



(51) International Patent Classification:

H01M 4/48 (2010.01) *H01M 4/36* (2006.01)
B32B 18/00 (2006.01) *H01M 4/587* (2010.01)
H01B 1/20 (2006.01)

(21) International Application Number:

PCT/US2016/047330

(22) International Filing Date:

17 August 2016 (17.08.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/215,363 8 September 2015 (08.09.2015) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

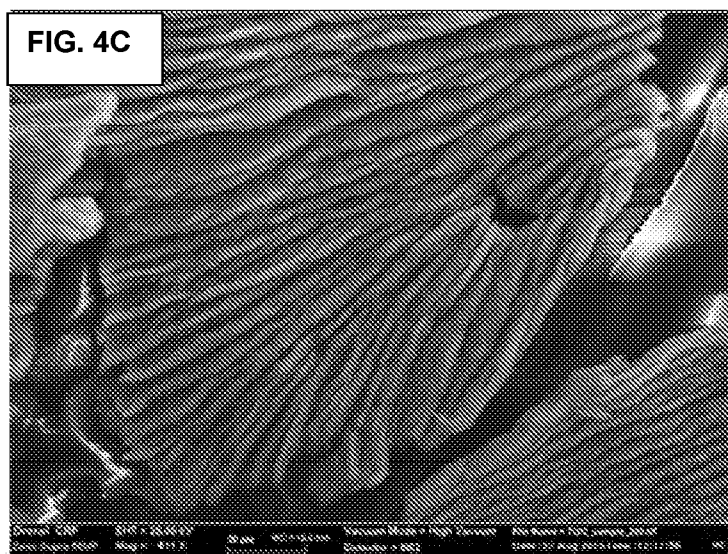
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

(54) Title: IMPROVED ROUTES TO MX-ENE CARBIDES



(57) Abstract: The present invention(s) relates to cost effective methods of preparing MXene carbide compositions having a formula $M_{n+1}C_n(T_s)$, especially those comprising titanium and carbon, the methods comprising reacting an oxide of M, elemental A, and carbon at elevated temperatures (e.g., greater than 800°C) under an inert or non-oxidizing atmosphere to form an intermediate product; optionally reducing the particle size of the intermediate product, and reacting the intermediate product directly with a source of aqueous hydrofluoric acid.

WO 2017/044262 A1



Published:

— *with international search report (Art. 21(3))*

IMPROVED ROUTES TO MX-ENE CARBIDES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application Ser. No. 62/215,363, filed September 8, 2015, the contents of which are incorporated by reference in its entirety herein.

GOVERNMENT RIGHTS

[0002] This invention was made with government support under Grant Number DMR-1310245 awarded by the National Science Foundation. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present invention(s) relates to cost effective methods of preparing MXene carbide compositions.

BACKGROUND

[0004] Recently, a new family of 2D early transition metal carbides and carbonitrides have been discovered, the class being described as MXenes, which are derived from the corresponding MAX phase materials with a formula of $M_{n+1}AX_n$, where M is an early transition metal, A is a III or IV A-group element and X is carbon and/or nitrogen. The exfoliation process was carried out by selectively etching the A layers to provide compositions with 2D layers of $M_{n+1}X_n$ terminated with OH/F groups. These new phases were named as MXene to emphasize their graphene-like morphology.

[0005] MXenes have important application in many areas, such as hydrogen storage, lead adsorption, energy storage, and polymer composites. The theoretical specific capacity of Ti_3C_2 anode has been predicted to be 320mAh g^{-1} .

[0006] To date, Ti-based MXene carbides have been synthesized by etching, for example, Ti_3AlC_2 and Ti_2AlC powder using HF or other sources of aqueous HF, e.g., LiF/HCl. However currently, commercial Ti_3AlC_2 and Ti_2AlC are quite expensive, because they are synthesized starting with Ti elemental powder that is costly. This high cost may be an impediment to large-scale use of these interesting materials.

[0007] The present invention is directed to addressing at least some of these problems.

SUMMARY

[0008] Herein are reported methods to synthesize Ti-Al MAX phases starting with various mixtures of rutile, TiO_2 , graphite and Al as raw materials. The effects of the initial compositions in raw materials on the MAX-based carbide composites were investigated. The latter was then converted to MXene carbides by immersing the composites in an HF solution. This new approach to synthesis MXene carbides is economical and effective.

[0009] These methods are based on the reduction of TiO_2 using Al as reducing agent. The product is then converted to pure MXenes by etching. Previously, it was found to be impossible to make Ti_3AlC_2 or Ti_2AlC powders without the presence of other extraneous phases such as alumina and TiC. See, e.g., Jixin Chen, *et. al.*, *J. Mater. Sci. Technol.*, 22 (2006) 455-458 and A. Hendaoui, *et al.*, Ti-Al-C MAX Phases by Aluminothermic Reduction Process, *International Journal of Self-Propagating High-Temperature Synthesis*, 17 (2008) 125-128. And while the latter phases are certainly undesirable in the case of the MAX phases, if the end result is to fabricate MXene carbides, then these phases pose much less of a problem since they are inert and can be readily separated from the MXene flakes. The purpose of this work is to synthesize Ti_3AlC_2 and Ti_2AlC -containing powders starting with rutile. The latter are then etched to convert them to MXene carbides, e.g., $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x .

[0010] Certain specific embodiments provide methods of preparing a MXene material having a formula $\text{M}_{n+1}\text{C}_n(\text{T}_s)$, each method comprising

- (a) reacting a mixture comprising or consisting essentially of an oxide of M, elemental A, and carbon at elevated temperatures (e.g., greater than 800°C) under an inert or non-oxidizing atmosphere (e.g., comprising argon) to form an intermediate product; and
- (c) reacting the intermediate product directly with an aqueous hydrofluoric acid;

wherein M is at least one of Ti, Zr, Hf, V, Mn, Nb, Ta, Cr, Mo, W;

wherein the A element is at least one of Al, As, Ga, Ge, In, P, Pb, S, or Sn (provided A is capable of reducing oxide of M and then reacting with and dissolving into aqueous HF);

$n = 1, 2$, or 3 ; and

wherein at least one of said surfaces of the layers has surface terminations, T_s , independently comprising alkoxide, alkyl, carboxylate, halide, hydroxide, hydride, oxide, sub-oxide, nitride, sub-nitride, sulfide, sulfonate, thiol, or a combination thereof.

[0011] In certain preferred embodiments, M is titanium. In related embodiments, the oxide of M is titanium dioxide, TiO_2 , encompassing rutile.

[0012] In certain preferred embodiments, A is aluminum.

[0013] As described more fully in the examples, the reaction mixture may independently comprise (a) titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $3 \text{ TiO}_2 + 5 \text{ Al} + 2 \text{ C}$ or (b) titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $6 \text{ TiO}_2 + 11 \text{ Al} + 3 \text{ C}$.

[0014] So as to improve the intimacy of the reaction of step (c), the method may further comprise a step (b) following (a) and preceding (c), wherein step (b) comprises reducing the particle size of the intermediate product to less than 500 nm, preferably less than 250 nm, 100 nm, or less than 50 nm (the lower limit being defined by attrition technology for these materials).

[0015] In some embodiments, the aqueous hydrofluoric acid is

(a) provided as such, or derived from:

(b) aqueous ammonium hydrogen fluoride ($\text{NH}_4\text{F} \cdot \text{HF}$);

(c) an alkali metal bifluoride salt (i.e., QHF_2 , where Q is Li, Na, or K), or a combination thereof; or

(d) at least one fluoride salt, such as an alkali metal, alkaline earth metal, or ammonium fluoride salt (e.g., LiF, NaF, KF, CsF, CaF_2 , tetraalkyl ammonium fluoride (e.g., tetrabutyl ammonium fluoride)) in the presence of at least one mineral acid that is stronger than HF (such as HCl, HNO_3 , or H_2SO_4); or

(d) a combination of two or more of (a)-(d).

