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(54) Title: TRANSITION METAL MXENE CATALYSTS FOR CONVERSION OF CARBON DIOXIDE TO HYDROCARBONS

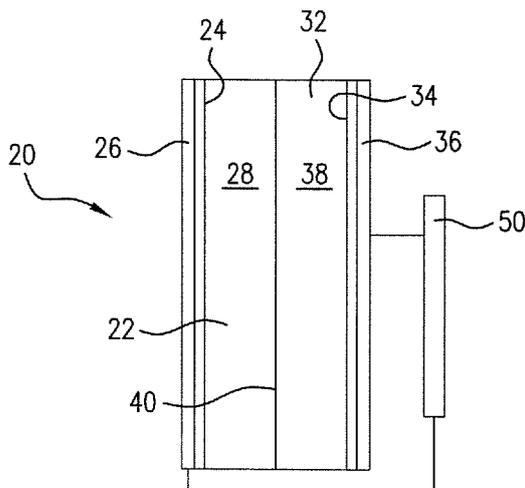


FIG. 1

(57) Abstract: Transition metal MXene catalysts and methods for using with electrochemical cells for reduction of carbon dioxide and production of hydrocarbons. The transition metal catalysts include nanostructured transition metal carbides, nitrides, or carbonitrides. The method includes electrochemically reducing carbon dioxide in an electrochemical cell, by contacting the carbon dioxide with at least one transition metal carbide, nitride, or carbonitride catalyst in the electrochemical cell and applying a potential to the electrochemical cell.

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**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))*
- *of inventorship (Rule 4.17(iv))*

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TRANSITION METAL MXENE CATALYSTS FOR CONVERSION  
OF CARBON DIOXIDE TO HYDROCARBONS  
CROSS REFERENCE TO RELATED APPLICATION

5 This application claims the benefit of U.S. Application, Serial No. 62/691,726,  
filed on 29 June 2018. The co-pending parent application is hereby incorporated by reference  
herein in its entirety and is made a part hereof, including but not limited to those portions which  
specifically appear hereinafter.

BACKGROUND OF THE INVENTION

Field of the Invention

10 The invention relates generally to photoelectrochemical cells, and more  
particularly, methods for using cells for reduction of carbon dioxide and/or production of  
hydrocarbons.

Description of Related Art

15 Today, the rapid growth of the population is draining the finite resources of the  
Earth's crust, i.e., fossil fuels, coals, and minerals, to supply their energy needs. Although fossil  
fuels have been widely used as the energy resource, when burnt, are the primary cause of global  
warming due to the released CO<sub>2</sub>. Therefore, developing a net zero carbon cycle, in which the  
released CO<sub>2</sub> can be transformed into valuable products and fuels using renewable and sustainable  
energy is quite desirable.

20 Electrochemical reduction of carbon dioxide to value-added chemicals using  
renewable energy sources is one of the promising approaches to reach to this goal. Thus far, most  
of the efforts have been focused to reduce CO<sub>2</sub> into CO as a final product in a electrocatalysis  
process. However, CO is known as an intermediate product and must be mixed with hydrogen  
(H<sub>2</sub>) in the desired ratio to produce syngas. The produced syngas also has to feed into a less  
25 efficient thermal process (Fischer-Tropsch) to produce value-added chemicals such as methanol.  
Therefore, reaching to the goal of the net-zero carbon emission process by producing syngas is  
not economically feasible.

Among various possible products of a CO<sub>2</sub> reduction reaction, hydrocarbon fuels, such  
as methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>), that have much higher energy density  
30 compared with carbon monoxide (CO), a common gas phase product of this reaction. The  
energy densities of CH<sub>4</sub> (891.1 kJ mol<sup>-1</sup>), C<sub>2</sub>H<sub>4</sub> (1411.2 kJ mol<sup>-1</sup>) and C<sub>2</sub>H<sub>6</sub> (1554 kJ mol<sup>-1</sup>) are  
three, five and about six times higher than CO (283.4 kJ mol<sup>-1</sup>), respectively. Moreover, these  
gases can be utilized directly as fuels or fed into various petrochemical/chemical processes to  
produce other valuable chemicals. To date, numerous types of copper catalysts such as oxide

drive copper, copper nanoparticles, and nanorods have been used to reduce CO<sub>2</sub> into hydrocarbon fuels such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. However, despite enormous efforts, none of them are capable of efficiently producing hydrocarbon fuels directly from carbon dioxide. Therefore, developing catalysts that can directly result in hydrocarbon formation is highly desirable.

