



(51) International Patent Classification:

B01J 23/75 (2006.01) **B01D 53/02** (2006.01)
B01J 23/83 (2006.01) **B01D 53/62** (2006.01)
B01J 23/89 (2006.01) **C07C 1/02** (2006.01)
B01J 37/00 (2006.01) **B82B 3/00** (2006.01)
B01J 20/02 (2006.01) **B82Y 30/00** (2011.01)

(21) International Application Number:

PCT/US2016/049164

(22) International Filing Date:

28 August 2016 (28.08.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/212,086 31 August 2015 (31.08.2015) US

(71) Applicant: **UNIVERSITY OF MASSACHUSETTS**
[US/US]; One Beacon Street, 31st Floor, Boston, MA
02110 (US).

(72) Inventors: **SHEN, Mengyan**; 34 Cottage Street, Belmont,
MA 02478 (US). **WANG, Cong**; 11 Phoebe Ave., Lowell,
MA 01854 (US). **REN, Haizhou**; 381 Hildreth St, Apt
209, Lowell, MA 01850 (US).

(74) Agent: **ZHANG, Yin, Philip**; Milstein Zhang & Wu LLC,
2000 Commonwealth Ave. Suite 400, Newton, MA 02466
(US).

(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).

Published:

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

(54) Title: COMPOSITIONS AND METHODS FOR CO₂ ADSORPTION AND CONVERSION TO LONG-CHAIN HYDROCARBONS

(57) Abstract: The invention provides novel, low-cost catalysts and methods for their preparation and application in CO₂ adsorption and conversion to long-chain hydrocarbons via photosynthesis with ambient CO₂ and solar energy.



WO 2017/040355 A1

COMPOSITIONS AND METHODS FOR CO₂ ADSORPTION AND CONVERSION TO LONG-CHAIN HYDROCARBONS

Statement of Federally Sponsored Research

[0001] The United States Government has certain rights to the invention pursuant to Grant No. 1161475 awarded by National Science Foundation and Grant No. ARPA-E 0670-2061 awarded by Department of Energy.

Priority Claims and Related Patent Applications

[0002] This application claims the benefit of priority from U.S. Provisional Application Serial No. 62/212,086, filed on August 31, 2015, the entire content of which is incorporated herein by reference in its entirety.

Technical Fields of the Invention

[0003] The invention generally relates to sequestration of CO₂ and generation of renewable energy. More particularly, the invention relates to novel, low-cost catalysts and their application in CO₂ adsorption and conversion to long-chain hydrocarbons and fuels via photosynthesis using ambient CO₂ and solar energy, and compositions and methods of preparation and use thereof.

Background of the Invention

[0004] Significant research efforts around the world have been directed to the development of artificial photosynthesis technologies that can efficiently and effectively convert CO₂ to energy, which would greatly reduce the dependence on crude oil and make use of the increasing amount of carbon dioxide emissions that is contributing to climate change. A continued effort has been placed on replicating or imitating the natural process of photosynthesis, for example, by various photocatalytic reactions that have been studied to convert CO₂ and H₂O to hydrocarbons to store solar energy in the form of chemical compounds. (Ghadimkhani, *et al.* **2013** *Chem. Commun.* 49, 1297-1299; Hou, *et al.* **2011** *ACS Catal.* 1 (8), pp 929-936; Varghese, *et al.* **2009** *Nano Letters* 9, 731-737; Mendoza, *et al.* **2012** *Korean J. Chem. Eng.* 29(11), 1483-1486.)

[0005] Most efforts so far have only been limited success in producing short-chain (C_1 - C_2) hydrocarbons or carbohydrates. The solar-to-chemical efficiencies remain at 1 or 2 order of magnitude lower than natural photosynthesis 1~7%. (G. Karp, "*Cell and Molecular Biology*", 5th Ed., Wiley, 2008.) There have been reports of conversion of CO_2 to long-chain hydrocarbons or carbohydrates, for example, via a photocatalytic process that converts carbon dioxide, water, and sunlight by using Co/CoO nanostructures. (Wang, *et al.* **2011 AIP Advances** 1, 042124; Wang, *et al.* **2009 Int'l J. of Modern Physics B** 23(31), 5849-5857.) The high cost of catalyst and requirement for pure grade CO_2 , however, place challenges on industrial application.

[0006] It is desirable to develop a low-cost, stable catalyst that can be efficiently applied in large-scale photosynthetic settings. It is also strongly desired that the photosynthetic procedure can use ambient CO_2 .

Summary of the Invention

[0007] The invention is based, in part, on the unexpected discovery of low-cost, acid-etching and base-etching methods for the fabrication of nanostructured catalysts. These nanostructured catalysts not only can be used for photocatalytic reduction of CO_2 but also can efficiently adsorbing CO_2 from atmosphere at the same time.

[0008] In one aspect, the invention generally relates to an acid-treated or base-treated metal or alloy material exhibiting a nanostructured surface, produced respectively by acid-etching or base-etching of a metal or alloy material having an oxide coating.

[0009] In another aspect, the invention generally relates to a method for forming a nanostructured surface on a metal or alloy material having an oxide coating. The method includes: etching a metal or alloy material with an acid or a base; and washing the acid- or base-etched metal or alloy material. In certain preferred embodiments, the method further includes exposing the washed acid- or base-etched metal or alloy material to ambient air or concentrated oxygen.

[0010] In yet another aspect, the invention generally relates to a method for forming a hydrocarbon from CO_2 via photosynthesis. The method includes: providing an acid-or base-treated metal or alloy material exhibiting a nanostructured surface capable of catalyzing photosynthesis; contacting the acid-or base-treated metal or alloy material CO_2 to allow adsorption of CO_2 onto the surfaces of the acid-or base-treated metal or alloy material; mixing

the CO₂-adsorbed, acid-or base-treated metal or alloy material with water forming a reaction mixture; and irradiating the reaction mixture with a light source to produce a hydrocarbon.

[0011] In yet another aspect, the invention generally relates to a method for absorbing CO₂. The method include: providing an acid-treated or base-treated metal or alloy material exhibiting a nanostructured surface capable of catalyzing photosynthesis; and contacting the acid-treated or base-treated metal or alloy material CO₂ to allow adsorption of CO₂ onto the surfaces of the acid-treated or base-treated metal or alloy material.

Brief Description of the Drawings

[0012] The invention will be better understood from a reading of the following detailed description taken in conjunction with the drawings in which like reference designators are used to designate like elements, and in which:

[0013] **FIG. 1** shows exemplary scanning electron microscope (SEM) images of the surfaces of a cobalt microparticle. (A) Co particles before treatment; (B) Co particles treated with 3.5 % aqueous HCl solution for 10 min. and washed with distilled water; (C) Nano-flake structures grew on surfaces of Co microparticles after 10 ~ 20 hours to air (oxygen).

[0014] **FIG. 2** shows exemplary GC chromatography of hydrocarbon products.

[0015] **FIG. 3** shows exemplary MS spectrum of ¹²C hydrocarbons and ¹³C incorporated decane formed from photosynthesis. The ¹³C isotope incorporation data confirms that hydrocarbons were produced directly from photocatalytic reduction of CO₂.

