Russian Chemical Reviews **82** (8) 735 – 746 (2013) © 2013 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2013v082n08ABEH004398

Graphene-like transition-metal nanocarbides and nanonitrides

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Contents

I.	Introduction	735
II.	Synthesis, properties and possible fields of application	736
III.	Theoretical simulation	739
IV.	Conclusion	744

Abstract. The review concerns the synthesis of a new family of graphene-like d-metal nanocarbides and nanonitrides based on MAX phases (MXenes), exhibiting unusual properties and offering interesting prospects for application in technology. The available experimental data on the synthesis and properties of 2D d-metal nanocarbides and nanonitrides and on possible fields of their application are generalized. The results of theoretical simulation of the structure, stability conditions, electronic and magnetic properties of a wide range of MXenes and their oxidized, fluorinated, hydroxylated and methylated derivatives, as well as nanoscrolls and nanotubes based on them are summarized. Promising avenues of research on this unique family of 2D nanomaterials in the nearest future are outlined. The bibliography includes 67 references.

I. Introduction

Among various carbides and nitrides, 3d – 5d-transition metal carbides and nitrides have long attracted the attention of researchers and engineers as materials for mechanical engineering, nuclear power engineering, chemical industry and for production of structural ceramics. Indeed, these systems exhibit unique combinations of physicochemical properties (*e.g.*, high thermomechanical parameters, radiation, chemical stability, magnetic, superconducting properties, *etc.*) and are used in production of abrasives, protective coatings or wear-resistant materials.[1 – 9]

Recently, new avenues of research on the synthesis and properties of transition-metal carbides and nitrides and on the design of promising materials based on them have been developed. A particular investigation line is related to the discovery and setting of comprehensive studies of crystalline platinum-metal carbides and nitrides.[10]

Yet another investigation line is aimed at studying nanoscale d-metal carbides and nitrides and at preparing novel nanoforms with their own morphologies (molecular clusters, nanocrystallites, nanospheres, nanofibres, nanowires, *etc.*) and characteristic particle sizes of less than 100 nm. Such systems can have variable chemical compositions [metal : nitrogen(carbon) ratio], differ in atomic structures and be significantly different from corresponding crystalline phases in physicochemical properties. It also involves fabrication of carbide and nitride nanomaterials in the form of nanopowders or compacted nanopowders, nanostructured films, alloys, ceramics, composites, *etc.* having unusual operational properties.

A remarkable recent event is the development of a method for synthesis and the synthesis of the first representatives of a novel family of graphene-like (quasi-2D) d-metal nanocarbides and nanonitrides.[11] Particular attention of researchers to this fact is due to the following reasons.

Successful synthesis,[12, 13] unusual properties and great prospects for graphene applications (see reviews [14 – 34]) gave an impetus to the search for related non-carbon graphene-like 2D materials. Here, layered phases (*e.g.*, hexagonal boron nitride, metal dichalcogenides, *etc.*) with pronounced anisotropy of atom – atom interactions seem to be the best candidates. Monolayers of such phases are characterized by the existence of a system of strong directed bonds while adjacent atomic sheets interact through weak (*e.g.*, van der Waals) forces. Isolated monolayers of such phases (the desired 2D materials) are successfully prepared by micromechanical cleavage (mechanical exfoliation) which was used for, *e.g.*, the preparation of graphene sheets.[12, 13]

Obtaining graphene-like nanomaterials based on phases having nearly isotropic 3D systems of strong covalent bonds is a much more complicated task. Here, typical examples are provided by transition-metal carbides and nitrides.[7 – 9] The synthesis of corresponding 2D forms, investigations of their properties and search for possible fields of application represent sophisticated problems and are of considerable scientific and technological interest.

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Received 15 April 2013
Uspekhi Khimii **82** (8) 735 – 746 (2013); translated by A M Raevskiy

A very interesting method for the synthesis of graphene-like carbides of variable composition M_2C and M_3C_2 (M are d-metals) involves[11] chemical separation of carbide (nitride) blocks of the layered MAX phases also known as nanolaminates.[35] This novel class of graphene-like carbides (nitrides) was named MXenes.[11] This designates the method of synthesis (from MAX phases) on the one hand and similarity to graphene on the other hand.

In this review, we tried to generalize the results obtained in the first steps of research on the novel group of graphene-like 2D materials, *viz*., transition-metal nanocarbides and nanonitrides (MXenes), which immediately followed the discovery of these systems.[11] Experimental data on the synthesis and properties of MXenes are discussed and potential fields of their application are outlined. We will analyze the results of theoretical simulation of the structure, stability conditions, electronic and magnetic properties of a wide range of MXenes, their oxidized, fluorinated, hydroxylated and methylated derivatives, as well as models for nanotubes based on MXenes. Promising avenues of research on this unique family of 2D nanomaterials in the nearest future are outlined.

II. Synthesis, properties and possible fields of application

Prior to describing the method for the synthesis of MXenes, we will briefly outline key information on the crystal structure and the character of atom–atom interactions in MAX phases representing precursors of the 2D materials in question.

1. MAX phases as precursors of 2D nanocarbides and nanonitrides: atomic structure and chemical bonding

MAX phases form a large family[35] of compounds of formal stoichiometry $M_{n+1}AX_n$ (n = 1, 2, 3, ...), where M is a transition d-metal, A is a p-element (*e.g*., Si, Ge, Al, S, Sn, *etc*.) and X is carbon or nitrogen (Fig. 1). Pioneering studies on the synthesis of MAX phases date back to the 1960s.[36–40]

Intensive research on the physicochemical properties of MAX phases began in the mid-1990s. It was shown that these systems represent a unique class of anisotropic materials combining chemical, physical, electrical and mechanical properties typical of both metals and ceramics.[35] For instance, MAX phases have high thermal and electrical conductivity similarly to metals and are refractory, have low densities and exhibit high oxidative and corrosion stability similarly to ceramics. A classical example is provided by titanium silicon carbide Ti_3SiC_2 characterized by high melting point, oxidative stability, good thermal and electrical conductivity, high uniaxial compression strength and Young modulus, low hardness and very low friction coefficient.[35] Also, Ti_3SiC_2 exhibits good plasticity at room temperature. This allows the material to be processed with admissible energy expenditures. At present, MAX phases are treated as promising materials for preparation of protective coatings, polyfunctional high-temperature ceramics, electrical contacts, catalysts, *etc*.[41–43]

The state of the art in the research on MAX phases is characterized by elaboration of methods for the synthesis of these compounds (including films and nanocrystals), intensive studies on their functional properties and considerable advances in theoretical materials science.[41–45]

In the context of this review, we will dwell on the structural properties and on the character of atom–atom bonds in the MAX phases.

A key feature of the MAX phases is their structure formed by nanosized layers (blocks) of different chemical composition with different stoichiometry and packing motifs. The structures of the 'classical' MAX phases $M_{n+1}AX_n$ (n = 1, 2, 3, ...) comprise alternating blocks of d-metal carbide (nitride) $[MC(N)]_k$ and flat atomic sheets of p-elements: ... A/$[MC(N)]_k$/A/$[MC(N)]_k$/A... (Fig. 2). The $[MC(N)]_k$ blocks formed by edge-sharing $M_6C(N)$ octahedra can have different thickness.

For example, a well-known phase Ti_3SiC_2 has a hexagonal structure (space group $P63/mmc$, Z = 2) comprised of alternating titanium carbide [TiC] blocks and flat atomic sheets of silicon ...Si/[TiC]/Si/[TiC]/Si... (see Fig. 2). In turn, the [TiC] blocks contain two layers of Ti_6C octahedra connected through the edges adjacent to the Si atomic sheets; therefore, the structure of Ti_3SiC_2 is often treated as periodic stacking of hexagonal layers ...[Si–Ti(2)–C–Ti(1)–C–Ti(2)]... along the z axis.