[0016] The invention also contemplates any and all MXene compositions prepared by the inventive methods described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The present application is further understood when read in conjunction with the appended drawings. For the purpose of illustrating the subject matter, there are shown in the drawings exemplary embodiments of the subject matter; however, the presently disclosed subject matter is not limited to the specific methods, devices, and systems disclosed. In addition, the drawings are not necessarily drawn to scale. In the drawings:

[0018] **FIGs. 1(A-C)** shows powder XRD patterns of mixtures of, (**FIG. 1A**) $3\text{TiO}_2\text{-5Al-2C}$, (**FIG. 1B**) $3\text{TiO}_2\text{-5.1Al-1.9C}$, (**FIG. 1C**) $3\text{TiO}_2\text{-5.1Al-1.8C}$ and (**FIG. 1D**) $3\text{TiO}_2\text{-5.5Al-1.8C}$ after heating $10^\circ\text{C}/\text{min}$ to 1500°C for 1 h.

[0019] **FIGs. 2(A-C)** shows powder XRD patterns of starting compositions: (**FIG. 2A**)

6TiO₂-11Al-3C, (**FIG. 2B**) 6TiO₂-11Al-2.7C and (**FIG. 2C**) 6TiO₂-12.3Al-2.7C after heating at a rate of 10°C/min 1500°C and holding at that temperature for 1 h.

[0020] FIGs. 3(A-C) shows powder XRD patterns of the products of compositions: (**FIG. 3A**) 6TiO₂-11Al-2.7C after HF treatment, but before purification, (**FIG. 3B**) after purification, (**FIG. 3C**) 6TiO₂-12.3Al-2.7C after HF etching and purification. Note the loss of Al₂O₃ peaks after purification.

[0021] FIGs. 4(A-C) shows SEM images of (**FIG. 4A**) Ti₂C-based; (**FIG. 4B**) Ti₃C₂-based and (**FIG. 4C**) Low magnification image of Ti₂C.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0022] The present invention may be understood more readily by reference to the following description taken in connection with the accompanying Figures and Examples, all of which form a part of this disclosure. It is to be understood that this invention is not limited to the specific products, methods, conditions or parameters described or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of any claimed invention. Similarly, unless specifically otherwise stated, any description as to a possible mechanism or mode of action or reason for improvement is meant to be illustrative only, and the invention herein is not to be constrained by the correctness or incorrectness of any such suggested mechanism or mode of action or reason for improvement. Throughout this text, it is recognized that the descriptions refer to compositions and methods of making and using said compositions. That is, where the disclosure describes or claims a feature or embodiment associated with a composition or a method of making or using a composition, it is appreciated that such a description or claim is intended to extend these features or embodiment to embodiments in each of these contexts (i.e., compositions, methods of making, and methods of using).

[0023] Certain embodiments of the present invention include those methods of preparing a MXene material having a formula M_{n+1}C_n(T_s) comprising

- (a) reacting a mixture comprising or consisting essentially of an oxide of M, elemental A, and carbon at elevated temperatures (e.g., greater than 800°C, for example to about 1800°C) under an inert or non-oxidizing atmosphere to form an intermediate product; and
- (c) reacting the intermediate product directly with a source of an aqueous hydrofluoric acid;

wherein M is at least one of Ti, Zr, Hf, V, Mn, Nb, Ta, Cr, Mo, W;

the A element is at least one of Al, As, Ga, Ge, In, P, Pb, S, or Sn; and

$n = 1, 2, \text{ or } 3$.

[0024] The MXene composition has previously been reported and is more fully described below. The present invention is specifically directed to the reduction of the oxide of M with an A element. The method is operable, provided that the A element is capable of reducing the oxide of M and then reacting with and/or dissolving into the source of aqueous HF.

[0025] As exemplified below, but not necessarily limited to these materials, the methods work well when M is titanium. In certain embodiments, the oxide of M is titanium dioxide, TiO_2 .

[0026] Also as exemplified below, but not necessarily limited to this material, in certain embodiments, A is aluminum.

[0027] Also as exemplified below, but not necessarily limited to these materials or stoichiometries, in some embodiments, the reaction mixture independently contains (a) titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $3 \text{ TiO}_2 + 5 \text{ Al} + 2 \text{ C}$; and (b) titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $6 \text{ TiO}_2 + 11 \text{ Al} + 3 \text{ C}$.

[0028] The reaction between the oxide of M, the A element, and carbon is conducted at elevated temperatures (e.g., greater than 800°C) under conditions used previously for the preparation of MAX phase materials. These conditions are also found useful in the preparation of other oxide, nitride, or carbide ceramics. Such reactions conditions typically include a ramp to a hold temperature, typically in a range of from about 1000°C to about 1800°C , and a hold or soak at that temperature for 1 to 4 hours, followed by a ramp return to ambient temperature. Soak temperatures may be any temperature in a range of from about 600°C to about 800°C , from about 800°C to about 1000°C , from about 1000°C to about 1200°C , from about 1200°C to about 1400°C , from about 1400°C to about 1600°C , from about 1600°C to about 1800°C , or any combination of two or more of these ranges, in series, for soak times at any given temperature in a range of from about 30 min to one hour, from about one hour to about 2 hours, from about 2 hours to about 4 hours, from about 4 hours to about eight hours, or any combination of two or more of these ranges.

[0029] The reactions are also conducted in inert (or non-oxidizing) environments. The term “inert,” as understood by the skilled artisan is the absence of substantial levels of oxygen or air, which otherwise render the atmosphere oxidizing to the A element and carbon. In certain embodiments, the inert atmosphere is or comprises argon or nitrogen, or both. In other

embodiments, the inert atmosphere is or comprises argon. In other embodiments, the inert atmosphere may comprise hydrogen.

[0030] As exemplified in the Examples, following the production of the intermediate product, which likely includes a mixture of the desired MXene material but also extraneous oxides and mixed oxide phases of the M and A elements, the method provides that the intermediate product is reacted with, or extracted by a source of aqueous hydrofluoric acid. Such sources are described further below. But such reactions or extractions proceed more efficiently with high surface area powders, such as exist with small particles. Accordingly, it is preferred that the methods further comprise an additional step, designated herein as step (b) which follows the reaction in step (a) and precedes the HF reactions/extractions of step (c), wherein step (b) comprises reducing the particle size of the intermediate product to less than 50 nm. Such particle size reductions can be accomplished by any suitable physical means, such as ball mill attrition, grinding, pulverizing, or any other method suitable for reducing the particles. In independent embodiments, the intermediate product is reduced to particles to less than 500 nm, 250 nm, 100 nm, or 50 nm. Again, smaller is better to improve intimacy of subsequent HF reaction / extraction. The resulting particles may be sieved to constant size, so as to improve consistency of the next step, or may be used as provided by the attrition method.

[0031] The intermediate reaction product from steps (a), optionally reduced in particle size in step (b), is then further contacted with a source of aqueous hydrofluoric acid so as to reduce any oxides of the A metal, or other extraneous materials, to form the MXene material. This source of aqueous is described elsewhere herein.

[0032] Additional embodiments include any composition provided by any of the methods described herein, especially the MXene compositions, as well as any device or composition incorporating these MXene materials. The skilled artisan would unambiguously understand the scope of this embodiment.

Terms

[0033] In the present disclosure the singular forms “a,” “an,” and “the” include the plural reference, and reference to a particular numerical value includes at least that particular value, unless the context clearly indicates otherwise. Thus, for example, a reference to “a material” is a reference to at least one of such materials and equivalents thereof known to those skilled in the art, and so forth.

[0034] When a value is expressed as an approximation by use of the descriptor “about,” it will be understood that the particular value forms another embodiment. In general, use of the term “about” indicates approximations that can vary depending on the desired properties sought by the disclosed subject matter and is to be interpreted in the specific context in which it is used, based on its function. The person skilled in the art will be able to interpret this as a matter of routine. In some cases, the number of significant figures used for a particular value may be one non-limiting method of determining the extent of the word “about.” In other cases, the gradations used in a series of values may be used to determine the intended range available to the term “about” for each value. Where present, all ranges are inclusive and combinable. That is, references to values stated in ranges include every value within that range.