5 Metals such as copper, silver, nickel, etc., have also been employed in the catalytic conversion of CO<sub>2</sub> into high-value products. However, none of them show a reasonable faradaic efficiency for CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> formation with respect to the applied overpotential. Therefore, an economical methane formation system cannot be obtained because of the low energy efficiency of the conventional metal catalysts.

## 10 SUMMARY OF THE INVENTION

A general object of the invention is to provide an improved method and system for carbon dioxide reduction into valuable end products such as hydrocarbons. Embodiments of this invention incorporate a catalyst that can selectively produce, for example, CH<sub>4</sub> (natural gas) with 100-fold higher turnover frequency, 40 times higher selectivity at four times less energy compared to state of the art catalysts (e.g., copper). Other exemplary hydrocarbon fuels possible  
15 by this invention include, without limitation, ethylene (C<sub>2</sub>H<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>) with 1411.2 and 1554 kJ mol<sup>-1</sup> energy density, respectively. The type of hydrocarbon can depend on the stoichiometric ratio of the catalyst used.

The invention includes a catalyst composition for carbon dioxide reduction,  
20 including at least one transition metal MXene catalyst. The transition metal catalyst comprises a nanostructured MXene carbide, nitride, or carbonitride, such as M<sub>y</sub>X<sub>z</sub>, wherein M is a transition metal, X is carbon, nitrogen or carbonitride (e.g., M<sub>x</sub>C<sub>y</sub>N<sub>z</sub>), and y and z are stoichiometric ratio integers. The transition metal can be, for example, molybdenum, tungsten, titanium, or cobalt. In embodiments of this invention, the transition metal MXene catalyst  
25 comprises a nanoparticle form, such as having an average size between about 1 nm and 400 nm. The transition metal MXene catalyst can further be a nanoflake, nanosheet, or nanoribbon form.

The invention further includes an electrochemical cell having a cathode with at least one transition metal catalyst, and in contact with an electrolyte. The electrolyte, such as  
30 a solution of 1M KHCO<sub>3</sub>, is saturated with the carbon dioxide to be treated, which can be fed into the electrolyte through any known manner.

The invention further includes a method of electrochemically reducing carbon dioxide, including: introducing the carbon dioxide to a catalyst comprising a transition metal catalyst in an electrochemical cell; applying a potential to the electrochemical cell; and

converting the carbon dioxide to a hydrocarbon. Embodiments of the invention further include steps of providing the electrochemical cell including a cathode coated with the catalyst, and an electrolyte in contact with the cathode and the catalyst; providing carbon dioxide to the electrochemical cell; and applying the potential to the electrochemical cell in the presence of the carbon dioxide to reduce the carbon dioxide to the hydrocarbon.

Other objects and advantages will be apparent to those skilled in the art from the following detailed description taken in conjunction with the appended claims and drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic sectional view of an electrochemical device according to one embodiment of this invention.

FIG. 2 representatively illustrates a two-compartment three-electrode electrochemical cell according to one embodiment of this invention.

#### DESCRIPTION OF THE INVENTION

This invention relates generally to reduction of carbon dioxide ( $\text{CO}_2$ ) to hydrocarbons such as methane ( $\text{CH}_4$ ) and, more particularly, to MXene materials as catalysts for this reduction.