Other MAX phases forming in the Ti–Si–C system (Ti_2SiC, Ti_4SiC_3, Ti_5SiC_4, see Fig. 2) also consist of carbide blocks of different thickness, separated by flat atomic sheets of silicon. Therefore, the thickness and chemical composition of the carbide (nitride) blocks and the composition of the A atomic sheets are the main variable parameters in the $M_{n+1}AX_n$ phases.

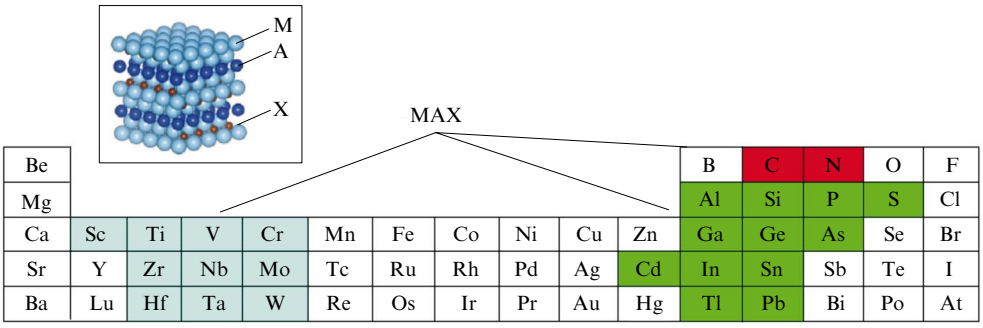


Figure 1. Fragment of the Periodic table. Shown are elements forming MAX phases of the general composition $M_{n+1}AX_n$ [n = 1, 2, 3, ...; M is a transition d-metal, A is a p-element (Si, Ge, Al, S, Sn, *etc*.), X is carbon or nitrogen].
Inset: an example of packing motif for the MAX phases.

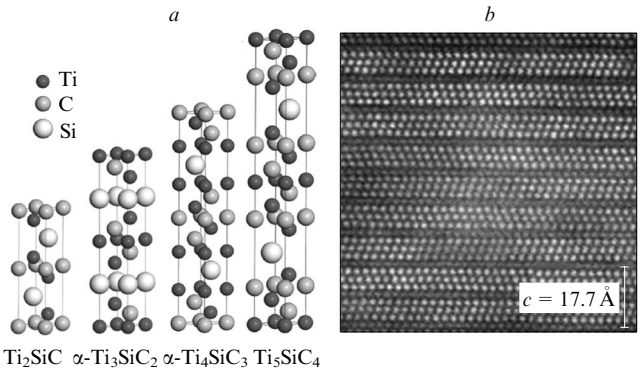


Figure 2. Crystal structures of the MAX phases $Ti_{n+1}SiC_n$ (n = 1, 2, 3 and 4) (*a*)[46] and a micrograph of atomic sheets for the Ti_3SiC_2 phase (*b*).[43]

Note that recently, the attention of researchers has been drawn to yet another family of layered phases, namely, $Hf_3Al_3C_5$ or $Hf_2Al_3C_4$, which also belong to nanolaminates. The structures of these phases comprise alternating d-metal carbide $[MC]_k$ and p-element carbide $[XC]_l$ blocks (see Ref. 34): ...$[XC]_l/[MC]_k/[XC]_l/[MC]_k/[XC]_l$... .

Layered structure of the MAX phases determines the main feature of the system of chemical bonds in these crystals, namely, a strong anisotropy of atom–atom interactions due to the coexistence of strong M–C(N) bonds in the carbide (nitride) blocks and weaker bonds between these blocks and atomic sheets of the A elements.

At present, this feature of atom–atom interactions in the MAX phases was substantiated experimentally and theoretically.[41–45] As an example, Fig. 3 presents the valence electron density distribution maps in the characteristic cross-sections of two MAX phases, Ti_2AlC and Ti_2AlN.[47] They clearly demonstrate significant differences between chemical bonds within [TiC(N)] blocks and between atomic sheets of Al and [TiC(N)] blocks.

2. Synthesis of MXenes

The method for preparation of graphene-like carbides and nitrides based on the MAX phases[11] originates from the idea of chemical removal of the A atoms and subsequent separation of the carbide (nitride) blocks $[M_{n+1}X_n]$ representing the desired novel 2D nanomaterials.

Pioneering experimental studies[11] were carried out using Ti_3AlC_2 as the MAX phase; Al atoms were removed upon treatment of Ti_3AlC_2 with HF. In this case, the following reactions proceeded:

$$Ti_3AlC_2 + 3\,HF = AlF_3 + 3/2\,H_2 + Ti_3C_2 \quad (1)$$

$$Ti_3C_2 + 2\,H_2O = Ti_3C_2(OH)_2 + H_2 \quad (2)$$

$$Ti_3C_2 + 2\,HF = Ti_3C_2F_2 + H_2 \quad (3)$$

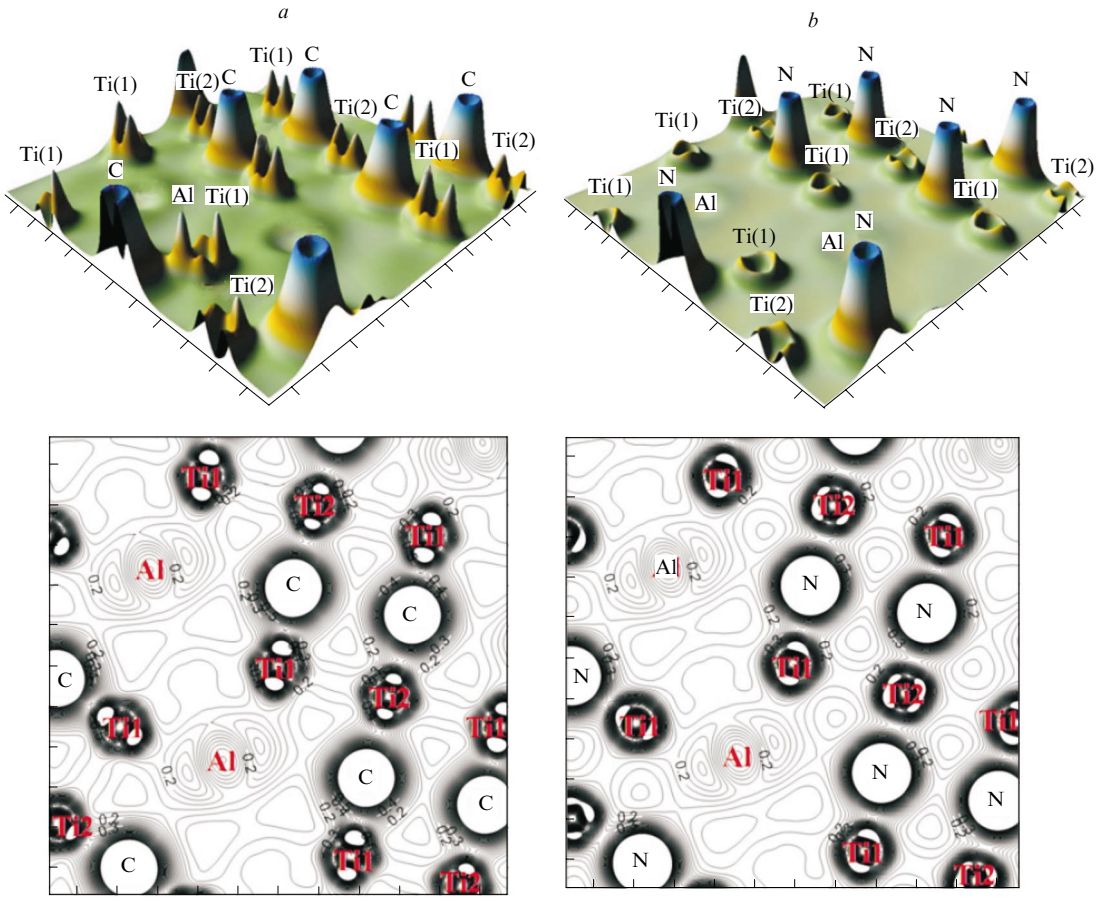


Figure 3. The valence electron density distribution at the characteristic cross-sections of the MAX phases Ti_2AlC (*a*) and Ti_2AlN (*b*).[47] Shown are the structurally nonequivalent titanium atoms Ti(1), Ti(2); the value of scale division on the axes of coordinates is 0.6 Å.