[0035] It is to be appreciated that certain features of the invention which are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. That is, unless obviously incompatible or specifically excluded, each individual embodiment is deemed to be combinable with any other embodiment(s) and such a combination is considered to be another embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. Finally, while an embodiment may be described as part of a series of steps or part of a more general structure, each said step may also be considered an independent embodiment in itself, combinable with others.

[0036] When a list is presented, unless stated otherwise, it is to be understood that each individual element of that list, and every combination of that list, is a separate embodiment. For example, a list of embodiments presented as “A, B, or C” is to be interpreted as including the embodiments, “A,” “B,” “C,” “A or B,” “A or C,” “B or C,” or “A, B, or C.”

[0037] Throughout this specification, words are to be afforded their normal meaning, as would be understood by those skilled in the relevant art. However, so as to avoid misunderstanding, the meanings of certain terms will be specifically defined or clarified.

[0038] As previously described, in some embodiments, MX-enes are materials comprising or consisting essentially of a $M_{n+1}X_n(T_s)$ composition having at least one layer, each layer having a first and second surface, each layer comprising

a substantially two-dimensional array of crystal cells.

each crystal cell having an empirical formula of $M_{n+1}X_n$, such that each X is positioned within an octahedral array of M,

wherein M is at least one Group 3, 4, 5, 6, or 7,

wherein each X is and

$n = 1, 2, \text{ or } 3$;

wherein at least one of said surfaces of the layers has surface terminations, T_s , independently comprising alkoxide, alkyl, carboxylate, halide, hydroxide, hydride, oxide, sub-oxide, nitride, sub-nitride, sulfide, sulfonate, thiol, or a combination thereof;

[0039] As described elsewhere within this disclosure, the $M_{n+1}X_n(T_s)$ materials produced in these methods and compositions have at least one layer, and sometimes a plurality of layers, each layer having a first and second surface, each layer comprising a substantially two-dimensional array of crystal cells; each crystal cell having an empirical formula of $M_{n+1}X_n$, such that each X is positioned within an octahedral array of M, wherein M is at least one Group 3, 4, 5, 6, or 7 metal (corresponding to Group IIIB, IVB, VB, VIB or VIIB metal), wherein each X is C and $n = 1, 2, \text{ or } 3$; wherein at least one of said surfaces of the layers has surface terminations, T_s , comprising alkoxide, alkyl, carboxylate, halide, hydroxide, hydride, oxide, sub-oxide, nitride, sub-nitride, sulfide, sulfonate, thiol, or a combination thereof.

[0040] Supplementing the descriptions above, $M_{n+1}X_n(T_s)$ compositions may be viewed as comprising free standing and stacked assemblies of two dimensional crystalline solids. Collectively, such compositions are referred to herein as " $M_{n+1}X_n(T_s)$," "MXene," "MXene compositions," or "MXene materials." Additionally, these terms " $M_{n+1}X_n(T_s)$," "MXene," "MXene compositions," or "MXene materials" also refer to those compositions derived by the chemical exfoliation of MAX phase materials, whether these compositions are present as free-standing 2-dimensional or stacked assemblies (as described further below). Reference to the carbide equivalent to these terms reflects the fact that X is carbon, C, in the lattice. Such compositions comprise at least one layer having first and second surfaces, each layer comprising: a substantially two-dimensional array of crystal cells; each crystal cell having an empirical formula of $M_{n+1}X_n$, where M, X, and n are defined above. These compositions may be comprised of individual or a plurality of such layers. In some embodiments, the $M_{n+1}X_n(T_s)$ MXenes comprising stacked assemblies may be capable of, or have atoms, ions, or molecules, that are intercalated between at least some of the layers. In other embodiments, these atoms or ions are lithium. In still other embodiments, these structures are part of an energy-storing device, such as a battery or supercapacitor. In still other embodiments these structures are added to polymers to make polymer composites.

[0041] The term “crystalline compositions comprising at least one layer having first and second surfaces, each layer comprising a substantially two-dimensional array of crystal cells” refers to the unique character of these materials. For purposes of visualization, the two-dimensional array of crystal cells may be viewed as an array of cells extending in an x-y plane, with the z-axis defining the thickness of the composition, without any restrictions as to the absolute orientation of that plane or axes. It is preferred that the at least one layer having first and second surfaces contain but a single two-dimensional array of crystal cells (that is, the z-dimension is defined by the dimension of approximately one crystal cell), such that the planar surfaces of said cell array defines the surface of the layer; it should be appreciated that real compositions may contain portions having more than single crystal cell thicknesses.

[0042] That is, as used herein, “a substantially two-dimensional array of crystal cells” refers to an array which preferably includes a lateral (in x-y dimension) array of crystals having a thickness of a single cell, such that the top and bottom surfaces of the array are available for chemical modification.

[0043] Metals of Group 3, 4, 5, 6, or 7 (corresponding to Group IIIB, IVB, VB, VIB, or VIIB), either alone or in combination, said members including Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. For the purposes of this disclosure, the terms “M” or “M atoms,” “M elements,” or “M metals” may also include Mn. Also, for purposes of this disclosure, compositions where M comprises Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, or mixtures thereof constitute independent embodiments. Similarly, the oxides of M may comprise any one or more of these materials as separate embodiments. For example, M may comprise any one or combination of Hf, Cr, Mn, Mo, Nb, Sc, Ta, Ti, V, W, or Zr. In other preferred embodiments, the transition metal is one or more of Ti, Zr, V, Cr, Mo, Nb, Ta, or a combination thereof. In even more preferred embodiments, the transition metal is Ti, Ta, Mo, Nb, V, Cr, or a combination thereof.

[0044] In certain specific embodiments, $M_{n+1}X_n$ comprises $M_{n+1}C_n$ (i.e., where $X = C$, carbon) which may be Ti_2C , V_2C , V_2N , Cr_2C , Zr_2C , Nb_2C , Hf_2C , Ta_2C , Mo_2C , Ti_3C_2 , V_3C_2 , Ta_3C_2 , Mo_3C_2 , $(Cr_{2/3} Ti_{1/2})_3C_2$, Ti_4C_3 , V_4C_3 , Ta_4C_3 , Nb_4C_3 , or a combination thereof.

[0045] In more specific embodiments, the $M_{n+1}X_n(T_s)$ crystal cells have an empirical formula Ti_3C_2 or Ti_2C . In certain of these embodiments, at least one of said surfaces of each layer of these two dimensional crystal cells is coated with surface terminations, T_s , comprising alkoxide, fluoride, hydroxide, oxide, sub-oxide, sulfonate, or a combination thereof.

[0046] The range of compositions available can be seen as extending even further when one considers that each M-atom position within the overall $M_{n+1}X_n$ matrix can be represented by more than one element. That is, one or more type of M-atom can occupy each M-position within

the respective matrices. In certain exemplary non-limiting examples, these can be $(M^A_x M^B_y)_2 C$, $(M^A_x M^B_y)_3 C_2$, or $(M^A_x M^B_y)_4 C_3$, where M^A and M^B are independently members of the same group, and $x + y = 1$. For example, in but one non-limiting example, such a composition can be $(V_{1/2} Cr_{1/2})_3 C_2$.

