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SUNDARA et al.(10) **Pub. No.: US 2015/0345034 A1**(43) **Pub. Date: Dec. 3, 2015**(54) **SYSTEMS, METHODS, AND MATERIALS
FOR PRODUCING HYDROCARBONS FROM
CARBON DIOXIDE**(71) Applicant: **INDIAN INSTITUTE OF
TECHNOLOGY MADRAS**, Chennai
(IN)(72) Inventors: **Ramaprabhu SUNDARA**, Chennai
(IN); **Tamilarasan PALANISAMY**,
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C25B 11/0405 (2013.01); **C25B 11/0489**
(2013.01); **C25B 11/12** (2013.01)(57) **ABSTRACT**

Disclosed herein are systems and methods to effectively convert carbon dioxide to hydrocarbons by electrochemical and/or photoelectrochemical methods. In one embodiment, a photoelectro-chemical cell may include an anode, a cathode comprising a carbon material, wherein the carbon material is surface functionalized with at least one poly(ionic) liquid, and wherein at least one metallic nanoparticle is disposed on the functionalized carbon material surface, and an energy source configured to irradiate the anode.

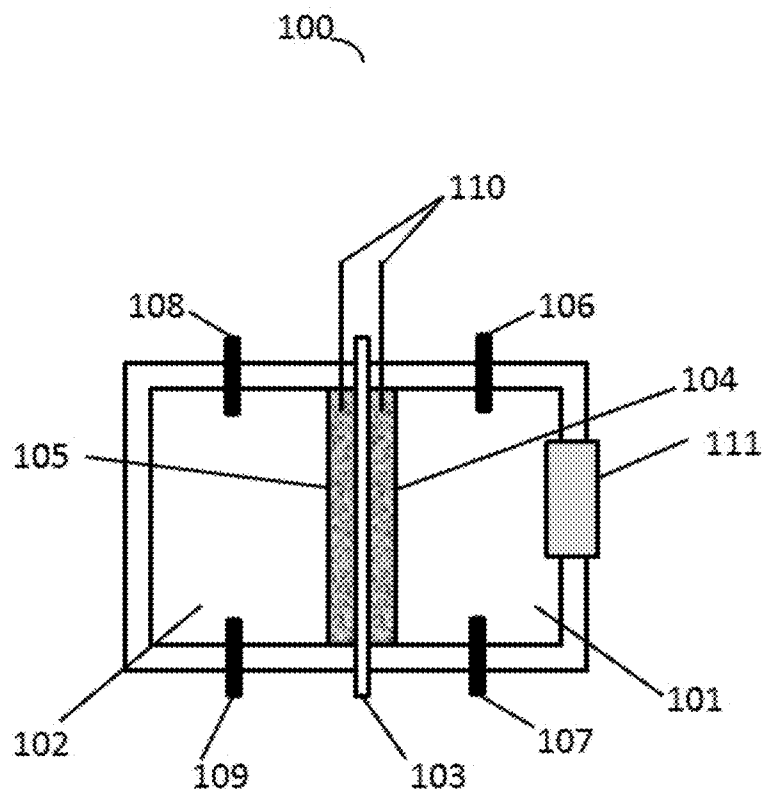


FIG. 1

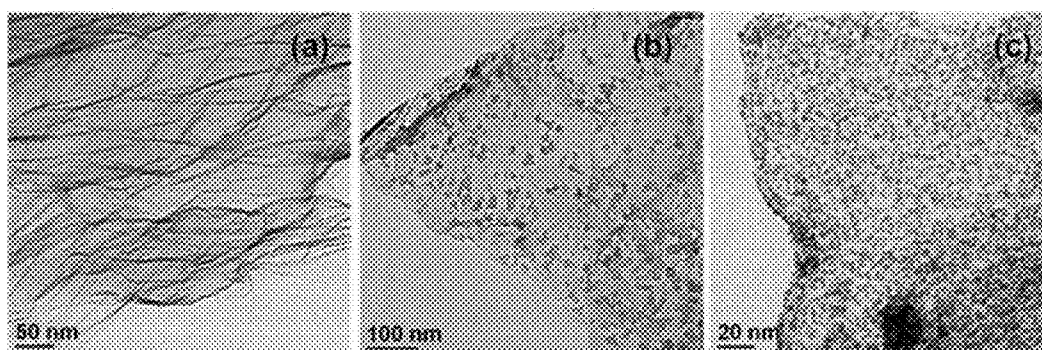


FIG. 2

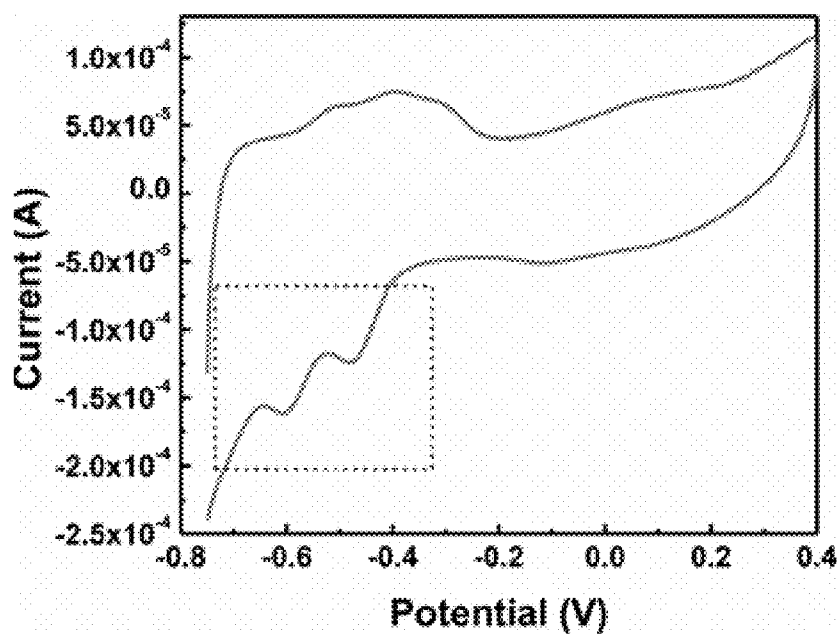


FIG. 3

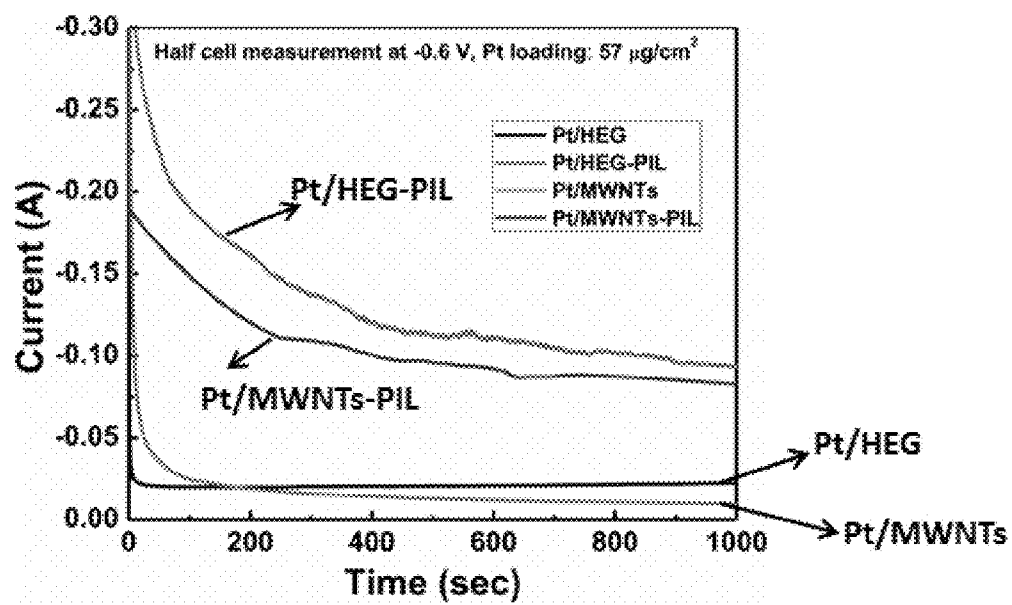