The invention provides transition metal catalysts and method of using the catalysts to reduce carbon dioxide, such as to hydrocarbons for use as fuel. Exemplary catalysts include nanostructured MXenes, such as typically in one of the following structures:  $\text{M}_2\text{X}$  (e.g.,  $\text{M}_2\text{N}$ ,  $\text{M}_2\text{C}$ , or  $\text{M}_2\text{CN}$ ),  $\text{M}_3\text{X}_2$  (e.g.,  $\text{M}_3\text{N}_2$ ,  $\text{M}_3\text{C}_2$ , or  $\text{M}_3\text{C}_2\text{N}$ ), and  $\text{M}_4\text{X}_3$  (e.g.,  $\text{M}_4\text{C}_3\text{N}$ ), wherein M is a transition metal and X is carbon, nitrogen, or a carbonitride. One presently preferred transition metal is molybdenum, such as in the form of  $\text{Mo}_2\text{C}$  or  $\text{Mo}_2\text{CN}$  nanoparticles or nanoflakes. Other exemplary MXenes include, without limitation, carbides, nitrides, or carbonitrides of cobalt, titanium, tungsten, etc. Multiple metals and/or multiple stoichiometries are also possible for the MXene catalysts.

Two ultimate goals in the electrochemical reduction of carbon dioxide can be addressed by using the transition metal MXene catalysts of this invention. First, it tackles the amount of required energy to reduce the  $\text{CO}_2$  into useful products. The observed onset overpotential for the  $\text{CH}_4$  formation ( $-0.15$  V vs. RHE) using  $\text{Mo}_2\text{C}$  is the lowest reported to date which shows its superior catalytic activity among commonly used catalysts. Second, employing  $\text{Mo}_2\text{C}$  catalysts provides production of  $\text{CH}_4$  having two orders of magnitude higher numbers of product formation compared to typical state of the art metal catalysts (e.g., copper).

FIG. 1 is a schematic sectional view of an electrochemical device (e.g., electrochemical cell) with a first compartment 22 including at least one transition metal MXene

24 disposed on a cathode 26. Device 20 includes a second compartment 32 including at least one water oxidizing catalyst 34 disposed on an anode 36. Compartments 22 and 32 include a first electrolyte 28 and a second electrolyte 38, respectively, and are in ionic contact through an ion-conductive membrane 40. An electrical potential source 50 is included. In 5 embodiments of this invention, the electrical potential source is a photovoltaic cell. The device 20 further includes a carbon dioxide inlet and a suitable hydrocarbon outlet, and a corresponding anode side inlet and outlet.

The transition metal MXene catalysts of embodiments of this invention have a general chemical formula of  $M_yX_z$ , wherein M is a transition metal, X is carbon and/or nitrogen, 10 and y and z are stoichiometric ratio integers (generally each one of 1-4, with y and z being equal or y one whole number greater than z; e.g.,  $M_2X$ ,  $M_3X_2$ , and/or  $M_4X_3$ ). In embodiments of this invention, the catalyst is or includes  $M_{n+1}X_n$ , wherein M is a transition metal, X is carbon and/or nitrogen, and n is zero or an integer. In additional embodiments of this invention, the catalyst is or includes  $M_xC_yN_z$  wherein M is a transition metal, C is carbon, N is nitrogen, and 15 x, y and z are each an stoichiometric ratio integer (e.g., with each of y and z being independently one of 0 to 3, with at least one of y and z not zero, and x, y and/or z being equal or x being one whole number greater than y or z (e.g., MC, MN,  $M_2C$ ,  $M_2N$ ,  $M_3C_2$ ,  $M_4C_3$ ,  $M_2CN$ ,  $M_3C_2N$ , and/or  $M_4C_3N$ ). Presently preferred transition metals include molybdenum, tungsten, titanium, or cobalt. Exemplary catalyst materials include, without limitation, WC, TiC,  $Co_2C$ , and/or 20  $Mo_2C$ .

The transition metal MXene catalysts can be provided in a variety of forms, for example, as a bulk material, in nanostructure form, as a collection of particles, and/or as a collection of supported particles. The MXene catalyst in bulk form can have a layered structure as is typical for such compounds. The MXene catalyst may have a nanostructure morphology, 25 including but not limited to monolayers, nanotubes, nanoparticles, nanoflakes (e.g., multilayer nanoflakes), nanosheets, nanoribbons, nanoporous solids, etc. As used herein, the term "nanostructure" refers to a material with a dimension (e.g., of a pore, a thickness, a diameter, as appropriate for the structure) in the nanometer range.