[0047] In other embodiments, the MXenes may comprise compositions having at least two Group 4, 5, 6, or 7 metals, and the $M_{n+1}X_n(T_s)$ composition is represented by a formula $M'_2 M''_m X_{m+1}(T_s)$, where $m = n - 1$. Typically, these are carbides (i.e., X is carbon). Such compositions are described in U.S. Patent Application No. 62/149,890, this reference being incorporated herein by reference for all purposes. In these double transition metal carbides, M' may be Ti, V, Cr, or Mo. In these ordered double transition metal carbides, M'' may be Ti, V, Nb, or Ta, provided that M' is different than M'' . These carbides may be ordered or disordered. Individual embodiments of the ordered double transition metal carbides include those compositions where $M'_2 M''_m X_{m+1}$ is independently $Mo_2 TiC_2$, $Mo_2 VC_2$, $Mo_2 TaC_2$, $Mo_2 NbC_2$, $Mo_2 Ti_2 C_3$, $Cr_2 TiC_2$, $Cr_2 VC_2$, $Cr_2 TaC_2$, $Cr_2 NbC_2$, $Ti_2 NbC_2$, $Ti_2 TaC_2$, $V_2 TaC_2$, $V_2 TiC_2$, or a combination thereof. In some other embodiments, $M'_2 M''_m X_{m+1}$ is independently $Mo_2 TiC_2$, $Mo_2 VC_2$, $Mo_2 TaC_2$, $Mo_2 NbC_2$, $Cr_2 VC_2$, $Cr_2 TaC_2$, $Cr_2 NbC_2$, $Ti_2 NbC_2$, $Ti_2 TaC_2$, $V_2 TaC_2$, $V_2 TiC_2$, or a combination thereof. In other embodiments, $M'_2 M''_m X_{m+1}$ is independently $Mo_2 Ti_2 C_3$, $Mo_2 V_2 C_3$, $Mo_2 Nb_2 C_3$, $Mo_2 Ta_2 C_3$, $Cr_2 Ti_2 C_3$, $Cr_2 V_2 C_3$, $Cr_2 Nb_2 C_3$, $Cr_2 Ta_2 C_3$, $Nb_2 Ta_2 C_3$, $Ti_2 Nb_2 C_3$, $Ti_2 Ta_2 C_3$, $V_2 Ta_2 C_3$, $V_2 Nb_2 C_3$, $V_2 Ti_2 C_3$, or a combination thereof. In still other embodiments, $M'_2 M''_m X_{m+1}$ is independently $Nb_2 VC_2$, $Ta_2 TiC_2$, $Ta_2 VC_2$, $Nb_2 TiC_2$ or a combination thereof.

[0048] Previously, these MXene materials, described above as either $M_{n+1}X_n(T_s)$ or $M'_2 M''_m X_{m+1}$, may be prepared by selectively removing an A group element from a precursor MAX-phase material. Depending on the specific MAX being considered, these A group elements may be independently defined as including Al, As, Cd, Ga, Ge, P, Pb, In, S, Sn, or Tl. These same materials are contemplated as independent embodiments for the A element used in the present invention. Some of these A-group elements may be removed in aqueous media, for example, by a process comprising a treatment with a fluorine-containing acid. For example, Al, As, Ga, Ge, In, P, Pb, S, or Sn may be removed in this way, although Al is especially amenable to such extractions. Aqueous hydrofluoric acid is particularly suitable for this purpose, whether used as provided, or generated *in situ* by other conventional methods. Such methods include the use of any one or more of the following:

- (a) aqueous ammonium hydrogen fluoride ($NH_4F.HF$);

(b) an alkali metal bifluoride salt (i.e., QHF_2 , where Q is Li, Na, or K), or a combination thereof; or

(c) at least one fluoride salt, such as an alkali metal, alkaline earth metal, or ammonium fluoride salt (e.g., LiF, NaF, KF, CsF, CaF_2 , tetraalkyl ammonium fluoride (e.g., tetrabutyl ammonium fluoride)) in the presence of at least one mineral acid that is stronger than HF (i.e., has a higher K_a value) and can react with fluorides to form HF *in situ* (such as HCl, HBr, HI, H_3PO_4 , HNO_3 , oxalic acid, or H_2SO_4); or

(d) a combination of two or more of (a)-(c).

[0049] In specific embodiments, the fluorine-containing acid is derived from lithium fluoride and a strong aqueous mineral acid, such as HCl, HNO_3 , or H_2SO_4 , preferably HCl.

[0050] It also appears that the use of aqueous HF in the presence of one or more alkali halides, such as LiCl, provides advantages over using HF alone, or by reacting LiF with aqueous HCl. The use of LiF with aqueous HCl avoids the handling issues associated with the use of aqueous HF and provides higher yields of single-layer flakes, in some cases it may be difficult to remove LiF impurities and the removal of the A-element (e.g., Al) is slower. The use of LiCl with aqueous HF provides more crystalline MXene phases, with better control of the basal spacing (c parameter) and it is easier to vary the procedures especially for those involving ion intercalation.

[0051] Exemplary MAX phase materials include those wherein M is at least one of Hf, Cr, Mn, Mo, Nb, Sc, Ta, Ti, V, W, or Zr. Other preferred embodiments include those where the A in the MAX phase material is at least one of Al, As, Ga, Ge, In, P, Pb, S, or Sn.

[0052] The following listing of Embodiments is intended to complement, rather than displace or supersede, the previous descriptions.

[0053] Embodiment 1. A method of preparing a MXene material having a formula $\text{M}_{n+1}\text{C}_n(\text{T}_s)$ comprising

- (a) reacting a mixture comprising or consisting essentially of an oxide of M, elemental A, and carbon at elevated temperatures (e.g., greater than 800°C , for example to about 1800°C) under an inert or non-oxidizing atmosphere to form an intermediate product; and
- (c) reacting the intermediate product directly with an aqueous hydrofluoric acid;

wherein the MXene composition $\text{M}_{n+1}\text{C}_n(\text{T}_s)$ comprises at least one layer, each layer having a first and second surface, each layer comprising

a substantially two-dimensional array of crystal cells.

each crystal cell having an empirical formula of $M_{n+1}C_n$, such that each C (carbon) is positioned within an octahedral array of M,

wherein M is at least one of Ti, Zr, Hf, V, Mn, Nb, Ta, Cr, Mo, W;

wherein the A element is at least one of Al, As, Ga, Ge, In, P, Pb, S, or Sn, provided that the A element is capable of reducing oxide of M and then reacting with and dissolving into aqueous HF;

$n = 1, 2, \text{ or } 3$; and

wherein at least one of said surfaces of the layers has surface terminations, T_s , independently comprising alkoxide, alkyl, carboxylate, halide, hydroxide, hydride, oxide, sub-oxide, nitride, sub-nitride, sulfide, sulfonate, thiol, or a combination thereof.

[0054] Embodiment 2. The method of Embodiment 1, wherein M is titanium.

[0055] Embodiment 3. The method of Embodiment 1 or 2, wherein the oxide of M is titanium dioxide, TiO_2 .

[0056] Embodiment 4. The method of any one of Embodiments 1 to 3, wherein A is aluminum.

[0057] Embodiment 5. The method of any one of Embodiments 1 to 4, wherein the reaction mixture is one containing titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $3 \pm 1.5 TiO_2 + 5 \pm 2 Al + 2 \pm 0.3 C$ (or any composition in which the variances are within the limits described herein).

[0058] Embodiment 6. The method of any one of Embodiments 1 to 4, wherein the reaction mixture is one containing titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $6 \pm 2 TiO_2 + 11 \pm 2 Al + 3 \pm 0.5 C$ (or any composition in which the variances are within the limits described herein).

[0059] Embodiment 7. The method of any one of Embodiments 1 to 6, wherein the elevated temperature is in a range of from about $1000^\circ C$ to about $1800^\circ C$.

[0060] Embodiment 8. The method of any one of Embodiments 1 to 7, wherein the inert or non-oxidizing atmosphere comprises argon.

[0061] Embodiment 9. The method of any one of Embodiments 1 to 8, further comprising a step (b) following (a) and preceding (c), wherein step (b) comprises reducing the particle size of the intermediate product to less than 500 nm, 250 nm, 100 nm, or 50 nm.

[0062] Embodiment 10. The method of any one of Embodiments 1 to 9, wherein the aqueous hydrofluoric acid is

(a) provided as such, or derived from:

(b) aqueous ammonium hydrogen fluoride (NH₄F.HF);

(c) an alkali metal bifluoride salt (i.e., QHF₂, where Q is Li, Na, or K), or a combination thereof; or

(d) at least one fluoride salt, such as an alkali metal, alkaline earth metal, or ammonium fluoride salt (e.g., LiF, NaF, KF, CsF, CaF₂, tetraalkyl ammonium fluoride (e.g., tetrabutyl ammonium fluoride)) in the presence of at least one mineral acid that is stronger than HF (such as HCl, HNO₃, or H₂SO₄); or

(d) a combination of two or more of (a)-(d).