FIG. 4

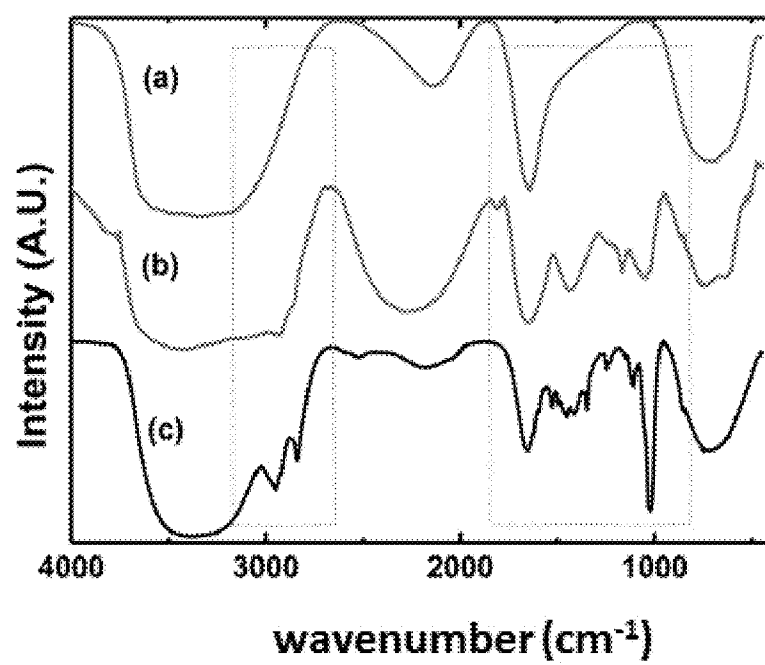


FIG. 5

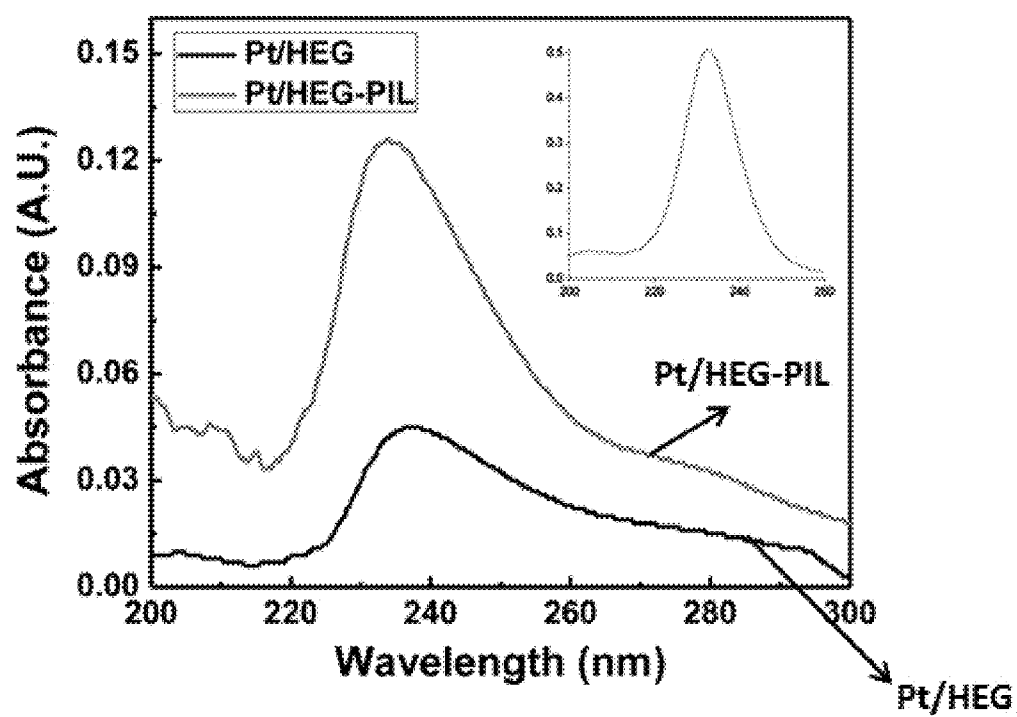


FIG. 6

SYSTEMS, METHODS, AND MATERIALS FOR PRODUCING HYDROCARBONS FROM CARBON DIOXIDE

RELATED APPLICATION

[0001] This application claims priority benefit under Title 35 § 119(a) of Indian Patent Application No. 1425/CHE/2014, filed Mar. 18, 2014, entitled, "SYSTEMS, METHODS, AND MATERIALS FOR PRODUCING HYDROCARBONS FROM CARBON DIOXIDE," the contents of which are herein incorporated by reference.

BACKGROUND

[0002] Photoelectrochemical conversion of carbon dioxide (CO_2) into hydrocarbons is one way of reducing the emission of carbon dioxide into the environment. This not only helps to reduce carbon dioxide levels, but also converts renewable energy, such as sunlight, into a chemical form that can be stored for later use. The electrochemical techniques and systems used in carbon dioxide reduction have many limitations, including the stability, efficiency and cost of materials used in such systems, the ability to control the processes effectively, and the rate at which carbon dioxide is converted. Thus, it is desirable to develop economical and efficient methods and systems to convert carbon dioxide to hydrocarbons.