[0016] **FIG. 4** shows exemplary MS spectrum of Heptane and D-Heptane formed by photosynthesis. The hydrogen isotope incorporation data confirms that hydrocarbons were produced directly from photocatalytic reduction of water.

[0017] **FIG. 5** shows exemplary FTIR data of hydrocarbon products by a photocatalytic reaction.

[0018] **FIG. 6** shows exemplary block flow diagram showing material balance for photocatalytic conversion of CO₂ and H₂O to hydrocarbons at 0.8 mJ/pulse energy intensity using 2 g of nanostructured Co microparticles of the invention under 2 atm CO₂ pressure and 3 hours of reaction time.

[0019] **FIG. 7** shows exemplary SEM images of the surfaces of a Nanostructured Co microparticle, treated with 3.5 % aqueous NaOH solution for 10 min, and then, after washing

with distilled water.

[0020] **FIG. 8** shows exemplary GC chromatogram of hydrocarbons produced from a larger reactor.

Definitions

[0021] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0022] As used herein, “acid” refers to a molecule or ion capable of donating a proton (a Brønsted acid or an Arrhenius acid) in an aqueous environment or, alternatively, capable of forming a covalent bond with an electron pair (a Lewis acid). An acid may be monoprotic (one proton per acid molecule) or polyprotic acid (two or more protons per acid molecule). Exemplary acids include boric acid (H_3BO_3), carboxylic acids ($-\text{COOH}$), chromic acid (H_2CrO_4), fluoroantimonic acid (HSbF_6), fluoroboric acid (HBF_4), fluorosulfuric acid (HSO_3F), halogen oxoacids (HClO , HClO_2 , HClO_3 , HClO_4 and bromine and iodine counterparts), hexafluorophosphoric acid (HPF_6), hydrogen halides (HX , where $\text{X} = \text{F}$, Cl , Br or I), nitric acid (HNO_3), phosphoric acid (H_3PO_4), sulfonic acids ($-\text{SO}_3\text{H}$), sulfuric acid (H_2SO_4), *etc.* Unless otherwise indicated, an embodiment disclosed herein that involves an acid can generally be carried out with a mixture of two or more acids and such embodiments are contemplated herein.

[0023] As used herein, “base” refers to a molecule or ion capable of donating a hydroxide ion OH^- or accepting a proton (a Brønsted base or an Arrhenius base) in an aqueous environment or, alternatively, capable of forming a covalent bond by donating an electron pair (a Lewis base). A base may be capable of accepting one proton per base molecule or two or more protons per base molecule. Examples of bases include hydroxides of alkali metals (*e.g.*, Lithium hydroxide (LiOH), Sodium hydroxide (NaOH), Potassium hydroxide (KOH), Rubidium hydroxide (RbOH), Cesium hydroxide (CsOH)) and hydroxides of alkaline earth metals (*e.g.*, Magnesium hydroxide (Mg(OH)), Calcium hydroxide (Ca(OH)), Strontium hydroxide (Sr(OH)), Barium hydroxide (Ba(OH))), alanine ($\text{C}_3\text{H}_5\text{O}_2\text{NH}_2$), ammonia (water) (NH_3 (NH_4OH)), dimethylamine ($(\text{CH}_3)_2\text{NH}$), *etc.* Unless otherwise indicated, an embodiment disclosed herein that involves an acid can generally be carried out with a mixture of two or more acids and such embodiments are contemplated herein.

[0024] As used herein, an “alloy material” refers to a mixture of metals or a mixture of one or more metals with one or more other elements. An alloy is a mixture of either pure or fairly pure chemical elements that retains the characteristics of a metal. Alloys can be made by mixing two or more elements, at least one of which being a metal.

[0025] As used herein, the term “nanoscopic scale” or “nano-scale” generally refers to a structure with at least one dimension in the nanometer range (*e.g.*, about 1 nm to about 100 nm).

[0026] As used herein, “nanostructured” refers to a structure displaying or characterized by one or more nanoscopic structural features.

Detailed Description of the Invention

[0027] The invention provides novel acid-etching and base-etching methods for the fabrication of nanostructured catalysts. The nanostructured catalysts of the invention can be used for photocatalytic reduction of CO₂ and for efficiently adsorbing CO₂ from atmosphere.

[0028] In one aspect, the invention generally relates to an acid-treated or base-treated metal or alloy material exhibiting a nanostructured surface, produced respectively by acid-etching or base-etching of a metal or alloy material having an oxide coating.

[0029] In certain embodiments, the metal or alloy is selected from Co or Co alloy with one or more of Ti, Ru, Rh, Pd, Os, Ir, La, Ce, Fe, Cu and Ni in the form of nano-scale flake-shaped particulates.

[0030] In certain preferred embodiments, the metal or alloy is selected from Co or Co alloy.

[0031] In certain embodiments, the acid- or base-etching is performed with an acid or a base capable of removing the oxide coating of the metal or alloy material.

[0032] Exemplary acids include: hydrochloric acid (HCl), nitric acid (HNO₃), hydrobromic acid (HBr), sulfuric acid (H₂SO₄), hydroiodic acid (HI), chloric acid (HClO₃) and perchloric acid (HClO₄). In certain preferred embodiments, the acid is HCl.

[0033] Exemplary bases include: sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH), rubidium hydroxide (RbOH), cesium hydroxide (CsOH), calcium hydroxide (Ca(OH)₂) and barium hydroxide (Ba(OH)₂). In certain preferred embodiments, the base is NaOH.

[0034] In certain preferred embodiments, the etching time is from about 1 minute to about 20 minutes (*e.g.*, from about 1 to about 15 min., from about 1 to about 10 min., from about 3 to

about 20 min., from about 5 to about 15 min., from about 5 to about 10 min.) followed by rinsing with water and then exposure to air or oxygen for about 1 hour to about 20 hours (*e.g.*, from about 1 to about 15 hrs., from about 1 to about 10 hrs., from about 1 to about 5 hrs., from about 3 to about 20 hrs., from about 5 to about 15 hrs., from about 5 to about 10 hrs.).

[0035] The nano-scale flake-shaped particulates produced from acid- or base-etching may have any suitable dimensions and shapes. In certain embodiment, they have the following dimensions: about 50 nm to about 1,000 nm in length, about 100 nm in height, and about 10 nm to about 50 nm in thickness. In certain embodiment, they have following dimensions: about 100 nm to about 500 nm in length, about 50 nm to 200 nm in height, and about 10 nm to about 30 nm in thickness.

[0036] Any suitable acid or base may be employed. Preferably, in the case of acid-etching the aqueous acid solution has a pH ranging from about 0.5 to about 2.0 (*e.g.*, about 0.5, 0.7, 1.0, 1.2, 1.5, 1.8, or 2.0). In certain embodiments, the acid is an aqueous HCl solution with a concentration from about 2.5 % to about 5% (*e.g.*, about 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5%). Preferably, in the case of base-etching the aqueous acid solution has a pH ranging from about 12.0 to about 13.5 (*e.g.*, about 12.0, 12.5, 13.0, 13.5). In certain embodiments, the base is an aqueous NaOH solution with a concentration from about 2.5 % to about 5% (*e.g.*, about 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5%).