In some embodiments, the catalyst is a layer-stacked bulk MXene with metal 30 atom-terminated edges. In other embodiments, MXene nanoparticles may be used in the devices and methods of the disclosure. In other embodiments, all MXene nanoflakes may be used in the devices and methods of the disclosure. Nanoflakes can be made, for example, via liquid exfoliation, as described in Coleman, J. N. et al., "Two-dimensional nanosheets produced by liquid exfoliation of layered materials." *Science* 331, 568-71 (2011) and Yasaei,

P. et al., "High-Quality Black Phosphorus Atomic Layers by Liquid-Phase Exfoliation." *Adv. Mater.* (2015) (doi:10.1002/adma.201405150), each of which is hereby incorporated herein by reference in its entirety. In other embodiments, transition metal MXene nanoribbons may be used in the devices and methods of the disclosure. In other embodiments, transition metal  
5 MXene nanosheets may be used in the devices and methods of the disclosure. The person of ordinary skill in the art can select the appropriate morphology for a particular device.

In some embodiments of the methods and devices as otherwise described herein, the transition metal MXene nanostructures (e.g., nanoflakes, nanoparticles, nanoribbons, etc.) have an average size between about 1 nm and 1000 nm. The relevant size  
10 for a nanoparticle is its largest diameter. The relevant size for a nanoflake is its largest width along its major surface. The relevant size for a nanoribbon is its width across the ribbon. The relevant size for a nanosheet is its thickness. In some embodiments, the transition metal MXene nanostructures have an average size between from about 1 nm to about 400 nm, or about 1 nm to about 350 nm, or about 1 nm to about 300 nm, or about 1 nm to about 250 nm, or about 1  
15 nm to about 200 nm, or about 1 nm to about 150 nm, or about 1 nm to about 100 nm, or about 1 nm to about 80 nm, or about 1 nm to about 70 nm, or about 1 nm to about 50 nm, or 50 nm to about 400 nm, or about 50 nm to about 350 nm, or about 50 nm to about 300 nm, or about 50 nm to about 250 nm, or about 50 nm to about 200 nm, or about 50 nm to about 150 nm, or about 50 nm to about 100 nm, or about 10 nm to about 70 nm, or about 10 nm to about 80 nm,  
20 or about 10 nm to about 100 nm, or about 100 nm to about 500 nm, or about 100 nm to about 600 nm, or about 100 nm to about 700 nm, or about 100 nm to about 800 nm, or about 100 nm to about 900 nm, or about 100 nm to about 1000 nm, or about 400 nm to about 500 nm, or about 400 nm to about 600 nm, or about 400 nm to about 700 nm, or about 400 nm to about 800 nm, or about 400 nm to about 900 nm, or about 400 nm to about 1000 nm.

In certain embodiments of the methods and devices as otherwise described herein, transition metal MXene nanoflakes have an average thickness between about 1 nm and about 100  $\mu\text{m}$  (e.g., about 1 nm to about 10  $\mu\text{m}$ , or about 1 nm to about 1  $\mu\text{m}$ , or about 1 nm to about 1000 nm, or about 1 nm to about 400 nm, or about 1 nm to about 350 nm, or about 1 nm to about 300 nm, or about 1 nm to about 250 nm, or about 1 nm to about 200 nm, or about 1  
30 nm to about 150 nm, or about 1 nm to about 100 nm, or about 1 nm to about 80 nm, or about 1 nm to about 70 nm, or about 1 nm to about 50 nm, or about 50 nm to about 400 nm, or about 50 nm to about 350 nm, or about 50 nm to about 300 nm, or about 50 nm to about 250 nm, or about 50 nm to about 200 nm, or about 50 nm to about 150 nm, or about 50 nm to about 100 nm, or about 10 nm to about 70 nm, or about 10 nm to about 80 nm, or about 10 nm to about