SUMMARY

[0003] Disclosed herein are systems and methods to convert carbon dioxide to one or more hydrocarbons by electrochemical and/or photoelectrochemical methods. In one embodiment, a photoelectrochemical cell may include an anode, a cathode comprising a carbon material, wherein the carbon material is surface functionalized with at least one poly(ionic) liquid, and wherein at least one metallic nanoparticle is disposed on the functionalized carbon material surface, and an energy source configured to irradiate the anode.

[0004] In another embodiment, a method of reducing carbon dioxide to one or more hydrocarbons includes introducing water to a first compartment of an electrochemical cell, wherein the first compartment includes an anode, introducing carbon dioxide dissolved in water to a second compartment of the electrochemical cell, wherein the second compartment includes a cathode, wherein the cathode comprises a carbon material that is surface functionalized with at least one poly(ionic) liquid and at least one metallic nanoparticle disposed on the functionalized carbon material surface, and applying an electrical potential between the anode and the cathode sufficient to reduce carbon dioxide to one or more hydrocarbons.

[0005] In an additional embodiment, a catalyst comprises an exfoliated graphene, wherein the exfoliated graphene is surface functionalized with at least one poly(ionic) liquid, and wherein at least one metallic nanoparticle is disposed on the functionalized graphene surface.

[0006] In a further embodiment, a method of preparing a catalyst includes oxidizing graphite to form graphite oxide, exfoliating graphite oxide to form one or more graphene nanosheets, contacting the one or more graphene nanosheets with a poly(ionic) liquid to form one or more coated graphene nanosheets, and contacting a metal compound with the one or more coated graphene nanosheets.

BRIEF DESCRIPTION OF THE FIGURES

[0007] FIG. 1 depicts a schematic diagram of a photoelectrochemical cell according to an embodiment.

[0008] FIG. 2 shows high resolution transmission electron microscopy (HRTEM) images of (a) HEG, (b) HEG-PIL, and (c) Pt/HEG-PIL according to an embodiment.

[0009] FIG. 3 shows a cyclic voltammogram of carbon dioxide reduction on Pt/HEG-PIL electrode. Electrolyte used was carbon dioxide saturated 0.5 M KHCO_3 , and reference electrode was saturated Ag/AgCl electrode, according to an embodiment.