[0037] In another aspect, the invention generally relates to a method for forming a nanostructured surface on a metal or alloy material having an oxide coating. The method includes: etching a metal or alloy material with an acid or a base; and washing the acid- or base-etched metal or alloy material. In certain preferred embodiments, the method further includes: exposing the washed acid- or base-etched metal or alloy material to ambient air or concentrated oxygen.

[0038] In certain preferred embodiments, the method further includes exposing the washed acid-etched or base-etched metal or alloy material to ambient air or concentrated oxygen.

[0039] In certain preferred embodiments of the method, the metal or alloy is selected from Co or Co alloy.

[0040] In certain preferred embodiments of the method, the etching time is from about 1 min. to about 20 min. followed and exposure to air or oxygen is for about 1 hour to about 20 hours (*e.g.*, from about 1 to about 15 min., from about 1 to about 10 min., from about 3 to about 20 min., from about 5 to about 15 min., from about 5 to about 10 min.) followed by rinsing with

water and then exposure to air or oxygen for about 1 hour to about 20 hours (*e.g.*, from about 1 to about 15 hrs., from about 1 to about 10 hrs., from about 1 to about 5 hrs., from about 3 to about 20 hrs., from about 5 to about 15 hrs., from about 5 to about 10 hrs.).

[0041] In yet another aspect, the invention generally relates to a method for forming a hydrocarbon from CO₂ via photosynthesis. The method includes: providing an acid-or base-treated metal or alloy material exhibiting a nanostructured surface capable of catalyzing photosynthesis; contacting the acid-or base-treated metal or alloy material CO₂ to allow adsorption of CO₂ onto the surfaces of the acid-or base-treated metal or alloy material; mixing the CO₂-adsorbed, acid-or base-treated metal or alloy material with water forming a reaction mixture; and irradiating the reaction mixture with a light source to produce a hydrocarbon.

[0042] In certain preferred embodiments of the method, the metal or alloy is selected from Co or Co alloy.

[0043] In certain embodiments of the method, the hydrocarbon is a long-chain hydrocarbon with at least three carbon atoms sequentially bonded.

[0044] In certain embodiments of the method, the hydrocarbon is a C₃-C₁₅ hydrocarbon. In certain preferred embodiments, the hydrocarbon(s) produced from the photosynthesis are long-chain hydrocarbons with at least three carbon atoms sequentially bonded (*e.g.*, C₃-C₁₅, C₃-C₁₂, C₆-C₁₅, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₂, C₁₅, *etc.*).

[0045] In certain preferred embodiments of the method, the photosynthesis is conducted at ambient temperature.

[0046] In certain preferred embodiments, the photosynthesis exhibits a solar-to-chemical conversion efficiency from about 1% to about 10% (*e.g.*, from about 3% to about 10%, from about 3% to about 8%, from about 3% to about 5%, about 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, or 10%).

[0047] In certain preferred embodiments, the photosynthesis is conducted at ambient temperature.

[0048] In certain preferred embodiments, CO₂ has a pressure from about 0.1 atm to about 5.0 atm (*e.g.*, from about 0.5 atm to about 5.0, from about 1.0 atm to about 5.0, from about 0.5 atm to about 3.0, from about 0.5 atm to about 2.0, from about 1.0 atm to about 4.0).

[0049] In yet another aspect, the invention generally relates to a method for absorbing CO₂. The method include: providing an acid-treated or base-treated metal or alloy material exhibiting a

nanostructured surface capable of catalyzing photosynthesis; and contacting the acid-treated or base-treated metal or alloy material CO₂ to allow adsorption of CO₂ onto the surfaces of the acid-treated or base-treated metal or alloy material.

[0050] To explore a novel photocatalytic process for direct synthesis of hydrocarbon fuels from carbon dioxide, water, and sunlight at high-rate by using Co/CoO nanostructures, ¹³CO₂ and D₂O was employed to further investigate the reaction mechanism. A series of long-chain hydrocarbon compounds, propane to pentadecane (C₃-C₁₅), were formed and then analyzed by Gas chromatography–mass spectrometry (GC-MS).

[0051] The isotope incorporation data confirm that hydrocarbons are produced directly from the photocatalytic reduction of CO₂. The results also support a unique reaction mechanism involving tunneling dissociation. The average photocatalytic CO₂ to fuels conversion rate at optimal conditions is about 0.76 mg per gram catalyst per hour, which is equivalent to a 4% solar-to-chemical conversion efficiency. (Farquhar, *et al.* **1989** *Annu. Rev. Plant Physiol. Plant Mol. Biol.* 40:503 37; R. P. Bell, “The Tunnel Effect in Chemistry”. *Chapman and Hall: New York, 1980*. L. Melander, W. H. Saunders, “Reaction Rates of Isotopic Molecules”. *Wiley: New York, 1980*.)

[0052] The acid-etching method and the base-etching method disclosed herein for nanostructure formation exhibits a number of advantages: First, the photosynthesis can now be efficiently catalyzed by a catalyst prepared by low cost materials and procedures. The acid-etching method employs low concentration acids while the base-etching method employs low concentration bases. Second, both the acid-treatment or the base-treatment procedures are hundreds of times faster than the previously disclosed laser-based technique. Thirdly, the acid-etching and base-etching methods are applicable to treating catalysts of different surface morphologies.

[0053] Importantly, the novel nanostructured catalysts of the invention have superior stability with regard to N₂ and O₂ as well as unique CO₂-adsorbing properties, which facilitate photosynthetic reactions. As a result, the photosynthesis does not require pure or high-grade CO₂ source. Instead, the photosynthesis can take from directly capturing CO₂ from the atmosphere. The method disclosed herein can even be adapted to capturing CO₂ from flue gas, combustion exhaust gas produced at power plants.

[0054] Thus, the low-cost and long-lasting catalysts plus the lesser requirement on purity of

CO₂ allows industrial scale, low cost operation of carbon capture and renewal energy production.

Examples

[0055] Photocatalytic experiments were conducted using ¹³CO₂ /¹²CO₂ mixture and water as reactants in order to investigate the photocatalytic process. Isotope-labeled long-chain hydrocarbon compounds were produced, and the mechanisms for the photocatalytic reaction were studied systematically by analyzing carbon isotope incorporation rate and distribution in the resulting compounds using GC-MS.

[0056] A total organic carbon analyzer (TOC) was used to measure the production output of the photosynthesis process. An average photocatalytic CO₂ to fuels conversion rate of about 0.76 mg per gram catalyst per hour was achieved. This is equivalent to a 4% solar-to-chemical conversion efficiency at average, which is compatible to natural photosynthesis, with the instantaneous efficiency higher than 4%.

[0057] Co(or Fe/Cu/Ni, or their alloy) particles or plates are mixed with 3.5 % aqueous HCl solution (any other acid solution can remove the oxide layer on the sample surfaces) for a few minutes, and then cleaned with distilled water. After 3 ~ 10 hours exposure of those metal samples to the air (or oxygen gas), nano-flakes structures were formed on the surface of the samples. Those nanostructures do not change further.

[0058] With the nanostructured metal/metal oxide catalysts, water and CO₂ can be converted to hydrocarbon fuels in glass pressure vessel by the sunlight. After being exposed to atmosphere, the nanostructured catalyst adsorbs CO₂ molecules and form strong bonds between those molecules and the catalyst's surfaces. Therefore, instead of using other CO₂ source, the nanostructured samples with the adsorbed CO₂ can be directly used in the photosynthesis reaction with water. After reaction, the catalyst retains its catalytic functionality and can continue to adsorb CO₂ and perform photosynthesis.