100 nm, or about 100 nm to about 500 nm, or about 100 nm to about 600 nm, or about 100 nm  
to about 700 nm, or about 100 nm to about 800 nm, or about 100 nm to about 900 nm, or about  
100 nm to about 1000 nm, or about 400 nm to about 500 nm, or about 400 nm to about 600  
nm, or about 400 nm to about 700 nm, or about 400 nm to about 800 nm, or about 400 nm to  
5 about 900 nm, or about 400 nm to about 1000 nm); and average dimensions along the major  
surface of about 20 nm to about 100  $\mu\text{m}$  (e.g., about 20 nm to about 50  $\mu\text{m}$ , or about 20 nm to  
about 10  $\mu\text{m}$ , or about 20 nm to about 1  $\mu\text{m}$ , or about 50 nm to about 100  $\mu\text{m}$ , or about 50 nm  
to about 50  $\mu\text{m}$ , or about 50 nm to about 10  $\mu\text{m}$ , or about 50 nm to about 1  $\mu\text{m}$ , or about 100  
nm to about 100  $\mu\text{m}$ , or about 100 nm to about 50  $\mu\text{m}$ , or about 100 nm to about 10  $\mu\text{m}$ , or  
10 about 100 nm to about 1  $\mu\text{m}$ ), The aspect ratio (largest major dimension:thickness) of the  
nanoflakes can be on average, for example, at least about 5:1, at least about 10:1 or at least  
about 20:1. For example, in certain embodiments the transition metal MXene nanoflakes have  
an average thickness in the range of about 1 nm to about 1000 nm (e.g., about 1 nm to about  
100 nm), average dimensions along the major surface of about 50 nm to about 10  $\mu\text{m}$ , and an  
15 aspect ratio of at least about 5:1.

The invention includes methods of electrochemically reducing carbon dioxide  
by introducing the carbon dioxide to a transition metal MXene catalyst in an electrochemical  
cell. Embodiments of this invention utilize nanostructured transition metal MXenes as  
catalysts in the electrocatalytic conversion of carbon dioxide ( $\text{CO}_2$ ) to produce hydrocarbon,  
20 such methane ( $\text{CH}_4$ ), the main component of natural gas, at remarkably low overpotentials.

The nanostructured transition metal MXenes can be synthesized using liquid  
exfoliation techniques, and were tested in a two-compartment three-electrode electrochemical  
cell as a working electrode, as shown in FIG. 2. FIG. 2 representatively illustrates the two-  
compartment three-electrode electrochemical cell according to embodiments of this invention  
25 used for testing. Transition metal carbides were drop-cast onto a glassy carbon substrate to  
form the working electrode 124. Platinum gauze or other suitable material can be used as the  
counter and reference electrodes 136 and 126, respectively. The working electrode 124,  
reference electrode 126, and counter electrode 136 are immersed in an aqueous electrolyte  
solution 128 and 138, respectively. The cathode and anode are separated by an ion-conductive  
30 membrane 140 to eliminate potential product oxidation at the anode 136 surface.

Testing results indicated that  $\text{Mo}_2\text{C}$  exhibited an onset potential of -0.15 V vs.  
RHE, which is a potential where the reduction reaction begins in a buffer electrolyte of 1 M  
 $\text{KHCO}_3$ . The recorded onset potential for  $\text{Mo}_2\text{C}$  is the lowest overpotential (-0.15 V), excess  
energy beyond thermodynamic potential, for  $\text{CH}_4$  formation reported so far, which is 650 mV less

than that of copper (- 0.8 V). Mo<sub>2</sub>C also exhibits significantly higher faradaic efficiency at a potential range of -0.15 to -0.8 V. For instance, at a potential of -0.4 V, methane formation F.E. for Mo<sub>2</sub>C nanoflake is 44% while copper has a negligible faradaic efficiency of less than 1%. Moreover, the calculated turnover frequency (TOF), the number of product (CH<sub>4</sub>) formation per active sites, for Mo<sub>2</sub>C indicated approximately two orders of magnitude higher CH<sub>4</sub> formation than that of copper at a potential range of -0.15 to -0.8 V vs. RHE.

Thus, the invention a method and system to recycle CO<sub>2</sub> into hydrocarbons, such as CH<sub>4</sub> (natural gas) in an energy efficient and economically feasible electrochemical process. A scale-up of the invention coupled with solar energy cells can develop a carbon-zero electrochemical system in which CO<sub>2</sub> from the air, wastes of the big industries, etc. can be reduced to a profitable product (natural gas) that can directly be used as a fuel.