[0010] FIG. 4 shows transient current generated by Pt/MWNTs (Pt loaded multi-walled nanotubes), Pt/HEG, Pt/MWNTs-PIL and Pt/HEG-PIL catalysts for carbon dioxide electrocatalytic conversion at -0.6 V in carbon dioxide saturated 0.5 M KHCO_3 aqueous solution, according to an embodiment.

[0011] FIG. 5 shows an FTIR spectrum of (a) deionized water, (b) cathode reservoir solution, and (c) commercial methanol, according to an embodiment.

[0012] FIG. 6 shows a UV-Vis spectrum of cathode reservoir solution with Pt/HEG and Pt/HEG-PIL cathode electrocatalyst, according to an embodiment.

DETAILED DESCRIPTION

[0013] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

[0014] In the detailed description below, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0015] Disclosed herein are methods and systems for electrochemical or photoelectro-chemical reduction of carbon dioxide to one or more hydrocarbons. FIG. 1 illustrates a system in accordance with some embodiments of the disclosure for catalyzed electrochemical and/or photoelectrochemical conversion of carbon dioxide to hydrocarbons. The reduction of carbon dioxide may suitably be achieved in an efficient manner in a divided electrochemical or photoelectrochemical cell 100 defining a first compartment 101 that includes an anode 104, and defining a second compartment 102 which includes a cathode 105. The cathode electrode comprises a metal nanoparticle catalyst disposed on a carbon support. The compartments are separated by an electrolyte 103 such as a proton exchange membrane (PEM) or any other ion-conducting bridge. The first compartment and the second compartment may also contain outlet valves 106 and 108, and inlet valves 107 and 109. Both the compartments may contain water. Further, carbon dioxide may continuously be introduced into the second compartment, to form carbon dioxide saturated water. The anode 104 and cathode 105 are further

connected via electrically conductive conduits **110**, in the case of a photoelectrochemical cell, to a current collector (not shown) or in the case of an electrochemical cell, to an external power source (not shown). Further, the cell **100** may optionally have a window **111** to allow a light source to illuminate the anode **104**. The hydrocarbons that may be produced from the systems and methods described herein include, but not limited to, methanol, methane, isopropanol, formic acid, formaldehyde, glyoxal, ethanol, butanol, or any combination thereof.

[0016] Carbon dioxide may be obtained from any source, for example, an exhaust stream from fossil fuel burning power plants, from geothermal or natural gas wells, or the atmosphere itself. Most suitably, the carbon dioxide may be obtained from concentrated point sources of generation prior to being released into the atmosphere. For example, high concentration carbon dioxide sources may be obtained from natural gas, flue gases of fossil fuel burning power plants, exhausts from cement factories, from fermenters used for industrial fermentation of ethanol, and from the manufacture of fertilizers and refined oil products, and other sources.

[0017] In some embodiments, the anode **104** in the electrochemical and/or the photoelectrochemical cell described herein may be a metal or a semiconductor, or any combination of metal and semiconductors. Non-limiting examples of the metal that may be used includes Au, Ag, Zn, Ga, Hg, In, Cd, Ti, Pd, or any combination thereof. Further, examples of semiconductors that may be used are TiO₂, ZnO, SnO₂, Nb₂O₅, NiO, CdSe, CdTe, InP, GaAs, CuInSe₂, Fe₂O₃, SiC, ZnSe, or any combination thereof. In some embodiments, the semiconductor materials described herein may be doped with metals, such as Ag, Au, Ru, Pt, Pd, Cd, In, Pb, Sn, or Ga. In some embodiments, the anode may be nanoparticles that are disposed on a carbon support. For example, the anode may be TiO₂ nanoparticles coated on a carbon fabric.