Reaction (1) is used to remove Al atoms from Ti_3AlC_2 and thus to obtain a desired material, MXene, with the formal chemical composition Ti_3C_2. The accompanying processes (2) and (3) describe the formation of hydroxylated or fluorinated derivatives of Ti_3C_2 as a result of replacement of Al atoms by fluorine atoms or OH groups in the reaction with HF which is carried out in water rich in F^- ions and OH groups. The second step involves sonication of the product to separate the MXenes Ti_3C_2. A scheme of this two-step process is shown in Fig. 4.

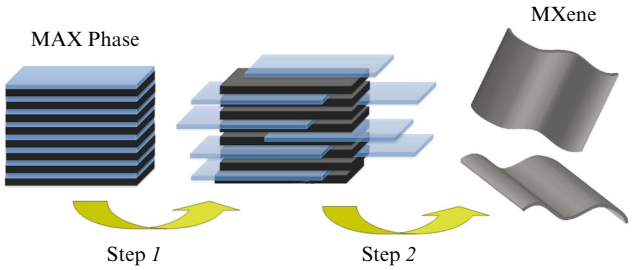


Figure 4. Two-step synthesis of MXenes from MAX phases.[48] Step *1* is chemical removal of A atoms from the MAX phases; step *2* is sonication-induced separation of carbide (nitride) blocks to give MXenes.

Table 1. Conditions of the synthesis of some MXenes from MAX phases.[48]

MAX phase	HF (%)	Time /h	Lattice constant *c* /nm	
			before treatment with HF	after treatment with HF
Ti_2AlC	10	10	1.360	1.504
Ta_4AlC_3	50	72	2.408	3.034
$(Ti_{0.5}Nb_{0.5})_2AlC$	50	28	1.379	1.488
$(V_{0.5}Cr_{0.5})_3AlC_2$	50	69	1.773	2.426
Ti_3AlCN	30	18	1.841	2.228
Ti_3AlC_2	50	2	1.842	2.051

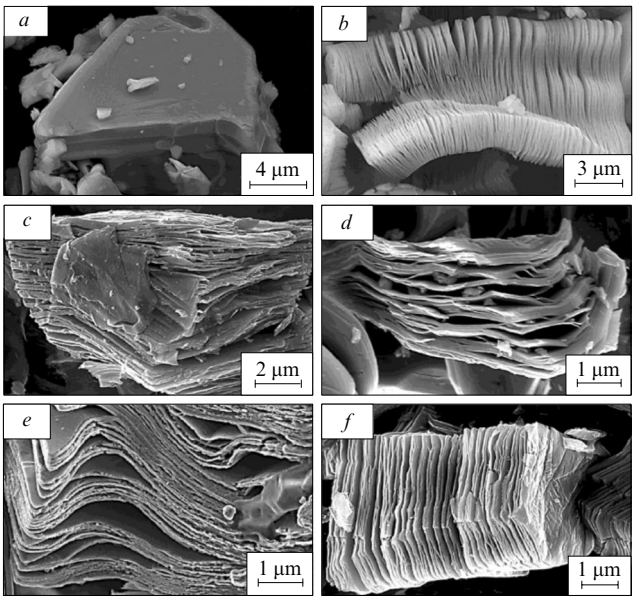


Figure 5. Micrographs of the parent MAX phase Ti_3AlC_2 before (*a*) and after treatment in HF solution (*b*); the MAX phases Ti_2AlC (*c*), Ta_4AlC_3 (*d*), TiNbAlC (*e*) and Ti_3AlCN (*f*) treated with HF.[48]

This method was employed[48] to prepare MXenes of different chemical composition, such as Ti_2C, Ta_4C_3, $(Ti_{0.5}Nb_{0.5})_2C$ and $(V_{0.5}Cr_{0.5})_3C_2$ using corresponding Al-containing MAX phases as precursors. The synthesis conditions and micrographs of some MXenes are presented in Table 1 and in Fig. 5.

It should be noted that at present this method for the preparation of MXenes is only applicable to a not so large group of Al-containing MAX phases. At the same time, a large number of MAX phases with A = Cd, Ga, In, Tl, Si, Ge, Sn, Pb, P, As or S are known.[41–46] Of course, elaboraton of methods for removal of these atoms from corresponding MAX phases is a priority; solving this problem will extend the family of MXenes in question.

3. Properties and possible fields of application of MXenes

A series of experimental studies on the properties of MXenes was reported.[11,48–50] In addition to the determination of structural parameters (as an example, Fig. 6 presents the X-ray diffraction patterns of the MAX phase Ta_4AlC_3 before and after treatment with HF[48]), their authors established that some MXene flakes are optically transparent in the visible light. The density of cold-pressed MXene disks varies in the range from 2.91 (for Ti_2C) to 6.82 g cm^{-3} for Ta_4C_3; the disks exhibit hydrophilic properties. The resistivities of a number of MXenes appeared to be higher than those of the parent MAX phases, probably,

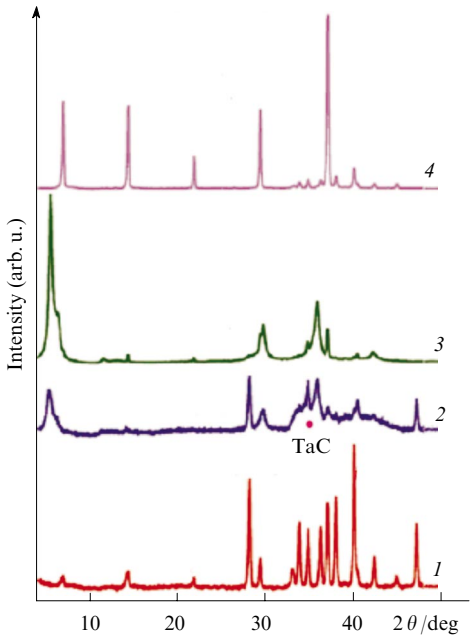


Figure 6. X-ray diffraction patterns of the MAX phase Ta_4AlC_3 (*1*), Ta_4AlC_3 treated with 50% HF for 72 h (*2*), cold-pressed MXene Ta_4C_3 (*3*) and MAX phase Ta_4AlC_3 before treatment with HF (*4*).[48]
Shown is the impurity phase TaC. The main structural effect, *viz.*, the loss of crystallinity of the 3D MAX phase after treatment with HF is clearly seen.

owing to replacement of Al atoms by OH groups or fluorine ions.[48]

To search for possible fields of application of MXenes, their electrochemical properties were studied. For instance, a cell was designed with a negative 2D electrode based on Ti_2C.[49] Also, the possibility of intercalation of lithium into multilayer Ti_2C was studied in order to design promising anode materials for lithium cells.[50]

By and large, preliminary results of studies on the properties of MXenes and the results of model calculations of these systems (see below) allow graphene-like d-metal nanocarbides and nanonitrides to be considered as possible materials for 2D electronics, lithium cells or sensors as well as for fabrication of novel polymer-containing composites.