Catalyst Preparation

[0059] Cobalt micro-particles (Goodfellow, purity: 99.9%, diameter: 50 um-100 um) were used for catalyst preparation. A scanning electron microscope (SEM) was used to characterize Co particle surfaces. As shown in **FIG. 1a**, Co particles (5~30 g) were mixed with 3.5% aqueous HCl solution for 10 min, and then, after washing with distilled water, the treated Co particles (as

shown in **FIG. 1b**) were dried in a vacuum oven. The treated Co particles were loaded into the reactor with water and CO₂. After 1~3 hours of light irradiation, self-assembled CoO/Co nano-flakes with nanostructures were obtained, as shown in **FIG.1c**. The dimensions of the random nano-flakes were about 100~500 nm in length, about 100 nm in height, and about 10~30 nm in thickness. The acid-etching process effectively removed the original oxide layer on the Co particles with the concurrent formation of nanostructured surfaces on the CoO/Co particles.

Photocatalytic Experiments

[0060] Nanostructured Co microparticles (2 g) and distilled water (350 mg) were placed on the bottom of a 15 mL glass pressure vessel (ACE Glass). The reaction chamber was vacuumed and then filled with research grade CO₂ gas to a pressure of 2 atm. Maintaining a three-phase (gas/liquid/solid) interface was found to be essential for the photocatalytic process; therefore, it was necessary to maintain this ratio of Co catalysts, water and CO₂ amount for all experiments. In the laboratory, a solar simulator (Honle SOL-500) was used to irradiate the samples at 120 mW/cm², and outdoor natural sunlight was also used to conduct photocatalytic experiments. Glass fibers were warped around the bottom part of the reactor as thermal insulator to keep the reactor around 60 °C, and the surface of Co catalysts can reach a temperature of 120 °C.

[0061] The irradiation time was generally 20 hours, and various lengths of 20~100 hours were also used for studies on the reaction mechanism. Isotopic enriched carbon dioxide gas (99:1, ¹³CO₂: ¹²CO₂, Aldrich) was used to provide labeled atoms. Similar experimental procedures were employed using unlabeled CO₂ and D₂O (99.9% pure Aldrich). After irradiation, the reaction products were either sampled directly from the gas stream to a TOC to measure the total production amount, or extracted by dichloromethane (CH₂Cl₂) and then analyzed by a GC-MS (Bruker Scion SQ, with ZB-624 column) to identify hydrocarbon compounds and its isotope incorporations.

Characterization of hydrocarbon productions by GC and MS

[0062] **FIG.2** is an exemplary GC chromatography, which shows that a series of long-chain hydrocarbon compounds, propane to pentadecane (C₃-C₁₅) were produced from the photocatalytic reaction. Methanol, ethanol, and branched alkanes were also identified but of relative lesser amounts comparing to the straight-chain alkanes.

[0063] **FIG. 3** shows an exemplary MS spectrum of comparing ^{12}C hydrocarbons and ^{13}C incorporated decane formed by this reaction. The ^{13}C isotope incorporation data confirms that hydrocarbons were produced directly from the photocatalytic reduction of CO_2 .

[0064] **FIG. 4** shows an exemplary MS spectrum of comparing heptane and D-heptane formed by this reaction. The hydrogen isotope incorporation data confirms that hydrocarbons were produced directly from the photocatalytic reduction of water.

Characterization of hydrocarbon productions by FTIR

[0065] Beside GC/MS, a Fourier Transform Infrared spectroscopy (FTIR) was used to characterize the production of the photocatalytic reaction. As shows in **FIG. 5**, the three absorptions peaks around 2900 wavenumbers are belong to C-H bond, and the two absorptions peaks in the range of 1200 to 1700 wavenumbers are belong to C-C bond. The large peak around 3300 wavenumbers is water, which come from the system and environment. This data indicated that saturated hydrocarbons (alkanes) are the main productions, which is consisted with the GC/MS tests.

Production Yield

[0066] **FIG. 6** shows the material balance across the photocatalytic converter. For this particular experiment the gas analysis showed that out of 103.3 mg of CO_2 input to the system, 97 mg CO_2 remained in the gas phase of the products. That is 6.3 mg CO_2 was consumed during the process, which is equivalent to 2.348 mmols of carbon. The GC-TCD analysis on the gas phase showed presence of 4.8 mL O_2 gas and 0.84 ml H_2 gas. The volume for the GC was 5 mL/test. The yield of hydrocarbons in this experiment was 2 mg.

[0067] **Table 1** shows the carbon and oxygen balance across the system for this particular experiment explained above. From the gas analysis, it was calculated that 6.3 mg (0.143 mmol carbon) of CO_2 was consumed. Assuming the average chemical formula of hydrocarbon as CH_2 , the number of carbon moles in the hydrocarbon product was calculated as 0.143 mmols. This resulted in carbon balance of 99.8% for this experiment. For oxygen balance, the theoretical oxygen produced from reaction 1 and 2 were calculated based on the amount hydrocarbon and hydrogen produced. Stoichiometric calculation showed that the amount of oxygen evolved should be 0.234 mmol (0.215 mmol from reaction 2 and 0.019 mmol from reaction 1). Based on

gas and liquid product analysis, 5 mL (0.223 mmol) of oxygen was obtained. This resulted in theoretical oxygen balance of 95.17% for the system.

[0068] Based on these calculations, the production yield was > 90%.

Table 1. Carbon and oxygen balance across the photocatalytic converter

Carbon Balance	mmol	Oxygen Balance	mmol
Carbon consumed	0.143	Oxygen in products (gas/liquid)	0.223
Carbon in hydrocarbons	0.143	Theoretical oxygen evolved from water dissociation (reaction 1)	0.019
		Theoretical oxygen evolved from hydrocarbon formation (reaction 2)	0.215
Carbon balance closure	99.8%	Theoretical oxygen balance closure	95.71%

Solar-to-chemical conversion efficiency

[0069] Based on TOC measurements, the generation rate of all hydrocarbon products is about 0.76 mg per gram of catalyst per hour. The solar-to-chemical conversion efficiency is defined as follows:

$$E = \frac{\text{Energy stored in products}}{\text{Irradiation energy}} \quad (1)$$

[0070] The energy stored in products was calculated by the average combustion of long-chain hydrocarbon (45 J/mg) times the amount of products. The irradiation energy was calculated by the solar intensity times the time and the irradiation area. In the glass pressure vessel, 2 g of catalyst paving on the bottom has about 4 cm² of irradiation area. Calculation revealed that a 4% solar-to-chemical conversion efficiency was achieved.

Scanning Electron Microscopy (SEM) image of Co treated with base solution

[0071] **FIG. 7** shows the SEM images of the surfaces of a cobalt microparticle, treated with 3.5 % aqueous NaOH solution for 10 min, and then, after washing with distilled water.

Nanostructures can be clearly observed, and they have similar dimensions as those treated with acid. These base solution treated Co were used to conducted photocatalytic reaction, and similar hydrocarbon products were formed. There is no difference can be observed comparing to those treated with acid.