[0063] Embodiment 11. The method of Embodiment 11, wherein the fluorine-containing acid is derived from lithium fluoride and an aqueous mineral acid that is stronger than HF, such as HCl, HNO₃, or H₂SO₄, preferably HCl.

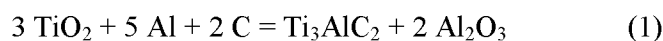
[0064] Embodiment 12. A MXene carbide composition prepared by a method of any one of Embodiments 1 to 12.

EXAMPLES

[0065] The following Examples are provided to illustrate some of the concepts described within this disclosure. While each Example is considered to provide specific individual embodiments of composition, methods of preparation and use, none of the Examples should be considered to limit the more general embodiments described herein.

[0066] Example 1. Experimental Details

[0067] **Example 1.1. Synthesis of MAX-containing composites.** Powders of TiO₂ (99.5%, 45 μm), aluminum (99.5%, < 44 μm), and graphite (98%, < 74 μm)(all sourced from Alfa Aesar) were mixed in the following nominal stoichiometric ratios:



with the goal of synthesizing Ti₃AlC₂ and Ti₂AlC, respectively. The powder mixtures were ball

milled for 10 h, heated at 10°C/min, under flowing argon, Ar, in a tube furnace for 1 h at 1500°C.

[0068] In order to decrease the TiC content in the final product, the following mixtures were also heated to 1500 °C for 1 h: 3TiO₂-5.1Al-1.9C and 3TiO₂-5.1Al-1.8C.

[0069] The resulting sintered compacts were firstly crushed using a hammer and then ground using a TiN coated milling bit and sieved through a 400 mesh sieve producing powder with a particle size less than 38 μm. The reaction products were characterized using a powder diffractometer (Rigaku SmartLab) using Cu-K_{α1} radiation ($\lambda = 1.54 \text{ \AA}$).

[0070] **Example 1.2. Synthesis of MXene.** The corresponding MAX-containing powders were immersed in 25% hydrofluoric acid, HF, (Acros Organics) at 40 °C for 24 h. Afterward the mixture was washed through ~ 5 cycles of distilled water, centrifugation (3500 rpm x 5 min. for each cycle), and decanting, until the supernatant reached a pH of ca. 6.

[0071] In other experiments yielding comparable results, the corresponding precursor powders were slowly added into 12M hydrochloric acid, HCl (Technical Grade, Fisher Scientific, Fair Lawn, NJ, USA), with 1 g of LiF pre-dissolved (98.5 %, Alfa Aesar, Ward Hill, MA, USA) and magnetically stirred at 35 °C for 24 h. In the case of pure Ti₂AlC, 1 g of the sieved powders were added to 10 mL of 6 M HCl with 0.66 g of LiF pre-dissolved instead. Afterwards the etched powder mixtures were washed three times with 6M HCl to remove residual LiF salts. Next the mixtures were washed with distilled water, centrifuged (3500 rpm x 2 min.), and the supernatant was decanted. This process was repeated five times until the supernatant reached a pH of approximately 6. In order to further separate the MXenes from the other extraneous phases present, the above products were shaken in 50 mL distilled water, sonicated in an ice-cooled bath sonicator for 0.5 h under a constant bubbling of Ar gas through the suspension, and followed by centrifugation at 3500 rpm for 1 h.

[0072] In order to further separate the MXenes from the other extraneous phases present, the above product was sonicated in cool water under argon for 1 hour, centrifuging at 3500 rpm for 15 minutes. Given that the extraneous phases do not form colloidal solutions, but the MXenes do, the supernatant resulting from this sonication step was a solution containing pure MXene.

[0073] To characterize the purity of the resulting MXenes, the supernatant was filtered through a polypropylene membrane with a pore size of 0.22 μm (Celgard LLC) to fabricate free-standing MXene films. The resulting films were easily peeled off from the PP membranes for further analysis.

[0074] Example 2. Characterization

[0075] The MAX-based powders and MXene films were characterized with a powder x-

ray diffractometer (Rigaku SmartLab, Tokyo, Japan) using CuK α radiation ($\lambda = 1.54 \text{ \AA}$). Samples were examined on a scanning electron microscope (SEM, Carl Zeiss Supra 50VP) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments) to obtain cross-sectional micrographs of the free-standing films and measure the chemical composition of various samples. Electrical resistivity measurements were performed on free-standing MXene films in a nitrogen-filled glovebox ($< 500 \text{ ppm O}_2$) using a Keithley 2634B SYSTEM Sourcemeter in a linear 4-point probe configuration with a probe spacing of 2.3 mm. The reported resistivity values and error indicate the arithmetic mean and standard deviations, respectively, of five measurements.

[0076] Example 3. Results and Discussion

[0077] Example 3.1 3TiO₂-5Al-2C (“3-5-2”) System and Variants Thereto

[0078] After heating the 3TiO₂-5Al-2C mixture to 1500 °C for 1 h, the XRD patterns (FIG. 1A) evidenced peaks for Ti₃AlC₂, Al₂O₃ and TiC. When the 3TiO₂-5.1Al-1.9C and 3TiO₂-5.1Al-1.8C compositions were used instead, the TiC content decreased as shown in FIG. 1B and FIG. 1C. These results are consistent with former work on producing Ti₃AlC₂/TiC-Al₂O₃ composites starting with TiO₂, Al and C powders. See, e.g., Jixin Chen, *et al.*, *J. Mater. Sci. Technol.*, 22 (2006) 455-458.

[0079] In an attempt to further increase the Ti₃AlC₂ content, a 3TiO₂-5.5Al-1.8C (“3-5.5-1.8”) mixture was heated to 1500 °C for 1 h. Interestingly in this case, peaks associated with Al₃Ti appeared, while those for Ti₃AlC₂ almost disappeared, as shown in FIG. 1D. Clearly, there is a limit to how far the C-content can be reduced before Al₃Ti is formed at the expense of Ti₃AlC₂.

[0080] Example 3.2 6TiO₂-11Al-3C (“6-11-3”) System and Variants Thereto

[0081] FIG. 2A shows the XRD pattern of the reaction products obtained when a 6TiO₂-11Al-3C mixture was heated to 1500 °C for 1 h. In this case, the phases that formed were Ti₂AlC, Ti₃AlC₂ and Al₂O₃.

[0082] To prepare powders containing a majority of Ti₂AlC or Ti₃AlC₂, adjustments to the Al and C contents in the raw materials were made, respectively. Reducing the C-content was beneficial to the formation of Ti₂AlC, while increasing the Al-content was beneficial to the formation of single phase Ti₃AlC₂. For the effect of Al-content on aluminothermic reduction process accords with Hendaoui’s study, as described in A. Hendaoui, *et al.*, *International Journal of Self-Propagating High-Temperature Synthesis*, 17 (2008) 125-128.

[0083] All compositions, when removed from the furnace, showed clear signs of combustion synthesis, such as a hollowed center surrounded by a sintered, deformed ring. In

general, the products of combustion reactions can show compositional variations between different experiments despite identical starting ratios of reactants. Also, it was observed that decreasing the Al-content was beneficial to the formation of Ti_2AlC , while increasing the Al-content, was beneficial to the formation of Ti_3AlC_2 . These caveats notwithstanding, these powders were, in turn, used as precursors to synthesize their respective MXenes.

[0084] **FIGs. 2B and 2C** showed, respectively, the XRD patterns of the reaction products of $6\text{TiO}_2\text{-}11\text{Al-}2.7\text{C}$ (“6-11-2.7”) and $6\text{TiO}_2\text{-}12.3\text{Al-}2.7\text{C}$ (“6-12.3-2.7”) mixtures heated to 1500°C for 1 h. From these results it was clear that relatively pure $\text{Ti}_2\text{AlC-Al}_2\text{O}_3$ and $\text{Ti}_3\text{AlC}_2\text{-Al}_2\text{O}_3$ composites can be synthesized starting with the $6\text{TiO}_2\text{-}11\text{Al-}2.7\text{C}$ (“6-11-2.7”) and $6\text{TiO}_2\text{-}12.3\text{Al-}2.7\text{C}$ (“6-12.3-2.7”) compositions, respectively. These powders were in turn used as precursors to synthesize their respective MXenes.