III. Theoretical simulation

Theoretical studies[11, 47, 51–58] of MXenes by quantum chemistry methods began soon after the discovery of these systems. The emphasis was placed on the calculations of structural parameters of MXenes and on comparison of the results obtained with the parameters of the corresponding parent MAX phases),[47, 51–53, 55, 58] on the problem of stability of these nanomaterials,[47, 51, 55] on prediction of their mechanical,[11, 58] electronic [11, 47, 51–58] properties, salient features of chemical bonding in them [47, 51] and on some specific problems including construction of models for hypothetical nanotubes based on MXenes [54] and simulation of Li/MXene systems as candidates for materials for lithium cells.[53] The results obtained for a number of synthesized and hypothetical MXenes are listed in Tables 2 and 3.

Table 2. Energies of formation ($-\Delta H_{form}$ /eV per unit cell) of 2D nanocarbides and nanonitrides functionalized with F or O adatoms or OH groups.[55]

MXene [a]	F	O	OH	MXene [a]	F	O	OH
Sc_2C	12.14	9.35	10.48	Hf_2N	10.55	11.75	9.62
Ti_2C	10.85	9.81	9.61	V_2C	9.30	8.92	8.26
Ti_2N	10.68	9.49	9.51	Nb_2C	9.36	8.92	8.32
Zr_2C	11.26	10.90	9.95	Ta_2C	9.03	9.73	8.26
Zr_2N	10.94	11.05	9.75	Cr_2C	8.04	6.89	7.0
Hf_2C	11.18	11.74	10.09	Cr_2N	8.61	7.70	7.47

[a] The most stable configurations (the surface of MXenes is completely covered with F and O adatoms or OH groups) correspond to the compositions $M_2(C,N)F_2$, $M_2(C,N)O_2$ and $M_2(C,N)(OH)_2$, respectively.

Table 3. Calculated energies of formation (ΔH_{form}, eV per atom) of some MAX phases $Ti_{n+1}AlX_n$ and corresponding MXenes $Ti_{n+1}X_n$ (X = C, N; n = 1, 2, 3).[47]

Reaction	ΔH_{form}	Reaction	ΔH_{form}
$Ti_2AlC \rightarrow TiC + Al + Ti$	−1.17	$Ti_2C \rightarrow TiC + Ti$	1.61
$Ti_2AlC \rightarrow TiC + TiAl$	−0.36	$Ti_2C + Al \rightarrow Ti_2AlC$	2.78
$Ti_3AlC_2 \rightarrow 2\,TiC + Al + Ti$	−1.32	$Ti_3C_2 \rightarrow 2\,TiC + Ti$	1.38
$Ti_3AlC_2 \rightarrow 2\,TiC + TiAl$	−0.51	$Ti_3C_2 + Al \rightarrow Ti_3AlC_2$	2.70
$Ti_3AlC_2 \rightarrow Ti_2AlC + TiC$	−0.15		
$Ti_4AlC_3 \rightarrow 3\,TiC + Al + Ti$	−1.32	$Ti_4C_3 \rightarrow 3\,TiC + Ti$	1.43
$Ti_4AlC_3 \rightarrow 3\,TiC + TiAl$	−0.51	$Ti_4C_3 + Al \rightarrow Ti_4AlC_3$	2.75
$Ti_4AlC_3 \rightarrow Ti_2AlC + 2\,TiC$	−0.15		
$Ti_4AlC_3 \rightarrow Ti_3AlC_2 + TiC$	0.0		
$Ti_2AlN \rightarrow TiN + Al + Ti$	−1.26	$Ti_2N \rightarrow TiN + Ti$	1.74
$Ti_2AlN \rightarrow TiN + TiAl$	−0.45	$Ti_2N + Al \rightarrow Ti_2AlN$	3.00
$Ti_3AlN_2 \rightarrow 2\,TiN + Al + Ti$	−1.28	$Ti_3N_2 \rightarrow 2\,TiN + Ti$	1.79
$Ti_3AlN_2 \rightarrow 2\,TiN + TiAl$	−0.47	$Ti_3N_2 + Al \rightarrow Ti_3AlN_2$	3.06
$Ti_3AlN_2 \rightarrow Ti_2AlN + TiN$	−0.02		
$Ti_4AlN_3 \rightarrow 3\,TiN + Al + Ti$	−1.46	$Ti_4N_3 \rightarrow 3\,TiN + Ti$	1.61
$Ti_4AlN_3 \rightarrow 3\,TiN + TiAl$	−0.65	$Ti_4N_3 + Al \rightarrow Ti_4AlN_3$	3.06
$Ti_4AlN_3 \rightarrow Ti_2AlN + 2\,TiN$	−0.20		
$Ti_4AlN_3 \rightarrow Ti_3AlN_2 + TiN$	−0.18		

1. MXenes and their oxo, fluorine and hydroxy derivatives

Atomistic models. Typical examples of atomistic models used in quantum chemical simulation of graphene-like d-metal nanocarbides and nanonitrides are shown in Fig. 7.[11, 47, 51–54, 56, 58] Corresponding 2D structures (MXenes) represent infinite isolated (noninteracting) blocks of parent MAX phases. Structural models for MXene derivatives with designation of possible adsorption sites on outer metal layers are also presented here.

Structural models for MXenes comprising a number of alternating graphene-like sheets M_2C and M_2N are available. Note that, according to calculations,[55] individual M_2C or M_2N sheets are separated by a distance of about 3 Å; *i.e.*, they will be separated by a 'van der Waals gap' and, correspondingly, interaction between sheets will be weak. The spectra of multilayer MXenes are very similar to those of isolated M_2C or M_2N (see below). Also, models for nanoblocks in the MAX phases $Ti_3Al_{0.5}C_2$ and $Ti_2Al_{0.5}C$ were considered;[51] namely, isolated blocks comprise two MXenes (Ti_3C_2 and Ti_2C) separated by an atomic sheet of Al; this simulates an intermediate stage of reaction (1), *viz.*, chemical removal of Al from the MAX phases.

Structural parameters. Structural features of the MXenes $Ti_{n+1}C_n$ and $Ti_{n+1}N_n$ compared to those of the parent MAX phases $Ti_{n+1}AlC_n$ and $Ti_{n+1}AlN_n$ (n = 1, 2, 3) have been studied in detail;[47, 51] key results are summarized in Table 4. Geometry optimization of these systems showed that MXenes by and large retain the structure of the $Ti_{n+1}C_n$ and $Ti_{n+1}N_n$ nanoblocks within the MAX phases; this suggests lattice stability in the graphene-like nanocarbides and nanonitrides. Main differences in the changes in structural parameters (see Table 4) are associated [47] with a decrease in the coordination numbers of the metal atoms in the outer layers in 2D MXenes as compared to the those of the metal atoms in the $Ti_{n+1}C_n$ and $Ti_{n+1}N_n$ nanoblocks in the 3D MAX phases.

Stability. The relative stability of MXenes is an important problem discussed in theoretical studies.[47, 51–53, 55–58] It can be evaluated using the cohesive energy (E_{coh}) equal to the difference between the total energy of the system and the sum of the total energies of the constituent atoms. According to calculations,[47, 51] the relative stabilities of the MXenes $Ti_{n+1}C_n$ and $Ti_{n+1}N_n$ (n = 1, 2, 3) increase with increasing n, *i.e.*, with increasing thickness of these 2D systems, graphene-like nanonitrides being less stable than corresponding nanocarbides.