[0018] In some embodiments, the cathode **105** present in the second compartment **102** of the electrochemical and/or the photoelectrochemical cell may be a carbon material, and the carbon material may be surface functionalized with at least one poly(ionic) liquid. Further, at least one metallic nanoparticle may be disposed on the functionalized carbon material surface. For example, the carbon material may be a carbon nanotube, graphene, graphene oxide, or any combination thereof. In some embodiments, a graphene cathode may be a plurality of exfoliated graphene nanosheets. In some embodiments, the graphene nanosheet may have a thickness of about 0.2 nanometer to about 100 nanometers, about 0.2 nanometer to about 50 nanometers, about 0.2 nanometer to about 10 nanometers, or about 0.2 nanometer to about 1 nanometer. Specific examples include about 0.2 nanometer, about 1 nanometer, about 5 nanometers, about 10 nanometers, about 2 nanometers, about 50 nanometers, about 100 nanometers, and ranges between any two of these values.

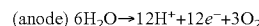
[0019] In some embodiments, the poly(ionic) liquid may be 3-ethyl-1-vinylimidazolium tetrafluoroborate, 1-methyl-3-vinylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-vinyl-3-methylimidazolium tetrafluoroborate, 1-isobutenyl-3-methylimidazolium tetrafluoroborate, 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-allyl-3-methylimidazolium bromide, 1,3-bis(cyanomethyl)imidazolium bis(trifluoromethylsulfonyl)imide, or any combination thereof. Further, any ionic liquid with back-bones, including imidazolium, ammonium, phosphonium and sulfonium, and with polymer-

izable side chains, such as vinyl, or allyl can be used. Further, the metallic nanoparticle that may be disposed on the poly(ionic) liquid functionalized carbon material surface may be Au, Ag, Pd, Co, Cu, Pt, Ni, Fe, Mn, Cr, V, Ti, Sc, Ce, or any combination thereof.

[0020] In some embodiments, an electrolyte **103** may be in contact with the first compartment **101** and the second compartment **102**, and the electrolyte may allow movement of protons from the first compartment **101** to the second compartment **102**. For example, the electrolyte **103** may be a proton exchange membrane (PEM), a salt bridge, a proton exchange polymer, a proton exchange ceramic, or any combination thereof. For example, the proton exchange membrane may be a sulfonated tetrafluoroethylene copolymer. In some embodiments, the first and the second compartments may be separated by a porous glass frit, microporous separator, ion exchange membrane, ion conducting bridge, and the like.

[0021] Also disclosed herein are methods of reducing carbon dioxide to one or more hydrocarbons. In some embodiments, the method involves introducing water to a first compartment of an electrochemical and/or a photoelectrochemical cell described herein, wherein the first compartment includes an anode. The method also includes introducing carbon dioxide dissolved in water to a second compartment of the electrochemical and/or a photoelectrochemical cell, wherein the second compartment includes a cathode. The carbon dioxide may be dissolved in a water stream prior to being introduced to the second compartment or carbon dioxide may be introduced into water in the second compartment to dissolve therein. In some embodiments, a combination may be used where additional carbon dioxide is introduced into water already containing dissolved carbon dioxide. Since carbon dioxide dissolves more freely in cold water, the water and/or the second compartment may be cooled or refrigerated. The cathode may comprise a carbon material that is surface functionalized with at least one poly(ionic liquid) and at least one metallic nanoparticle disposed on the functionalized carbon material surface.

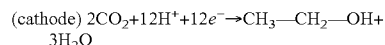
[0022] In some embodiments, the anode **104** in the first compartment of a photoelectrochemical cell is in contact with water. Further, the anode may be configured to oxidize water molecules. For example, when a semiconductor is photoactivated, this induces movement of electrons from the valence band to the conduction band. The reactive electron-hole pairs are created as a result of this migration and this may oxidize water molecules to produce oxygen molecules, protons and the electrons. An exemplary reaction at anode may be represented as follows:



[0023] The first compartment may also include inlet(s) and outlet(s) to allow continuous entry of water and exit of oxygen, during the process.