[0085] Example 3.3 MXene Syntheses

[0086] **FIG. 3A** plots the XRD pattern of the $6\text{TiO}_2\text{-}11\text{Al-}2.7\text{C}$ composition after HF etching. When this pattern was compared to its precursor (**FIG. 2B**), it was obvious that the (002) peak shifted from a 2θ of 13.1° to 7.7° . In other words, the c-lattice parameter, c-LP, increased from $13.6 \text{ \AA}$ to $22.9 \text{ \AA}$ (**FIG. 3B**). The same was true when **FIGs. 2C and 3C** were compared. In this case, the c-LP the (002) peak shifted from a 2θ of 9.5° to 7.1° which implied that the c-LP increased from $18.6 \text{ \AA}$ to $28.0 \text{ \AA}$ upon etching. In other words, like all MXenes, the XRD peaks not only shifted to lower angles, but also broadened significantly. Based on these results there was little doubt that the 3D MAX phase structure was converted to a 2D MXene structure in both cases. Like all other MXenes, the etching process was accompanied by an exothermic reaction and the generation of bubbles (presumably H_2).

[0087] **FIG. 3A** shows that after centrifugation, but before sonication, Al_2O_3 peaks were present. After sonication (**FIG. 2B**), however, the latter disappeared and a phase-pure MXene was obtained.

[0088] The HF-etched MXenes reported to date show the accordion-like morphology that is a comfortable bed for alumina particles implantation. After sonication process, the accordion-like MXene particle can become delaminated (confirmed by **FIG. 4**), and alumina can be easily separated.

[0089] **FIGs. 4A and 4B** show SEM images of the low-cost Ti_2C and Ti_3C_2 materials. As is mentioned above, the low-cost Ti-based MXenes did not show the accordion-like morphology; rather, delaminated flakes appeared tightly stacked. Interestingly, sonication process broke the accordion-like morphology particles, but the low-cost Ti-based MXene still appeared as a similar morphology at macro level (**FIG. 4C**).

[0090] To confirm the purity of the MXene films (i.e. after sonication that led to delamination), EDS was used for elemental analysis. The elemental composition of Ti_2CT_x and $Ti_3C_2T_x$ films were, respectively, 56.72Ti: 17.25C: 15.22O: 10.63F: 0.18Al and 61.02Ti: 18.92C: 9.16O: 10.91F. In the latter case, no Al signal was detected. These results are quite important because they conclusively confirm that not only was the Al-etched out the MAX phases and replaced by F and O/OH terminations, but as importantly, the extraneous alumina phase was also removed.

[0091] Example 4. Electrical Resistivities

[0092] The room temperature electrical resistivities of $Ti_3C_2T_x$ films made starting with pure Ti_3AlC_2 powders and those derived from the 6 – 12.3 – 2.7 mixture were compared. At $220 \pm 10 \mu\Omega \cdot cm$, the resistivity of the former was lower than the $380 \pm 100 \mu\Omega \cdot cm$ of the latter. Thus, the $Ti_3C_2T_x$ films made with the 6 – 12.3 – 2.7 low-cost precursors are $\sim 70\%$ more resistive than films made from pure Ti_3AlC_2 . The reason for the increased resistance is unclear at this time and requires further work. However, when these results are compared to previous results in Table 1, it is clear that the present values, including those for films made from the low-cost precursors, fall within the range of what has been published previously. It follows that this new approach to make Ti-based MXenes results in films whose transport properties are not too different from ones made with significantly cleaner precursors.

Table 1: Electrical resistivity of $Ti_3C_2T_x$ synthesized in this work compared to those reported in literature		
Sample	Resistivity ($\mu\Omega \cdot cm$)	Reference
Roll-cast thick film $Ti_3C_2T_x$	667	A
Spin-coated $Ti_3C_2T_x$	152	B
Isolated single flake $Ti_3C_2T_x$	1111	C
Epitaxial thin film $Ti_3C_2T_x$	176	D
Vacuum-filtered film from pure Ti_3AlC_2	220 ± 10	This work
Vacuum-filtered film from 6 – 12.3 – 2.7	380 ± 100	This work
Ref. A: Ghidui, <i>et al.</i> : <i>Nature</i> , 4, 1716, (2014).		
Ref. B: Dillon, A.D. <i>et al.</i> : <i>Adv. Funct. Mater.</i> , 1 – 7, (2016).		
Ref. C: Miranda, A., <i>et al.</i> : <i>Appl. Phys. Lett.</i> , 108, 033102, (2016).		
Ref. D: Halim, J., <i>et al.</i> , <i>Chem. Mater.</i> , 26, 2374 – 2381, (2014).		

[0093] Example 5. Comments on Examples 1 and 2. Powder compacts partially containing the Ti_2AlC and Ti_3AlC_2 MAX phases have been successfully synthesized using aluminothermic reduction of TiO_2 in the presence of C. When the latter powders were immersed in 40°C , 25% HF for 24 h the MAX powders were converted to their respective MXene powders and were readily separated from the other phases present after the thermic reaction like Al_2O_3 and TiC. This method is thus a low-cost method to synthesize Ti_2C and Ti_3C_2 MXenes.

[0094] The following references may be useful in understanding the background and various aspects of the present invention:

- [1] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M.W. Barsoum, Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2 , *Adv. Mater.* 23 (2011) 4248-4253.
- [2] Michael Naguib, Jérémy Come, Boris Dyatkin, Volker Presser, Pierre-Louis Taberna, Patrice Simon, Michel W Barsoum, Yury Gogotsi, MXene: a promising transition metal carbide anode for lithium-ion batteries, *Electrochemistry Communications*, 16 (2012) 61-64.
- [3] M.W. Barsoum, *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*, John Wiley & Sons, 2013.
- [4] M.W. Barsoum, Physical Properties of the MAX phases, *Encyclopedia of Materials: Science and Technology*, 2006.
- [5] Q. Hu, D. Sun, Q. Wu, H. Wang, L. Wang, B. Liu, A. Zhou, J. He, MXene: A New Family of Promising Hydrogen Storage Medium, *J. Phys. Chem. A* 117 (2013) 14253–14260.
- [6] Q. Hu, H. Wang, Q. Wu, X. Ye, A. Zhou, D. Sun, L. Wang, B. Liu, J. He, Two-dimensional Sc_2C : A reversible and high-capacity hydrogen storage material predicted by first-principles calculations, *Int. J. Hydrogen Energy* 39 (2014) 10606–10612.
- [7] Q. Peng, J. Guo, Q. Zhang, J. Xiang, B. Liu, A. Zhou, R. Liu, Y. Tian, Unique lead adsorption behavior of activated hydroxyl group in two-dimensional titanium carbide, *J. Am. Chem. Soc.* 136 (2014) 4113–4116.
- [8] Q. Tang, Z. Zhou, P. Shen, Are MXenes Promising Anode Materials for Li Ion Batteries? Computational Studies on Electronic Properties and Li Storage Capability of Ti_3C_2 and $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X} = \text{F}, \text{OH}$) Monolayer, *J. Am. Chem. Soc.* 134 (2012) 16909–16916.
- [9] M. Ghidui, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi, M. W. Barsoum. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. *Nature*, 516 (2014) 78-81.
- [10] Jixin Chen, Jialin Li and Yanchun Zhou, In-situ Synthesis of $\text{Ti}_3\text{AlC}_2/\text{TiC}-\text{Al}_2\text{O}_3$ Composite

- from TiO₂-Al-C System, *J. Mater. Sci. Technol.*, 22 (2006) 455-458.
- [11] A. Hendaoui, D. Vrel, A. Amara, A. Benaldjia, P. Langlois, Ti-Al-C MAX Phases by Aluminothermic Reduction Process, *International Journal of Self-Propagating High-Temperature Synthesis*, 17 (2008) 125-128.
- [12] Naguib, M., Mochalin, V. N., Barsoum, M. W. & Gogotsi, Y. Mxenes: A new family of two-dimensional materials. *Adv. Mater.* 26 (2014) 982-982.
- [13] Chang, F., Li, C., Yang, J., Tang, H. & Xue, M. Synthesis of a new graphene-like transition metal carbide by de-intercalating Ti₃AlC₂. *Mater. Lett.* 109 (2013) 295-298.

