or OH groups and become more stabilized, especially by F termination.

Finally, it is worth mentioning that there might be other ways to produce 2D Mo\textsubscript{2}C in addition to the exfoliation of the Mo\textsubscript{2}AC MAX phases. For example, it has been shown experimentally that thin films of Mo\textsubscript{2}C can be formed on the top of graphite surfaces resulting from MoO\textsubscript{3} reactions with the carbon atoms of graphite [65].

4. Summary

By using first-principles calculations, we have studied the electronic structures, elastic constants and exfoliation energies of Mo\textsubscript{2}AC (A = Al, Si, P, Ga, Ge, As or In) MAX phases. On the basis of the above analyses, it is predicted that Mo\textsubscript{2}InC has the best chance for exfoliation into 2D Mo\textsubscript{2}C nanosheets. We hope our results would stimulate experimentalists to synthesize various Mo-containing MAX phases and investigate their selective etching and exfoliation into novel 2D Mo\textsubscript{2}C nanosheets with potentially unique energy-related properties.

References

[1] Song X, Hu J and Zeng H 2013 J. Mater. Chem. C 1 2952
[2] Butler S Z et al 2013 ACS Nano 7 2898
[3] Balendrhan S, Walia S, Nili H, Ou J Z, Zhuifykov S, Kaner R B, Siriram S, Bhaskaran M and Kalantar-Zadeh K 2013 Adv. Funct. Mater. 23 3952
[4] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 Proc. Natl Acad. Sci. USA 102 10451
[5] Mars-Ballesté R, Gómez-Navarro C, Gómez-Herrero J and Zamora F 2011 Nanoscale 3 20
[6] Tang Q and Zhou Z 2013 Prog. Mater. Sci. 58 1244
[7] Naguib M, Kurtoglu M, Presser V, Lu J, Niu J, Heon M, Hultman L, Gogotsi Y and Barsoum M W 2011 Adv. Mater. 23 4248
[8] Naguib M, Mashtalir O, Carle J, Presser V, Lu J, Hultman L, Gogotsi Y and Barsoum M W 2012 ACS Nano 6 1322
[9] Naguib M, Come D, Dyatkin B, Presser V, Taberna P-L, Simon P, Barsoum M W and Gogotsi Y 2012 Electrochem. Commun. 16 61
[10] Mashtalir O, Naguib M, Mochalin V N, Agnese Y D, Heon M, Barsoum M W and Gogotsi Y 2013 Nature Commun. 4 1716
[11] Chang F, Li C, Yang J, Tang H and Xue M 2013 Mater. Lett. 109 295
[12] Zhang X, Xu J, Wang H, Zhang J, Yan H, Pan B, Zhou J and Xie Y 2013 Angew. Chem. Int. Edn Engl. 52 4361
[13] Naguib M, Halim J, Lu J, Cook K M, Hultman L, Gogotsi Y and Barsoum M W 2013 J. Am. Chem. Soc. 135 15966
[14] Lukatskaya M R, Mashtalir O, Ren C E, Dall’Agnese Y, Rozier P, Taberna P L, Naguib M, Simon P, Barsoum M W and Gogotsi Y 2013 Science 341 1502
[15] Sun Z M 2011 Int. Mater. Rev. 56 143
[16] Enyashin N and Ivanovskii A L 2012 Comput. Theor. Chem. 989 27
[17] Shein I R and Ivanovskii A L 2012 Comput. Mater. Sci. 65 104
[18] Kurtoglu M, Naguib M, Gogotsi Y and Barsoum M W 2012 MRS Commun. 2 133
[19] Enyashin A N and Ivanovskii A L 2013 J. Phys. Chem. C 117 13637
[20] Tang Q, Zhou Z and Shen P 2012 J. Am. Chem. Soc. 134 16909
[21] Khazaee M, Arab M, Sasaki T, Chang C-Y, Venkataramanan N S, Estili M, Sakya Y and Kawazoe Y 2013 Adv. Funct. Mater. 23 2185
[22] Xie Y and Kent P R C 2013 Phys. Rev. B 87 235441
[23] Gan L-Y, Huang D and Schwingenschlög L 2013 J. Mater. Chem. A 1 13672
[24] Enyashin A N and Ivanovskii A 2013 Solid State Chem. 207 42
[25] Khazaee M, Arab M, Sasaki T, Estili M and Sakya Y 2014 submitted
[26] Chen H Y, Chen L, Lu Y, Hong Q, Chua H C, Tang S B and Lin J 2004 Catal. Today 96 161
[27] Solymosi F, Németh R, Ovári L and Egri L 2000 J. Catal. 195 316
[28] Zhou B, Liu X, Cuervo J and Salahub D R 2012 Struct. Chem. 23 1459
[29] Ren J, Wang J, Huo C-F, Wen X D, Cao Z, Yuan S, Li Y and Jiao H 2007 Surf. Sci. 601 1599
[30] Shi X-R, Wang S-G, Hu J, Qin Z and Wang J 2012 Surf. Sci. 606 1187
[31] Tomina H and Nagai M 2007 Appl. Catal. A 328 35
[32] Pistonesi C, Juan A, Farkas A P and Solymosi F 2008 Surf. Sci. 602 2206
[33] Xing S-K and Wang G-C 2013 J. Mol. Catal. A 377 180
[34] Barsoum M W 2000 Prog. Solid State Chem. 28 201
[35] Jeitschko W, Nowotny H and Benesovsky F 1963 Monatsh. Chem. 94 672