The invention illustratively disclosed herein suitably may be practiced in the absence of any element, part, step, component, or ingredient which is not specifically disclosed herein.

While in the foregoing detailed description this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purposes of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

What is claimed is:

1. A method of electrochemically reducing carbon dioxide, comprising:  
introducing the carbon dioxide to a catalyst comprising a transition metal carbide, nitride, or carbonitride in an electrochemical cell;  
applying a potential to the electrochemical cell; and  
converting the carbon dioxide to a hydrocarbon, preferably methane.
2. A method of claim 1, wherein the electrochemical cell comprises a cathode, wherein the cathode is coated with the catalyst.
3. A method of claim 1, further comprising:  
providing the electrochemical cell including a cathode coated with the catalyst, and an electrolyte in contact with the cathode and the catalyst;  
providing carbon dioxide to the electrochemical cell; and  
applying the potential to the electrochemical cell in the presence of the carbon dioxide to reduce the carbon dioxide to the hydrocarbon.
4. The method of any one of claim 3, wherein the electrolyte, such as a solution of 1M  $\text{KHCO}_3$ , is saturated with the carbon dioxide.
5. A method of any one of claims 1 to 4, wherein the catalyst comprises a nanostructured MXene.
6. A method of any one of claims 1 to 5, wherein the catalyst comprises  $\text{M}_y\text{X}_z$ , wherein M is a transition metal, X is carbon and/or nitrogen, and y and z are stoichiometric ratio integers.
7. A method of any one of claims 1 to 6, wherein the transition metal comprises molybdenum, tungsten, titanium, or cobalt.
8. A method of any one of claims 1 to 7, wherein the catalyst comprises a nanoparticle form.

9. A method of claim 8, wherein the catalyst nanoparticles have an average size between about 1 nm and 400 nm.
10. A method of any of claims 1 to 9, wherein the catalyst comprises a nanoflake, nanosheet, or nanoribbon form.
11. An electrochemical cell having a cathode with at least one MXene catalyst, and in contact with an electrolyte.
12. An electrochemical cell of claim 11, wherein the MXene catalyst comprises a nanostructured transition metal carbide, nitride and/or carbonitride.
13. An electrochemical cell of claim 11, wherein the MXene catalyst comprises  $M_yX_z$ , wherein M is a transition metal, X is carbon and/or nitrogen, and y and z are stoichiometric ratio integers.
14. An electrochemical cell of any one of claims 11 to 13, wherein the MXene catalyst comprises molybdenum, tungsten, titanium, or cobalt.
15. An electrochemical cell of any one of claims 11 to 14, wherein the MXene catalyst comprises a nanoparticle form.
16. An electrochemical cell of claim 15, wherein the MXene catalyst nanoparticles have an average size between about 1 nm and 400 nm.
17. An electrochemical cell of any one of claims 11 to 16, wherein the MXene catalyst comprises a nanoflake, nanosheet, or nanoribbon form.
18. An electrochemical cell according to any one of claims 11 to 17 for use in reducing carbon dioxide.
19. A catalyst composition for carbon dioxide reduction, comprising at least one transition metal MXene.

20. A composition of claim 19, wherein the transition metal MXene comprises a nanostructured carbide, nitride, and/or carbonitride.

21. A composition of claim 19 or 20, wherein the transition metal MXene comprises  $M_yX_z$ , wherein M is a transition metal, X is carbon and/or nitrogen, and y and z are stoichiometric ratio integers.

22. A composition of any one of claims 19 to 21, wherein the transition metal MXene comprises molybdenum, tungsten, titanium, or cobalt.

23. A composition of any one of claims 19 to 22, wherein the transition metal MXene comprises a nanoparticle form.

24. A composition of claim 23, wherein the transition metal MXene nanoparticles have an average size between about 1 nm and 400 nm.

25. A composition of any one of claims 19-24, wherein the transition metal MXene comprises a nanoflake, nanosheet, or nanoribbon form.