The results obtained in calculations [47] of the energies of formation of these phases (see Table 3) led to similar conclusions. These energies are estimated using different formal reactions of formation of the desired systems. For instance, for the Ti_3C_2 MXene one can use the reaction of its

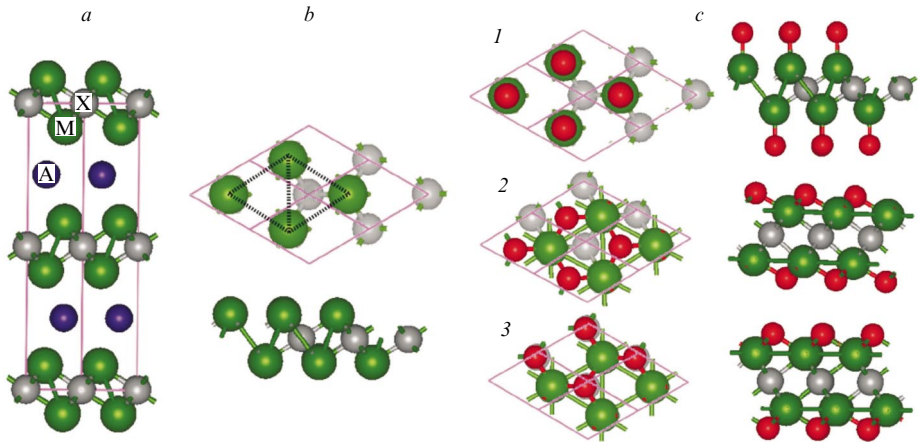


Figure 7. Atomistic models for the MAX phase of the composition M_2AX (*a*), MXene of the composition M_2X (*b*) (top view and side view) and the M_2X MXene derivatives of the formal composition M_2XA_2 for decoration of the M_2X outer sheets with adatoms on both sides of the sheet (*c*).[55]
(*1–3*) Possible adsorption sites (top view and side view).

Table 4. Optimized lattice constants (*a* and *c*), their ratios (*c*/*a*), interatomic distances (d_{Ti-X}), [$Ti_{n+1}X_n$] block thicknesses (*D*) in the MAX phases and corresponding MXenes, and the relative difference between the [$Ti_{n+1}X_n$] block thicknesses (δD) and the parameters of hexagonal lattices *a* (δa) for MXenes and corresponding MAX phases.[47]

Phase [a]	*a* /Å	*c* /Å	*c*/*a*	d_{Ti-X} /Å (see [b])	*D* /Å	δD (%)	δa (%)
Ti_2AlC	3.0694	13.7311	4.47	2.112	2.296	+0.56	−0.97
Ti_2C	3.0395	—	—	2.101	2.309		
Ti_3AlC_2	3.0824	18.6522	6.05	2.082	4.744	−0.04	+ 0.07
Ti_3C_2	3.0845	—	—	2.083	4.742		
Ti_4AlC_3	3.0861	23.5855	7.64	2.077	7.222	−1.06	+0.35
Ti_4C_3	3.0972	—	—	2.052	7.146		
Ti_2AlN	2.9965	13.6360	4.55	2.081	2.345	−2.45	−0.38
Ti_2N	2.9853	—	—	2.069	2.289		
Ti_3AlN_2	3.0065	18.4780	6.15	2.071	4.771	−4.63	−0.05
Ti_3N_2	3.0050	—	—	2.030	4.560		
Ti_4AlN_3	2.9975	23.4828	7.83	2.075	7.259	−0.50	−0.15
Ti_4N_3	2.9929	—	—	2.060	7.223		

[a] The synthesized phases are given in semi-bold; other phases were predicted theoretically.
[b] Distances between atoms of the outer sheets in [$Ti_{n+1}X_n$] blocks and X atoms in the adjacent atomic sheet of carbon (nitrogen).

decomposition to cubic titanium monocarbide and metallic titanium

$$Ti_3C_2 \rightleftharpoons 2\,TiC + Ti \qquad (4)$$

In this case, ΔH_{form} is calculated from the relation

$$\Delta H_{form}(Ti_3C_2) = [E_{tot}(Ti_3C_2) - 2\,E_{tot}(TiC) - E_{tot}(Ti)],$$

where E_{tot} are the total energies of corresponding components. Negative ΔH_{form} values thus defined indicate that the formation of the system under study from these reactants is energetically favourable.

Systematic calculations of the influence of d-metals on the stability of MXenes M_2C (M = Sc, Ti, V, Cr, Zr, Nb, Hf, Ta) and M_2N (M = Ti, Cr, Zr) were carried out for both 'untouched' and F-, O- or OH-functionalized systems.[55] Evaluation of the energies of formation of $M_2(C,N)O_2$, $M_2(C,N)F_2$ and $M_2(C,N)(OH)_2$ derivatives obtained assuming a complete coverage of MXene surfaces with F or O atoms or OH groups (see Table 2) showed that $\Delta H_{form} < 0$ and therefore the synthesis of these derivatives seems not to be improbable owing to energetically favourable formation conditions. Calculations predict the highest stability (maximum $|\Delta H_{form}|$ values) for F-functionalized Group IV metal nanocarbides where the metal is titanium, zirconium and hafnium. This is additionally substantiated by the results of calculations of the phonon spectra of these graphene-like systems.[55] Namely, MXenes meet the dynamic stability criterion [no imaginary normal vibrational frequencies of atoms for all wave vectors $\boldsymbol{k}$ within the Brillouin zone: $\omega^2(\boldsymbol{k}) > 0$]. As an example, Fig. 8 presents the phonon spectrum of Ti_2CO_2 MXene which clearly demonstrates no imaginary energy bands $\omega^2(\boldsymbol{k}) < 0$.

Electronic properties. The results of theoretical studies [11, 47, 51–53, 55–58] carried out to date suggest that all 'untouched' MXenes and a number of derivatives will exhibit metal-like properties. A distinctive feature of the electronic spectra of MXenes compared to those of the corresponding MAX phases consists in abrupt increase in

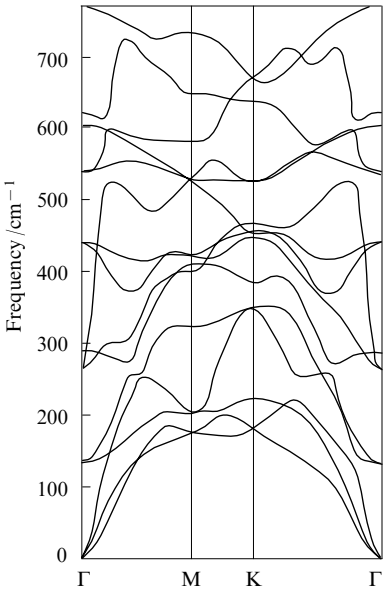


Figure 8. Phonon spectrum of MXene Ti_2CO_2.[55]

the density of states near the Fermi level (E_F, Fig. 9). This is explained by the appearance of dangling bonds of titanium atoms upon extraction of nanoblocks from the MAX phase. Also, it is important that the major contribution to the increase in the density of electron states near E_F comes from titanium atoms in the outer layers of MXenes.

Functionalization of MXenes with different atoms or atomic groups can lead to fundamental changes in their conductive properties, namely, from metal-like to semiconductor ones. According to calculations,[55] the MXene derivatives Ti_2CO_2, Zr_2CO_2, Hf_2CO_2, Sc_2CF_2, $Sc_2C(OH)_2$ and Sc_2CO_2 are semiconductors with energy gaps of 0.24, 0.88, 1.0, 1.03, 0.45 and 1.8 eV, respectively, $Sc_2C(OH)_2$ is a direct band-gap semiconductor, whereas all other systems are indirect band-gap semiconductors (Fig. 10). The change in the conductivity type is due to transfer of one (for F atom and OH group) or two electrons (for O atom) from the atoms M to the F or O atom or OH group accompanied by corresponding changes in the electronic spectrum.[55]

Magnetic properties. Prediction of magnetization for some 2D nanocarbides and nanonitrides in contrast to most corresponding 3D carbides and nitrides and MAX phases belonging to nonmagnetic materials is among the most interesting conclusions based on the results of calculations.[47, 51, 55]

The nature of the effect becomes clear from analysis of the distribution of the density of electron states in MXenes. Graphene-like nanocarbides and nanonitrides are characterized by the appearance of strong peaks of metal atoms near the Fermi level, which indicate the possibility of their magnetization.