Production Scaleup

[0072] Original lab scale photocatalytic reaction with nano-Co was done in a tubing reactor with 2 cm² reaction area. Currently, a larger reactor with 80 cm² reaction area was built, and as **FIG. 8** shows, similar long-chain hydrocarbon products were obtained. The efficiency achieved in this larger reactor is comparable to the original reactor. This indicates that this photocatalytic reaction disclosed herein can be effectively scaled up.

[0073] Applicant's disclosure is described herein in preferred embodiments with reference to the Figures, in which like numbers represent the same or similar elements. Reference throughout this specification to "one embodiment," "an embodiment," or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment," "in an embodiment," and similar language throughout this specification may, but do not necessarily, all refer to the same embodiment.

[0074] The described features, structures, or characteristics of Applicant's disclosure may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are recited to provide a thorough understanding of embodiments of the invention. One skilled in the relevant art will recognize, however, that Applicant's composition and/or method may be practiced without one or more of the specific details, or with other methods, components, materials, and so forth. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the disclosure.

[0075] In this specification and the appended claims, the singular forms "a," "an," and "the" include plural reference, unless the context clearly dictates otherwise.

[0076] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and

materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described. Methods recited herein may be carried out in any order that is logically possible, in addition to a particular order disclosed.

Incorporation by Reference

[0077] References and citations to other documents, such as patents, patent applications, patent publications, journals, books, papers, web contents, have been made in this disclosure. All such documents are hereby incorporated herein by reference in their entirety for all purposes. Any material, or portion thereof, that is said to be incorporated by reference herein, but which conflicts with existing definitions, statements, or other disclosure material explicitly set forth herein is only incorporated to the extent that no conflict arises between that incorporated material and the present disclosure material. In the event of a conflict, the conflict is to be resolved in favor of the present disclosure as the preferred disclosure.

Equivalents

[0078] The representative examples are intended to help illustrate the invention, and are not intended to, nor should they be construed to, limit the scope of the invention. Indeed, various modifications of the invention and many further embodiments thereof, in addition to those shown and described herein, will become apparent to those skilled in the art from the full contents of this document, including the examples and the references to the scientific and patent literature included herein. The examples contain important additional information, exemplification and guidance that can be adapted to the practice of this invention in its various embodiments and equivalents thereof.

What is claimed is:

CLAIMS

1. An acid-treated or base-treated metal or alloy material exhibiting a nanostructured surface, produced by acid-etching or base-etching, respectively, of a metal or alloy material having an oxide coating.
2. The acid-treated or base-treated metal or alloy material of Claim 1, wherein the metal or alloy is selected from Co or Co alloy in the form of nano-scale flake-shaped particulates.
3. The acid-treated or base-treated metal or alloy material of Claim 2, wherein the metal or alloy comprises one or more of Ti, Ru, Rh, Pd, Os, Ir, La, and Ce, Fe, Cu and Ni.
4. The acid-treated or base-treated metal or alloy material of any of Claim 1-3, wherein the acid-etching is performed with an acid capable of removing the oxide coating of the metal or alloy material.
5. The acid-treated or base-treated metal or alloy material of any of Claim 1-3, wherein the base-etching is performed with a base capable of removing the oxide coating of the metal or alloy material.
6. The acid-treated or base-treated metal or alloy material of Claim 4 or 5, wherein the etching time is from about 1 minute to about 20 minutes followed by rinsing with water and then exposure to air or oxygen for about 1 hour to about 20 hours.
7. The acid-treated or base-treated metal or alloy material of Claim 6, wherein the etching time is from about 3 minutes to about 10 minutes followed by rinsing with water and then exposure to air or oxygen for about 3 hours to about 10 hours.
8. The acid-treated or base-treated metal or alloy material of any of Claims 1-7, wherein nano-scale flake-shaped particulates have the following dimensions: about 50 nm to about 1,000 nm in length, about 100 nm in height, and about 10 nm to about 50 nm in thickness.
9. The acid-treated or base-treated metal or alloy material of any of Claims 1-4 and 6-8, wherein the acid has a pH ranging from about 0.5 to about 2.
10. The acid-treated or base-treated metal or alloy material of any of Claims 1-3 and 5-8, wherein the base has a pH ranging from about 12.0 to about 13.5.
11. The acid-treated or base-treated metal or alloy material of any of Claims 1-4 and 6-8,

- wherein the acid is an aqueous HCl solution with a concentration from about 2.5 % to about 5%.
12. The acid-treated or base-treated metal or alloy material of any of Claims 1-3 and 5-8, wherein the base is an aqueous NaOH solution with a concentration from about 2.5 % to about 5%.
13. A method for forming a nanostructured surface on a metal or alloy material having an oxide coating, comprising
- etching a metal or alloy material with an acid or a base; and
 - washing the acid-etched or base-etched metal or alloy material.
14. The method of Claim 13, further comprising
- exposing the washed acid-etched or base-etched metal or alloy material to ambient air or concentrated oxygen.
15. The method of Claim 13 or 14, wherein the metal or alloy is selected from Co or Co alloy.
16. The method of any of Claims 13-15, wherein the etching time is from about 1 minute to about 20 minutes followed and exposure to air or oxygen is for about 1 hour to about 20 hours.
17. A method for forming a hydrocarbon from CO₂ via photosynthesis, comprising:
- providing an acid-treated or base-treated metal or alloy material exhibiting a nanostructured surface capable of catalyzing photosynthesis;
 - contacting the acid-treated or base-treated metal or alloy material CO₂ to allow adsorption of CO₂ onto the surfaces of the acid-treated or base-treated metal or alloy material;
 - mixing the CO₂-adsorbed, acid-treated or base-treated metal or alloy material with water forming a reaction mixture; and
 - irradiating the reaction mixture with a light source to produce a hydrocarbon.
18. The method of Claim 17, wherein the metal or alloy is selected from Co or Co alloy.
19. The method of Claim 17 or 18, wherein the hydrocarbon is a C₃-C₁₅ hydrocarbon.
20. The method of any of Claims 17-19, wherein the photosynthesis is conducted at ambient temperature and CO₂ has a pressure from about 0.1 atm to about 5.0 atm.