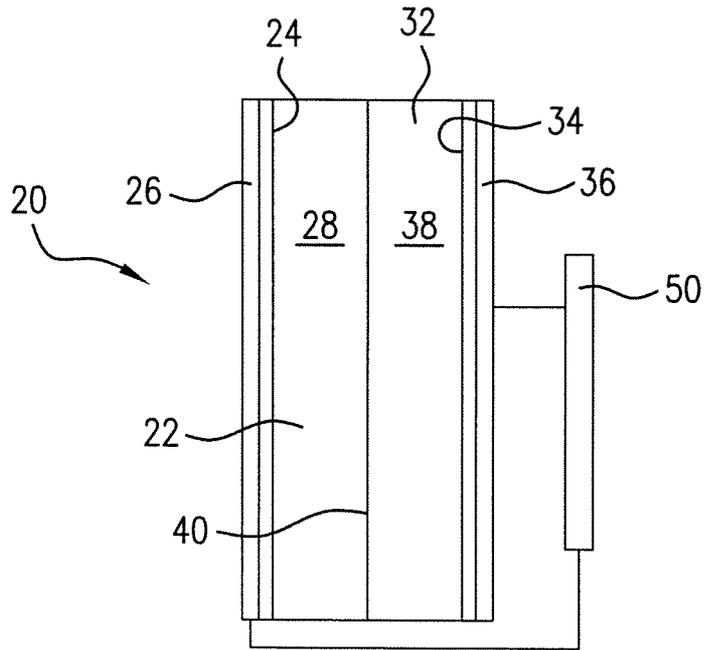


FIG. 1

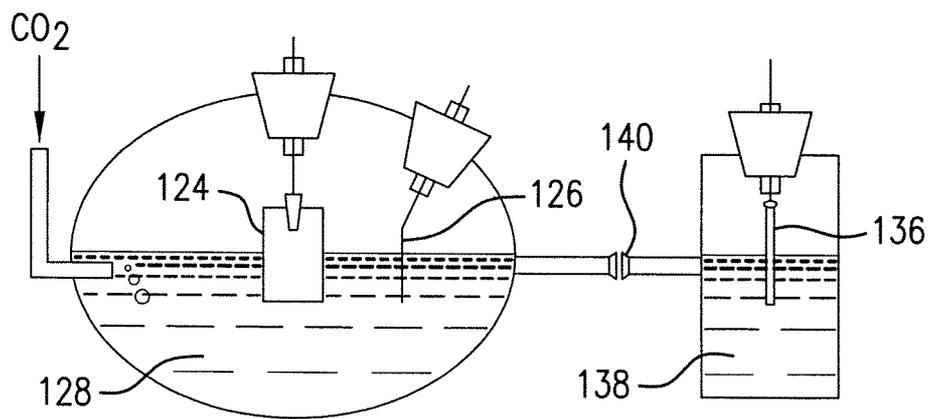


FIG. 2

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/35577

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 27/22, B01J 27/24, C25B 1/00 (2019.01)

CPC - B01J27/22; B01J27/24; C01B32/40; C25B1/00; C25B11/0447; C25B3/04

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)

See Search History Document

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

See Search History Document

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

See Search History Document

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2012/0018311 A1 (YOTSUHASHI et al. ) 26 January 2012 (26.01.2012); Entire document, especially Fig. 4, para [0030]-[0046]	1-4 ----- 5, 11-14, 19-21
Y	LI et al., "Understanding of Electrochemical Mechanisms for CO2 Capture and Conversion into Hydrocarbon Fuels in Transition-Metal Carbides (MXenes)" ACS Nano, 10825-10833, 11 September 2017 (2017); abstract, page 10825 [online] URL < <a href="https://pubs.acs.org/doi/abs/10.1021/acsnano.7b03738">https://pubs.acs.org/doi/abs/10.1021/acsnano.7b03738</a> >	5, 11-14, 19-21
A	US 2018/0023198 A1 (SIEMENS AKTIENGESELLSCHAFT) 25 January 2018 (25.01.2018), entire document	1-5, 11-14, 19-21

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

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"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

13 August 2019

Date of mailing of the international search report

10 SEP 2019

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

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Authorized officer:

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PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/35577

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 6-10,15-18,22-25  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.