Numerical calculations[47] of the magnetic structures of MXenes carried out using Ti_3C_2 and Ti_3N_2 as examples revealed that antiferromagnetic configuration with ferromagnetic spin ordering of titanium atoms in the same outer sheet is most energetically stable, whereas titanium atoms lying in different outer sheets are ordered antiferromagnetically. The magnetic moments per Ti atom were estimated as 0.74 for Ti_3C_2 and 0.34 μ_B for Ti_3N_2. At the same time, the 'inner' atomic sheet of Ti atoms, as well as the atomic sheets of C(N), remain nonmagnetic.

Of course, the type of magnetic structures and the values of the atomic magnetic moments of MXenes can vary in a wide range depending on the type of the transition metal atom, on the thickness of MXenes or on the type of coverage of their surface with different atoms. According to

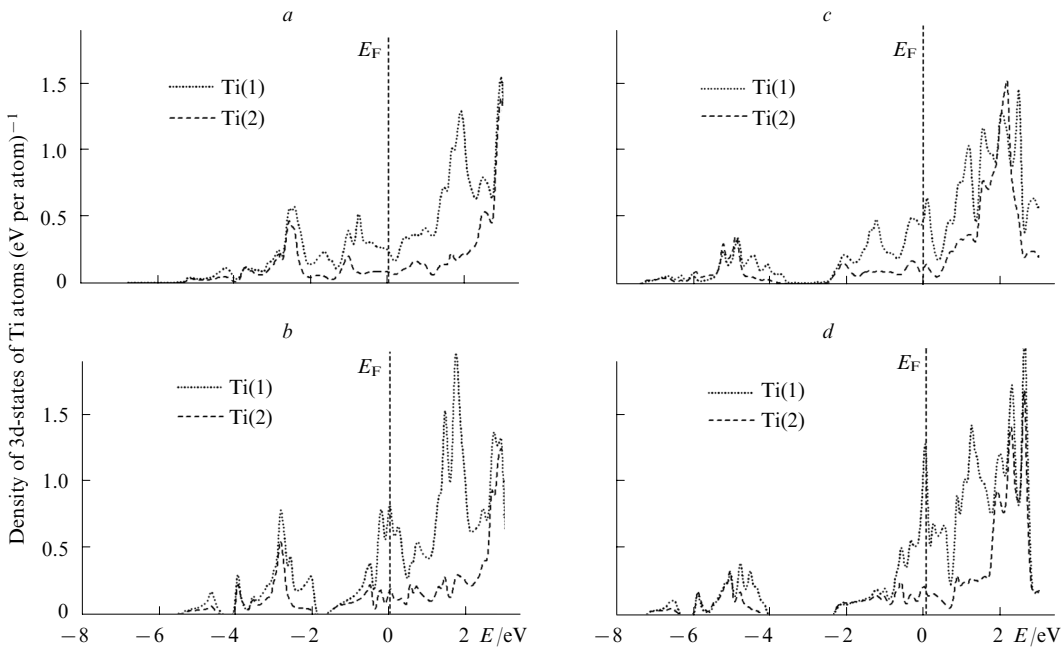


Figure 9. Density distribution of 3d-states for nonequivalent atoms Ti(1) (form outer sheets) and Ti(2) (form inner sheets) from nanoblocks of the MAX phases Ti_3AlC_2 (*a*), Ti_3AlN_2 (*c*) and MXenes Ti_3C_2 (*b*), Ti_3N_2 (*d*).[47]

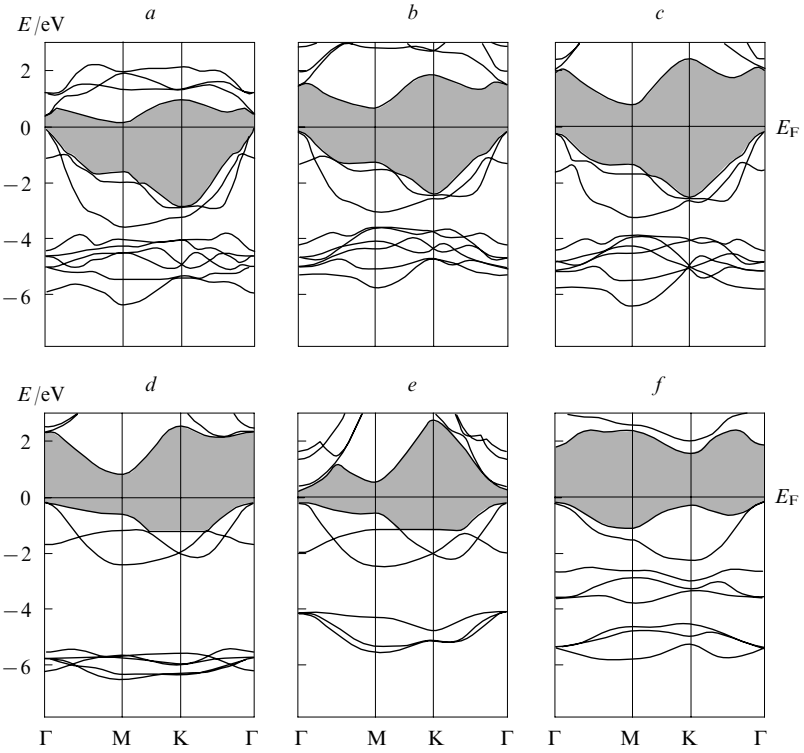


Figure 10. Energy bands of 2D semiconductor nanocarbides.[55]
Ti_2CO_2 (*a*), Zr_2CO_2 (*b*), Hf_2CO_2 (*c*), Sc_2CF_2 (*d*), $Sc_2C(OH)_2$ (*e*), Sc_2CO_2 (*f*). Horizontal lines denote the Fermi levels (E_F = 0 eV); band gaps are shown in dark.

calculations,[55] the MXenes Cr_2C and Cr_2N have a ferromagnetic ground state, the energy difference between the ferromagnetic and nonmagnetic solutions being rather large (~0.08–0.49 eV per Cr atom); this suggests the possibility of retention of the ferromagnetic state of these materials at room temperature. The magnetic moments of, *e.g.*, F- or OH-functionalized Cr_2C are 2.71 and 2.24 μ_B per Cr atom, respectively, whereas O-functionalized Cr_2C is a nonmagnetic material.

2. 2D titanium carbonitrides $Ti_3C_{2-x}N_x$ and their hydroxy derivatives $Ti_3C_{2-x}N_x(OH)_2$

To date, in addition to binary MXenes (2D d-metal nanocarbides and nanonitrides), the first representatives of graphene-like titanium carbonitride of formal composition $Ti_3(C_{0.5}N_{0.5})_2$ were prepared.[48]

Note that crystalline (3D) transition-metal carbonitrides $MC_{1-x}N_y$ (mutual solid solutions of binary carbides MC and nitrides MN) have long attracted the attention of researchers as interesting materials for various applications in technology. Recently, considerable efforts were made to prepare their submicrometre and nanoscale forms (see, *e.g.*, Refs 59–61).

Simulation of 2D titanium carbonitrides $Ti_3C_{2-x}N_x$ and their hydroxy derivatives $Ti_3C_{2-x}N_x(OH)_2$ (see Ref. 57) revealed that the electronic spectra of these systems have a metal-like type. The stability of $Ti_3C_{2-x}N_x$ MXenes depends strongly on the mutual distribution of C and N atoms, which can be ordered (carbon and nitrogen atoms form their own atomic sheets) or mixed (C and N atoms are in some way distributed between adjacent sheets). In addition, nitrogen-rich 2D carbonitrides (N : C > 1) should be more stable. The type of adsorption sites for OH groups is also an important factor influencing the properties of hydroxylated derivatives of 2D titanium carbonitrides. Adsorption sites located between three adjacent carbon (nitrogen) atoms appeared to be most favourable.[57]

The properties of these interesting graphene-like materials can further be modified by, *e.g.*, introducing variable numbers of structural vacancies into the C/N sublattice (note that structural vacancies are present [62,63] in the MAX phases, *i.e.*, precursors of the materials in question) or by partial replacement of d-metal atoms by other sort of atoms, or by the formation of various adsorption sites, probably, with variable degree of coverage.