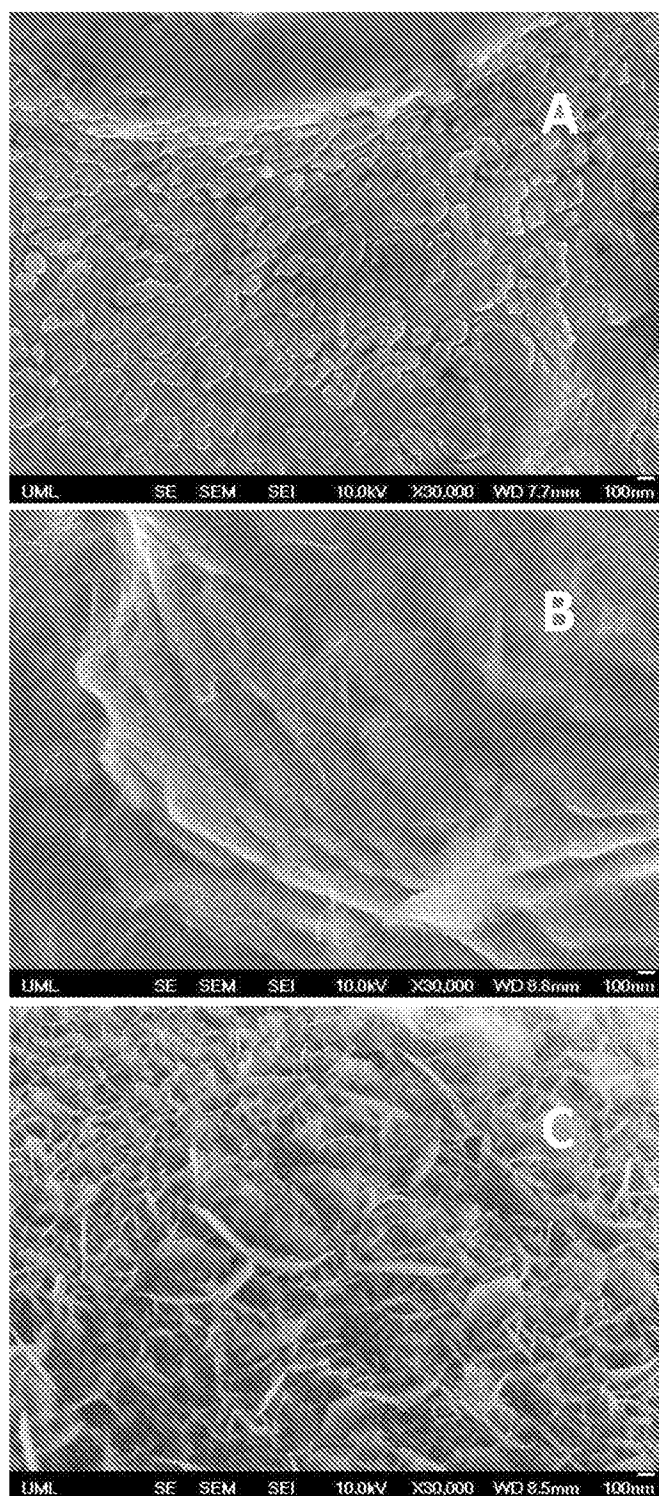


FIG. 1. Scanning electron microscope (SEM) images of the surfaces of a cobalt microparticle. (A) Co particles before treatment; (B) Co particles treated with 3.5 % aqueous HCl solution for 10 min. and washed with distilled water; (C) Nano-flake structures grew on surfaces of Co microparticles after 10 ~ 20 hours to air (oxygen).

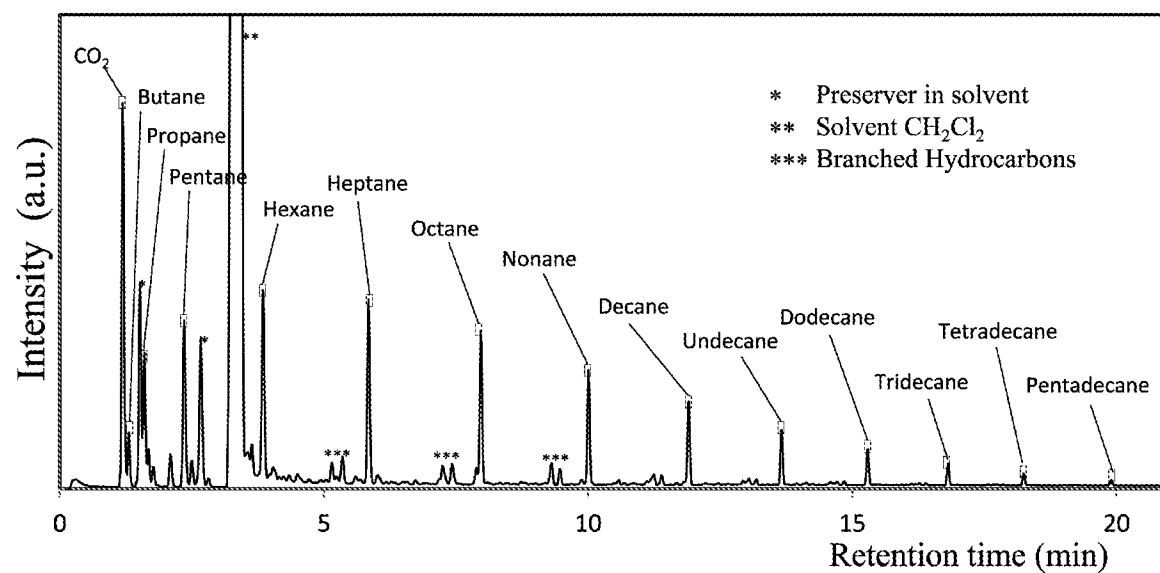


FIG. 2. GC chromatography of hydrocarbon products.