[0095] As those skilled in the art will appreciate, numerous modifications and variations of the present invention are possible in light of these teachings, and all such are contemplated hereby. For example, in addition to the embodiments described herein, the present invention contemplates and claims those inventions resulting from the combination of features of the invention cited herein and those of the cited prior art references which complement the features of the present invention. Similarly, it will be appreciated that any described material, feature, or article may be used in combination with any other material, feature, or article, and such combinations are considered within the scope of this invention.

[0096] The disclosures of each patent, patent application, and publication cited or described in this document and the Appendices attached to this specification are hereby incorporated herein by reference, each in its entirety, for all purposes, or at least for the purpose described in the context in which the reference was presented.

What is Claimed:

1. A method of preparing a MXene material having a formula $M_{n+1}C_n(T_s)$ comprising
 - (a) reacting a mixture comprising an oxide of M, elemental A, and carbon at temperatures in excess of 800°C under an inert or non-oxidizing atmosphere to form an intermediate product; and
 - (c) reacting the intermediate product directly with an aqueous hydrofluoric acid;
 wherein the MXene composition $M_{n+1}C_n(T_s)$ comprises at least one layer, each layer having a first and second surface, each layer comprising

a substantially two-dimensional array of crystal cells.

each crystal cell having an empirical formula of $M_{n+1}X_n$, such that each C is positioned within an octahedral array of M,

wherein M is at least one of Ti, Zr, Hf, V, Mn, Nb, Ta, Cr, Mo, W;

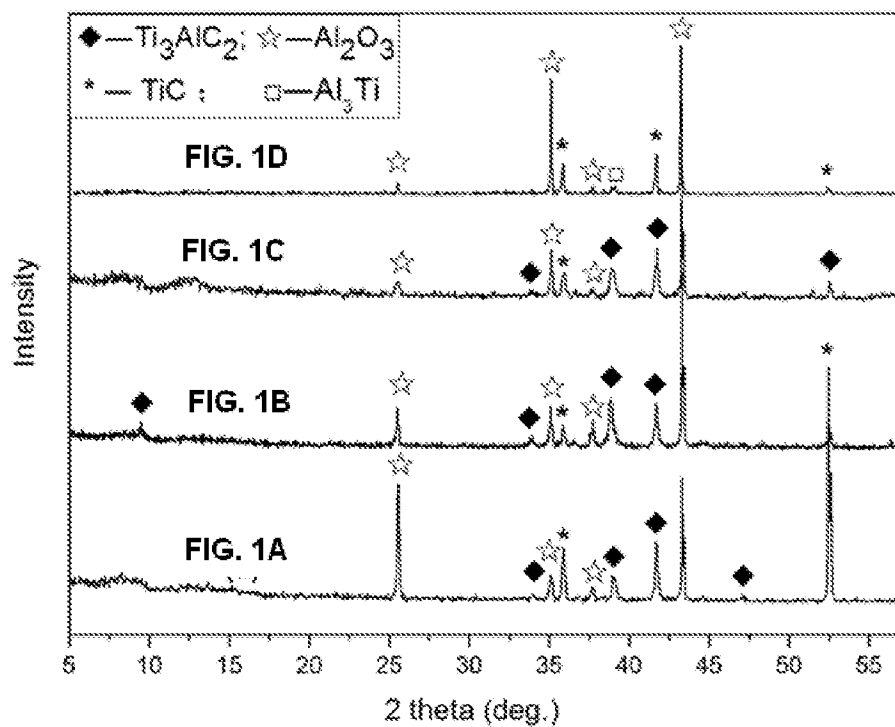
wherein the A element is at least one of Al, As, Ga, Ge, In, P, Pb, S, or Sn;

$n = 1, 2, \text{ or } 3$; and

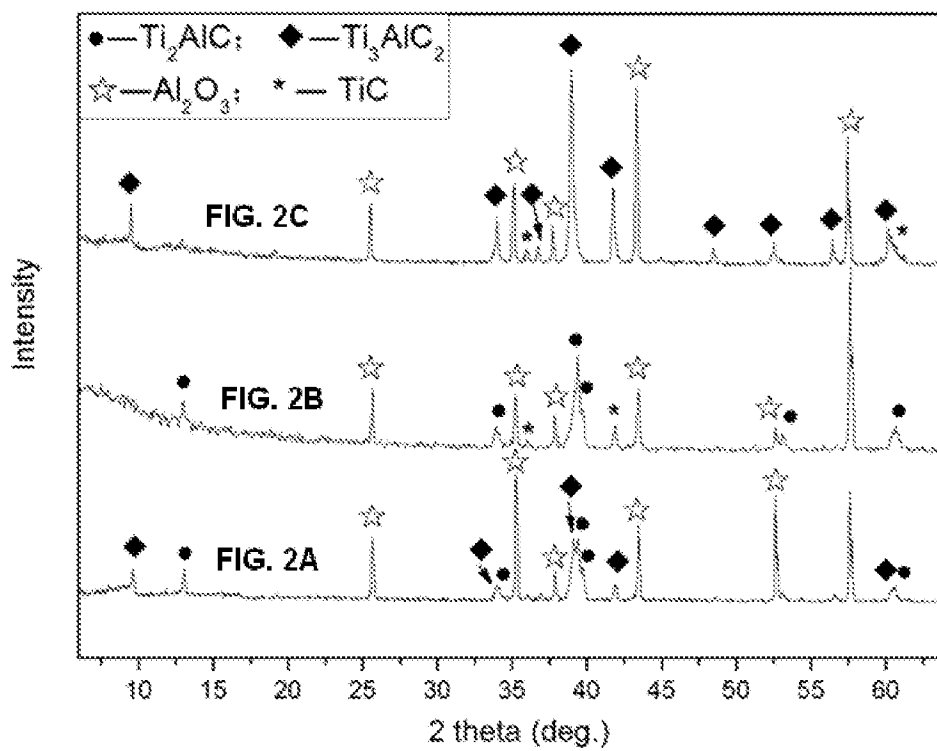
wherein at least one of said surfaces of the layers has surface terminations, T_s , independently comprising alkoxide, alkyl, carboxylate, halide, hydroxide, hydride, oxide, sub-oxide, nitride, sub-nitride, sulfide, sulfonate, thiol, or a combination thereof.
2. The method of claim 1, wherein M is titanium.
3. The method of claim 1, wherein the oxide of M is titanium dioxide, TiO_2 .
4. The method of claim 1, wherein A is aluminum.
5. The method of claim 1, wherein the reaction mixture is one containing titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $3 TiO_2 + 5 Al + 2 C$.
6. The method of claim 1, wherein the reaction mixture is one containing titanium dioxide, TiO_2 , aluminum, and carbon in a ratio of $6 TiO_2 + 11 Al + 3 C$.
7. The method of claim 1, wherein the elevated temperature is in a range of from about 1000°C to about 1800°C.
8. The method of claim 1, wherein the inert or non-oxidizing atmosphere comprises argon.

9. The method of claim 1, further comprising a step (b) following (a) and preceding (c), wherein step (b) comprises reducing the particle size of the intermediate product to less than 50 nm.
10. The method of claim 1, wherein the aqueous hydrofluoric acid is
- (a) provided as such, or derived from:
 - (b) aqueous ammonium hydrogen fluoride ($\text{NH}_4\text{F} \cdot \text{HF}$);
 - (c) an alkali metal bifluoride salt (i.e., QHF_2 , where Q is Li, Na, or K), or a combination thereof; or
 - (d) at least one fluoride salt, such as an alkali metal, alkaline earth metal, or ammonium fluoride salt in the presence of at least one mineral acid that is stronger than HF; or
 - (d) a combination of two or more of (a)-(d).
11. The method of claim 11, wherein the fluorine-containing acid is derived from lithium fluoride and an aqueous mineral acid that is stronger than HF.
12. A MXene carbide composition prepared by a method of claim 1.