3. Methoxylated and mixed derivatives of the MXenes Ti_2C and Ti_3C_2: $Ti_2C(OMe)_2$ and $Ti_3C_2(OMe)_2$

In addition to the synthesized MXene derivatives (see above) one can predict the possibility of obtaining various groups of related systems. In particular, replacement [11,48] of water by alcohol (or aqueous alcohol) for the acid treatment of MAX phases can lead to formation of alkoxylated MXene derivatives. In the case of Ti_3AlC_2, a possible route to the derivatives of the MXene Ti_3C_2 is as follows:

$$Ti_3C_2 + 2\,ROH = Ti_3C_2(OR)_2 + H_2 \quad (5)$$

or

$$Ti_3C_2(OH)_2 + 2\,ROH = Ti_3C_2(OR)_2 + 2\,H_2O \quad (6)$$

where R is an alkyl group.

A theoretical study of methoxylated MXenes Ti_2C and Ti_3C_2 functionalized with methoxy groups (OMe) with the maximum degree of coverage, *viz.*, $Ti_2C(OMe)_2$ and $Ti_3C_2(OMe)_2$, was carried out and specific features of their structural and electronic properties and the relative stabilities were determined.[56] It was found that the sites A located between three adjacent C atoms (see Fig. 7) are the most energetically favourable for the chemisorption of OMe

groups, the sites over titanium atoms being much less favourable. The energies of formation of these derivatives in the following formal reactions

$$Ti_3C_2(OH)_2 + 2\,MeOH = Ti_3C_2(OMe)_2 + 2\,H_2O \quad (7)$$

were estimated using the expression

$$\Delta H[Ti_3C_2(OMe)_2] = E_{tot}[Ti_3C_2(OMe)_2] + \\ + 2\,E_{tot}(H_2O) - E_{tot}[Ti_3C_2(OH)_2] - 2\,E_{tot}(MeOH)$$

It was found that $\Delta H < 0$ for most studied configurations of $Ti_2C(OMe)_2$ and $Ti_3C_2(OMe)_2$ (Table 5); *i.e.*, the formation of these derivatives is energetically favourable, which makes their synthesis not improbable.

According to calculations,[56] the most stable configurations of methoxylated MXene derivatives will exhibit metal-like properties; the near-Fermi energy bands are mainly composed of Ti 3d-orbitals. At the same time, for some metastable derivatives the character of dispersion of the near-Fermi valence bands and conduction bands suggests the existence of Dirac points for these materials, *e.g.*, graphene (Fig. 11).

A possible mechanism of formation of methoxylated MXenes in the interaction of $Ti_2C(OH)_2$ with methanol described by the formal reaction

$$Ti_2C(OH)_2 + 2\,MeOH = Ti_2C(OMe)_2 + 2\,H_2O \quad (8)$$

was discussed based on the results of a molecular dynamics simulation.[56]

Table 5. Optimized lattice constants (a/Å), relative energies (ΔE/eV per atom) and energies of formation (ΔH/eV per OMe group) of methoxy derivatives of Ti_2C and Ti_3C_2.[56]

Derivatives (configuration) [a]	a	ΔE	ΔH
$Ti_2C(OMe)_2$ (*AA*)	3.373	0	−0.335
$Ti_2C(OMe)_2$ (*BB*)	3.328	0.042	−0.240
$Ti_2C(OMe)_2$ (*AB*)	3.409	0.034	−0.234
$Ti_2C(OMe)_2$ (*AC*)	3.385	0.106	0.355
$Ti_2C(OMe)_2$ (*CC*)	3.390	0.215	1.060
$Ti_3C_2(OMe)_2$ (*AA*)	3.382	0	−0.357
$Ti_3C_2(OMe)_2$ (*BB*)	3.363	0.044	−0.283
$Ti_3C_2(OMe)_2$ (*AB*)	3.408	0.031	−0.282
$Ti_2C(OMe)(OH)$ (*AA*)	3.363	0	−0.331
$Ti_2C(OMe)(OH)$ (*BB*)	3.296	0.045	−0.241

[a] Types of configurations (*AA*, *AB*, *etc.*) are shown in Fig. 11.

4. Nanoscrolls and nanotubes

The pioneering study on the synthesis of MXenes [11] gave an experimental evidence that these sheets can be bent with no fracture up to radii less than 20 nm. Following an analogy with graphene that is used as a basis for a wide range of quasi-1D nanostructures (nanotubes and nanoscrolls), the authors of Ref. 11 suggested the possibility of formation of related 1D forms based on the novel 2D materials and constructed an atomistic model for nanoscrolls (Fig. 12).

Atomistic models (Fig. 13) were constructed and comparative numerical calculations of the stability and electronic properties of Ti_2C and Ti_3C_2 MXene nanotubes and their hydroxylated forms $Ti_2C(OH)_2$ and $Ti_3C_2(OH)_2$ were carried out.[54] It was found that the stability of these nanotubes (it can be estimated from the strain energy E_{str}, *i.e.*, the energy difference between nanotubes and the corresponding flat atomic sheet) increases with increasing nanotube radii. Also, nanotubes with thinner walls [Ti_2C, $Ti_2C(OH)_2$] will be more stable than analogous Ti_3C_2 or $Ti_3C_2(OH)_2$ nanotubes provided the same radius. Yet another key factor influencing the stability of MXene nanotubes is related to decoration of their walls with adatoms or functional groups.

According to calculations,[54] all nanotubes studied have metal-like density of states spectra (unlike corresponding flat 2D MXenes, which exhibit the properties of metals or

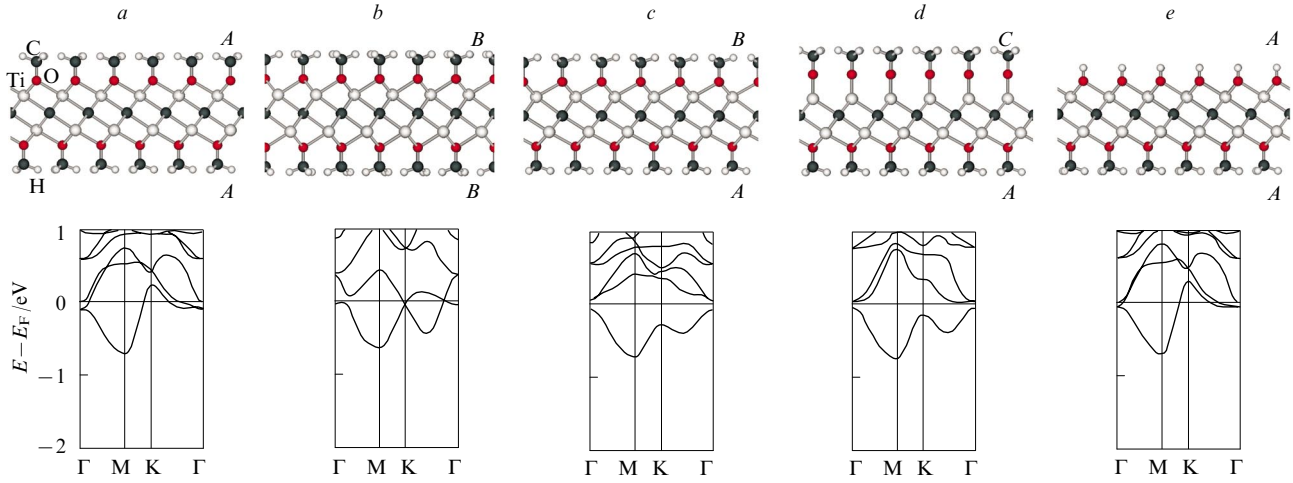


Figure 11. Models for possible atomic configurations (above) and corresponding near-Fermi energy bands (below) for methoxy derivatives of Ti_2C.[56]
(a–d) $Ti_2C(OMe)_2$ with different types of adsorption of OMe groups, (e) 'mixed' derivative of Ti_2C MXene (with simultaneous functionalization with methoxy and hydroxyl groups) of the composition $Ti_2C(OH)(OMe)$. The formation of Dirac points was found for model (b).