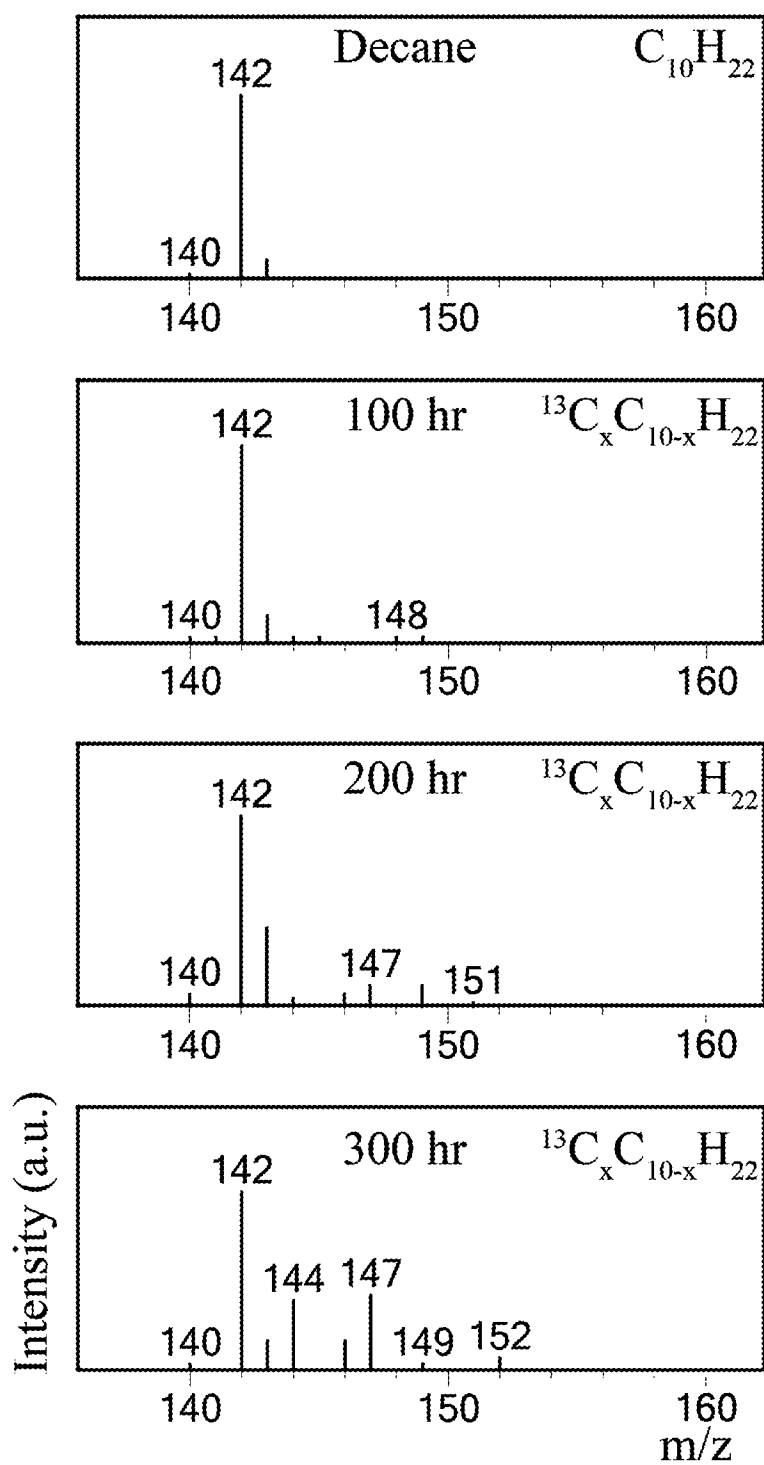


FIG. 3. MS spectrum of ^{12}C hydrocarbons and ^{13}C incorporated decane formed from photosynthesis. The ^{13}C isotope incorporation data confirms that hydrocarbons were produced directly from photocatalytic reduction of CO_2 .

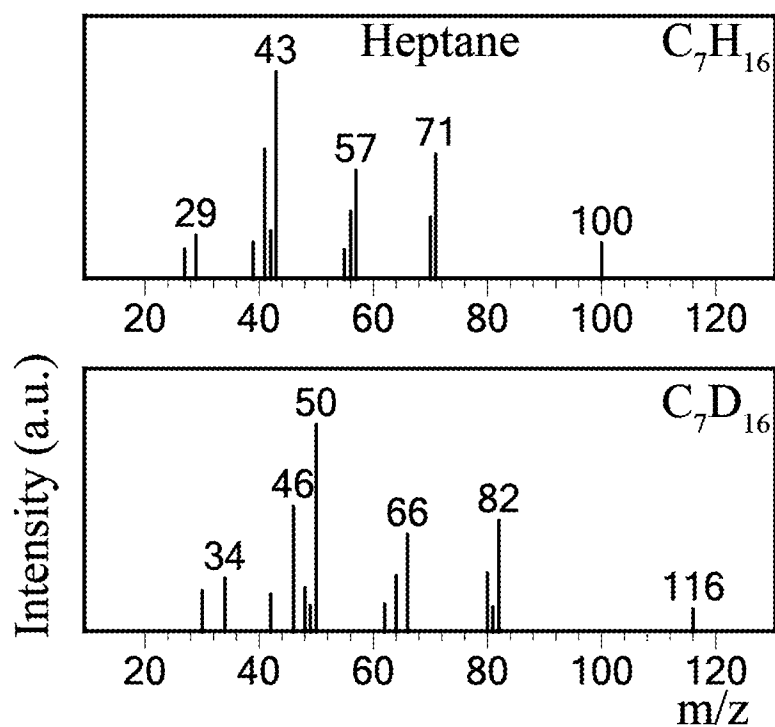


FIG. 4. MS spectrum of Heptane and D-Heptane formed by photosynthesis. The hydrogen isotope incorporation data confirms that hydrocarbons were produced directly from photocatalytic reduction of water.

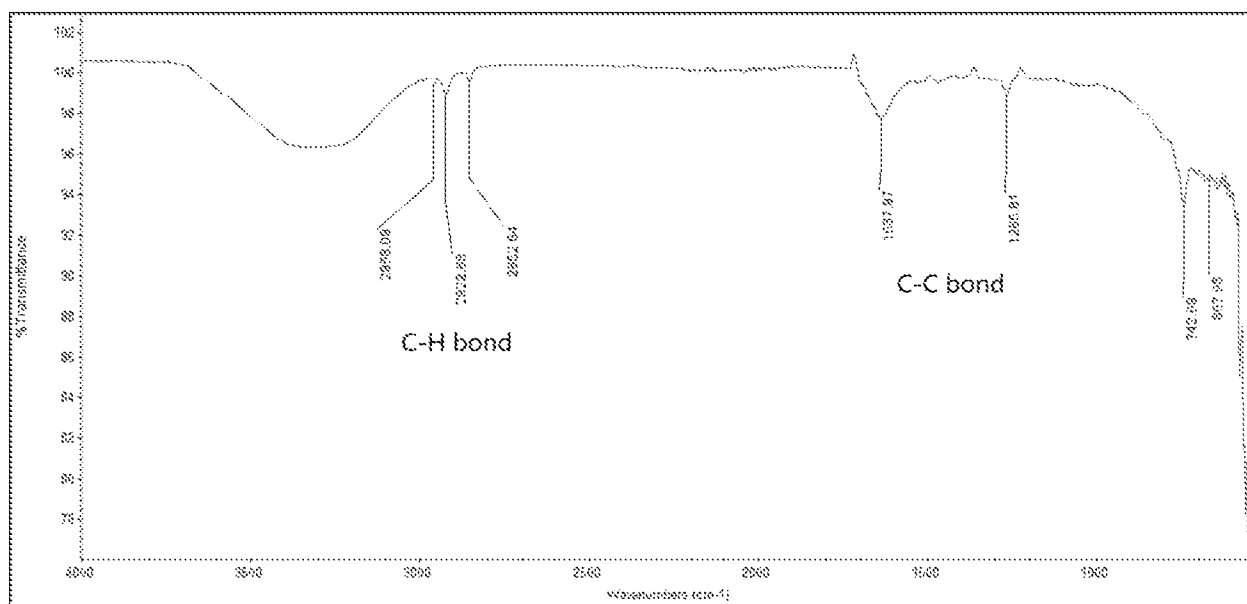


FIG. 5. FTIR data of hydrocarbon products by this photocatalytic reaction

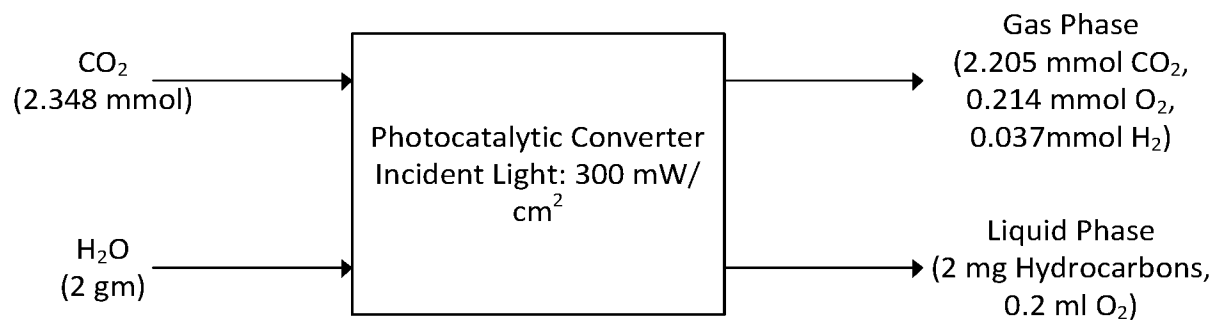


FIG. 6. Block flow diagram showing material balance for photocatalytic conversion of CO₂ and H₂O to hydrocarbons at 0.8 mJ/pulse energy intensity using 2 g of nanostructured Co microparticles of the invention under 2 atm CO₂ pressure and 3 hours of reaction time.