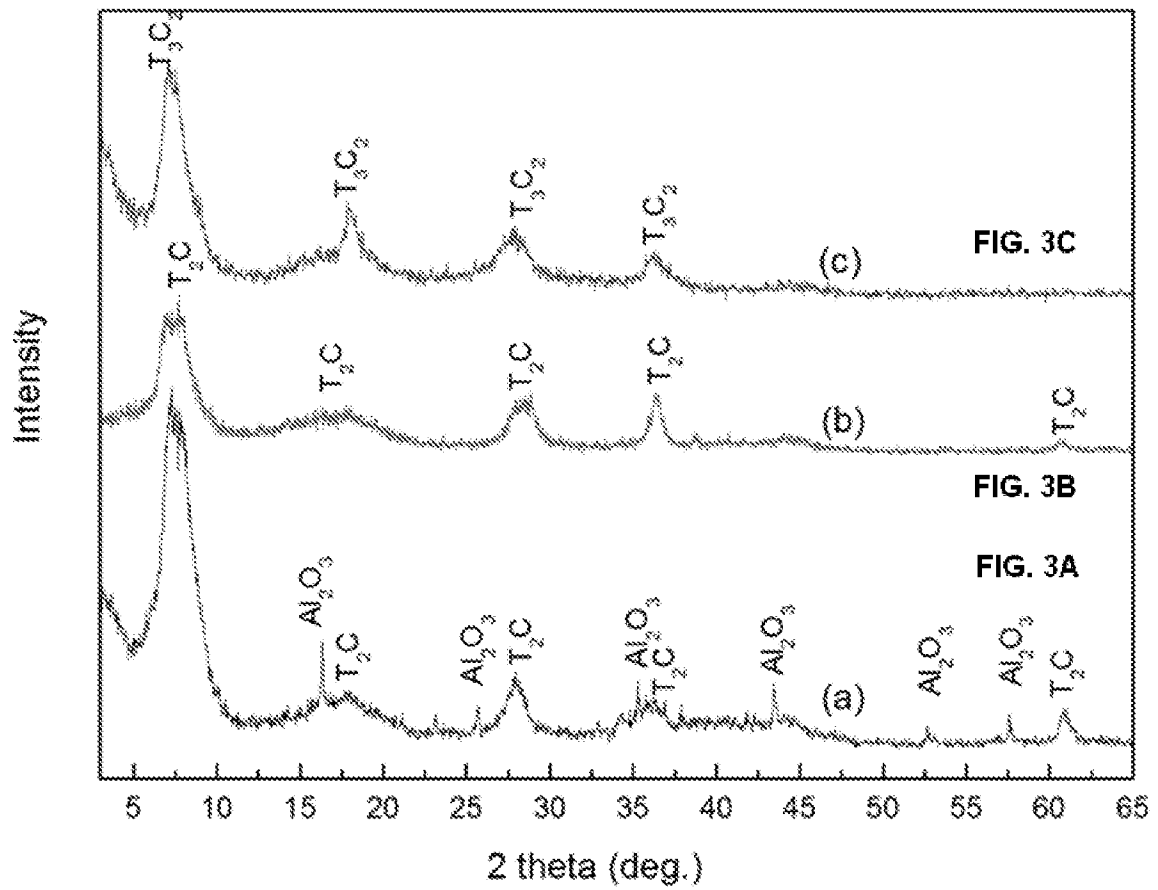
FIGs. 1(A-D)



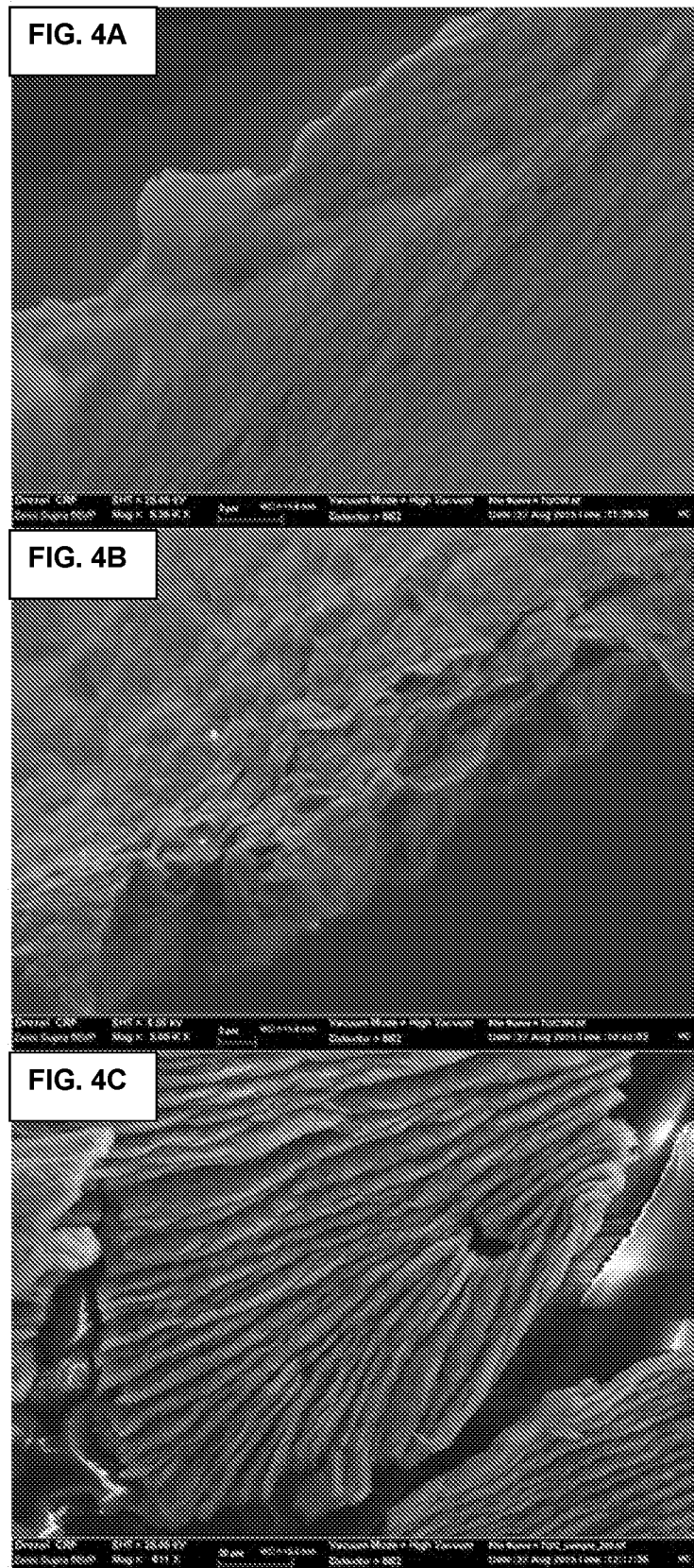
FIGs. 2(A-C)



FIGs. 3(A-C)



FIGs. 4(A-C)



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/047330

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 4/48; B32B 18/00; H01B 1/20; H01M 4/36; H01M 4/587 (2016.01)

CPC - H01M 4/48; B32B 18/00; H01B 1/20; H01M 4/36; H01M 4/587 (2016.08)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - B32B 18/00; H01B 1/20; H01M 4/36; H01M 4/48; H01M 4/587 (2016.01)

CPC - B32B 18/00; H01B 1/20; H01M 4/36; H01M 4/48; H01M 4/587 (2016.08)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 423/371; 423/414; 423/439; 429/218.1; 429/231.8; IPC(8) - B32B 18/00; H01B 1/20; H01M 4/36; H01M 4/48; H01M 4/587; CPC - B32B 18/00; H01B 1/20; H01M 4/36; H01M 4/48; H01M 4/587 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Orbit, Google Patents, Google Scholar

Search terms used: mxenes, titanium dioxide, aluminum, carbon

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/0210044 A1 (DREXEL UNIVERSITY) 30 July 2015 (30.07.2015) entire document	1-12

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

06 October 2016

Date of mailing of the international search report

24 OCT 2016

Name and mailing address of the ISA/

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