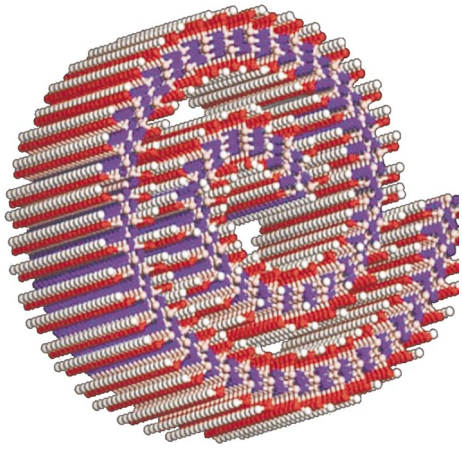


Figure 12. Model for nanoscroll based on Ti_3C_2 MXene.[11]

semiconductors depending on the atomic configuration). Note also that the density of states spectra of these nanotubes near the Fermi level are mainly formed by d-states of transition-metal atoms for both nanotubes based on the MAX phases[64, 65] and for hypothetical hollow 1D nanostructures based on B(1)-carbides[66] or d-metal oxocarbides.[67]

IV. Conclusion

The aim of this review was to generalize the results of investigations of a novel family of quasi-2D (graphene-like) transition-metal nanocarbides and nanonitrides named MXenes, which were discovered in 2011 and synthesized from the MAX phases.[11] Key results are as follows.

An original method of synthesis of 2D transition-metal nanocarbides and nanonitrides by selective removal of A atoms from layered MAX phases followed by separation of molecular carbide (nitride) sheets was developed. A representative group of MXenes of different stoichiometry [metal : carbon(nitrogen) ratio] and different chemical composition, *e.g.*, Ti_2C, Ti_3C_2, Ta_4C_3, $Ti_3(C_{0.5}N_{0.5})_2$, $(Ti_{0.5}Nb_{0.5})_2C$, *etc.*, as well as their fluorinated and hydroxylated derivatives were synthesized.

Some properties of MXenes were studied. In particular, it was established that the materials are suitable for cold pressing and their conductivities are comparable with those of multilayer graphenes. The materials can be intercalated with lithium, which offers prospects for their application as anode materials for lithium cells. Other promising fields of application of MXenes include materials for 2D electronics, for the synthesis of novel polymer-containing composites and for sensors.

A series of theoretical calculations of a representative group of synthesized and hypothetical MXenes was performed. Specific features of the electronic spectra of MXenes were determined, the possibility of spontaneous magnetization was predicted for some of these materials, factors influencing the stabilities of the systems in question and salient features of atom–atom interactions were analyzed, as well as mechanical properties were predicted.

These preliminary results point to interesting future development in physical chemistry and materials science of graphene-like transition-metal nanocarbides and nanonitrides whose investigations are now in the early stage of development. Emphasize that more than 100 MAX phases were synthesized and predicted to date. They serve as 'reservoir' for the search and design of novel MXenes with possible unusual properties and unique functionality.

At the same time, many problems concerning this group of graphene-like nanomaterials are still to be solved. For instance, the available method of synthesis of MXenes is only applicable to the Al-containing MAX phases. Elaboration of methods for removal of A atoms from corresponding MAX phases is a priority. Solving this problem will allow the family of MXenes to be extended. Also, the problem of nonstoichiometry and the possible role of structural vacancies in controlling the properties of MXenes

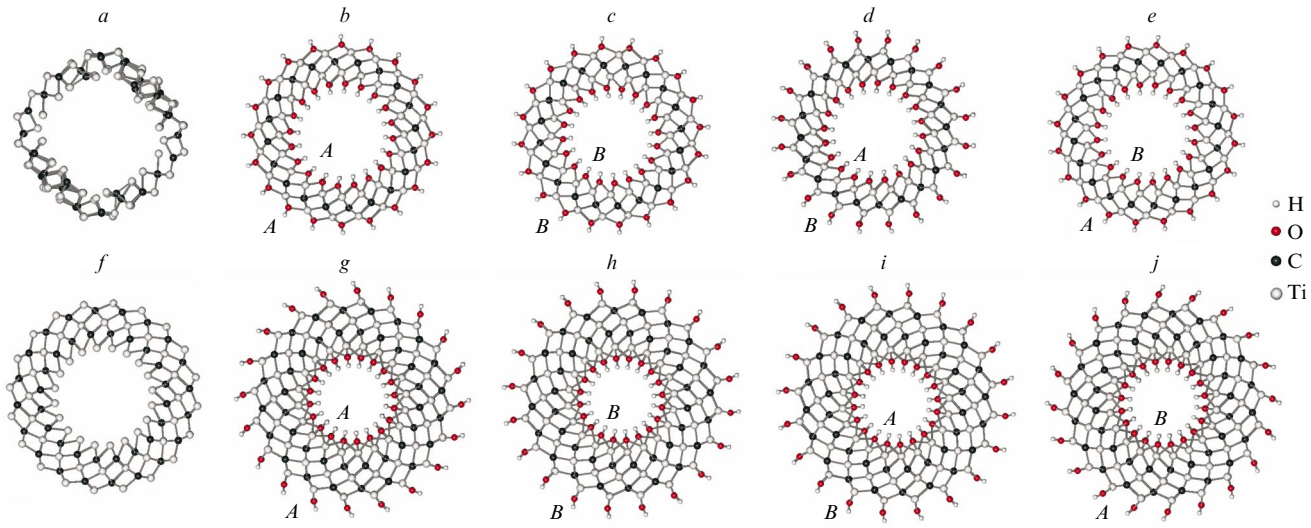


Figure 13. Optimized atomic structures (cross-sections) of (10,10) nanotubes based on the MXenes Ti_2C (*a*), Ti_3C_2 (*f*) and their hydroxy derivatives $Ti_2C(OH)_2$ (*b*–*e*) and $Ti_3C_2(OH)_2$ (*g*–*j*).[54]
A and *B* denote possible types of attachment of OH groups to the outer and inner nanotube walls.

seems to be interesting. Yet another important task is to develop methods of targeted modification of the properties of MXenes. This can be attained by varying the chemical compositions (by introducing various impurities into the M- or X-sublattices of these 2D phases) or by adsorption of atoms (molecules) on the MXene surface.

The design of 1D (ribbons) and 0D (platelets) MXenes also seems to be a promising investigation line. A key feature of such systems consists in a large number of dangling bonds at the termini (ribbons) or along the perimeter (platelets). This will both determine some features of the properties of these novel 1D and 0D materials and offer prospects for further control of their properties through functionalization at terminal positions. One more interesting method of modification of MXene nanoribbons involves mechanical deformation, *e.g.*, rolling or twisting. It should be emphasized that rolling of MXene nanoribbons may lead to such 1D-materials as nanotubes or nanoscrolls.

Eventually, the evolution of the ideas of 2D nanocarbides and nanonitrides should involve the search for not only new MAX phases, but also other systems, possible precursors of the desired graphene-like structures. These can be, *e.g.*, orthorhombic phases M_3AlN (M = Zr, Hf) comprised of $[M_3N]$ blocks separated by atomic sheets of Al; here, M–Al bonds are much weaker than M–N bonds. Probably, these phases may appear to become precursors of novel 2D nanonitrides with the atomic ratio M : N = 3.

We believe that the development of research activity in these fields will be important for progress in materials science of novel graphene-like nanomaterials.

This review has been written with the financial support from the Russian Foundation for Basic Research (Project No. 11-03-00156).

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[b] — *Theor. Exp. Chem. (Engl. Transl.)*