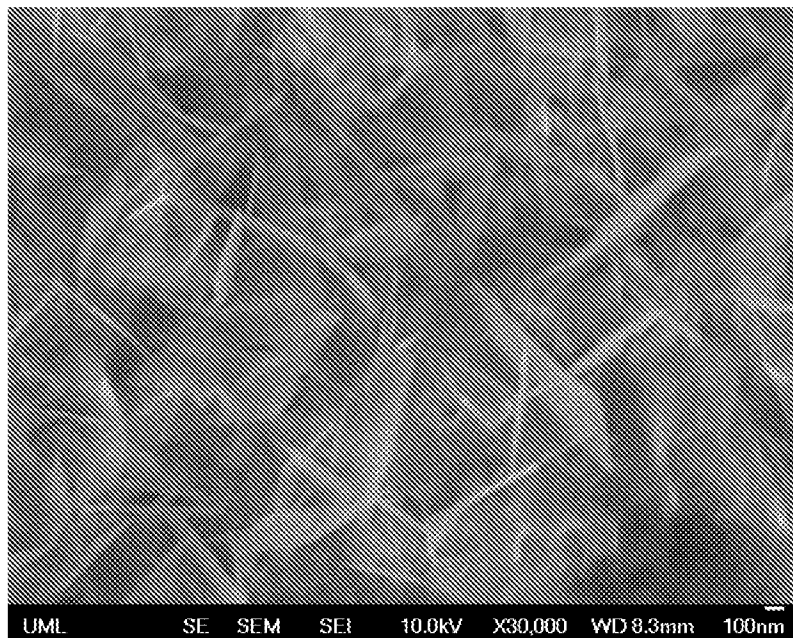


FIG. 7. SEM images of the surfaces of a cobalt microparticle, treated with 3.5 % aqueous NaOH solution for 10 min, and then, after washing with distilled water.

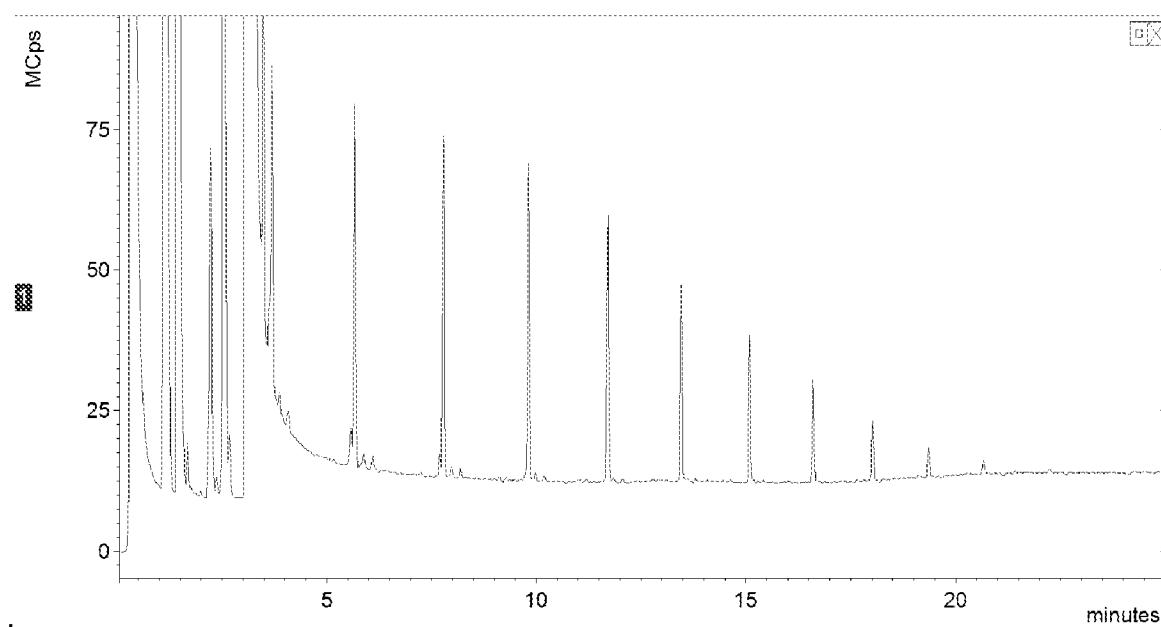


FIG. 8. GC chromatogram of hydrocarbons produced from a larger reactor.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/049164

A. CLASSIFICATION OF SUBJECT MATTER (see extra sheet) 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) B01J 20/00-20/02, 23/00, 23/70, 23/74, 23/74-23/76, 23/83, 23/89, 37/00, 37/06, 38/00, 38/04, 38/12, 38/48, 38/60, 38/64, C07C 1/02, B01D 53/02, 53/62, B82B 3/00, B82Y 30/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PatSearch (RUPTO internal), DWPI, Espacenet, RUPAT, SIPO, Patentscope		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RU 2434678 C1 (UCHREZHDENIE ROSSIYSKOY AKADEMII NAUK INSTITUT STRUKTURNY MAKROKINETIKI I PROBLEM MATERIALOVEDENIYA RAN et al.) 27.11.2011, abstract, p. 5, example 1, p. 6, lines 7-9, claim 1	1-5, 8-10, 13, 15
A		6, 7, 14, 16-20
X	RU 2469744 C1 (ABDULLAEV FIKRET MAVLUDINOVICH) 20.12.2012, abstract, p. 5, lines 5-15	1, 4
Y		11, 12
A	RU 2533710 C1 (FEDERALNOE GOSUDARSTVENNOE BYUDZHETNOE UCHREZHDENIE NAUKI INSTITUT KATALIZA IM. G.K. BORESKOVA SIBIRSKOGO OTDELENIYA ROSSIYSKOY AKADEMII NAUK) 20.11.2014, abstract	1-20
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
*	Special categories of cited documents:	“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 “&” document member of the same patent family
“A”	document defining the general state of the art which is not considered to be of particular relevance	
“E”	earlier document 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	
Date of the actual completion of the international search 18 November 2016 (18.11.2016)		Date of mailing of the international search report 08 December 2016 (08.12.2016)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer V. Kochetkova Telephone No. (499)240-25-91

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/049164

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JPS 6458346 A (TANAKA PRECIOUS METAL IND) 06.03.1989, abstract	11
Y	US 7592292 B2 (JAPAN SCIENCE TECHNOLOGY AGENC et al.) 22.09.2009, claim 1	12

INTERNATIONAL SEARCH REPORT

Classification of subject matter

International application No.

PCT/US 2016/049164

B01J 23/75 (2006.01)***B01J 23/83 (2006.01)******B01J 23/89 (2006.01)******B01J 37/00 (2006.01)******B01J 20/02 (2006.01)******B01D 53/02 (2006.01)******B01D 53/62 (2006.01)******C07C 1/02 (2006.01)******B82B 3/00 (2006.01)******B82Y 30/00 (2011.01)***