[0024] In some embodiments, carbon dioxide may be continuously introduced into the second compartment **102** through an inlet **109** to form carbon dioxide saturated water or the water in the second compartment may be pre-saturated with carbon dioxide. For example, the concentration of carbon dioxide present in the second compartment may range from about 20 mM to about 200 mM. The cathode **105** may be in contact with water containing dissolved carbon dioxide and may reduce carbon dioxide to one or more hydrocarbons. The electrons generated in the anode compartment travel through

the external circuit 110 and protons may travel through the proton exchange membrane 103. In the second compartment, the cathode described herein may act as a catalyst and may catalyze reduction of carbon dioxide to one or more hydrocarbons. An exemplary reaction taking place at cathode may be represented as follows:



[0025] The electrochemical and/or the photoelectrochemical cell of the present disclosure may be used to reduce carbon dioxide to a variety of hydrocarbons including, but not limited to, methanol, methane, isopropanol, formic acid, formaldehyde, glyoxal, ethanol, butanol, or any combination thereof.

[0026] Further, in some embodiments, the method includes applying an electrical potential between the anode and the cathode sufficient to reduce carbon dioxide to one or more hydrocarbons. The electrical potential may be applied from an external electrical power source, irradiation, or any combination thereof. The electrical energy for the electrochemical reduction of carbon dioxide can come from a conventional energy source, including nuclear and alternatives (hydroelectric, wind, solar power, geothermal, etc.), from a solar cell or other non-fossil fuel source of electricity.

[0027] In some embodiments, the carbon dioxide may be reduced by photoelectrochemical reduction. In these embodiments, the anode is a semiconductor, and is suitably illuminated with an electromagnetic radiation of energy equal to or greater than the band gap of the semiconductor. A window may be provided in the photoelectrochemical cell to allow the electromagnetic radiation to illuminate the anode. For example, electromagnetic radiation may be provided by any suitable source, such as sunlight, and/or an artificial light source, such as visible light, UV, or any combination thereof. In an exemplary embodiment, the electromagnetic radiation is provided by sunlight. In some embodiments, light may be provided by sunlight at certain times of operation of a system (for example, during daytime, on sunny days, etc.) and artificial light may be used at other times of operation of the system (for example, during night time, on cloudy days, and the like.). Non-limiting examples of artificial light sources include a lamp (mercury-arc lamp, a xenon-arc lamp, a quartz tungsten filament lamp, and the like.), a laser (for example, argon ion), and/or a solar simulator. In some embodiments, optical fibers may be used to guide the electromagnetic radiation to illuminate the anode.

[0028] During photoelectrochemical reduction of carbon dioxide, the photoelectrochemical cell may produce electrical current due to the difference in voltage potential between the anode and the cathode. For example, the electrical current that may be produced may be in the range of about 50 $\mu\text{A}/\text{cm}^2$ to about 500 milliamperes/ cm^2 , about 50 $\mu\text{A}/\text{cm}^2$ to about 50 milliamperes/ cm^2 , about 50 $\mu\text{A}/\text{cm}^2$ to about 5 milliamperes/ cm^2 , or about 50 $\mu\text{A}/\text{cm}^2$ to about 500 $\mu\text{A}/\text{cm}^2$. This electrical current may be collected or stored by a current collector. These methods help to convert renewable energy, such as sunlight, into a chemical form that can be stored for later use.

[0029] In some embodiments, the methods described herein may be carried out at temperatures of about 5° C. to about 40° C., and pressures of about 1 to about 6 atmospheres.

[0030] The hydrocarbons produced by the reactions described herein may be isolated from the second compartment of the electrochemical cell. In some embodiments, these hydrocarbons may further be used as reactants. For example, the hydrocarbons may be used as a feedstock for the produc-

tion of plastics or for production of higher carbon-content hydrocarbons. It is further possible to convert the hydrocarbons to synthetic petrochemicals. The hydrocarbons may also be used as fuels or stored in a fuel container. It is possible to use the hydrocarbons produced in an internal or external combustion engine. The hydrocarbons may be oxidized, burned, or combusted in an engine or a fuel cell installed in any suitable vehicle, such as an automobile, aircraft, or military vehicle. Additionally, the devices/reactors described herein may also be installed into any such combustion engine, and the hydrocarbons produced by the reactor may be oxidized to power the engine.

[0031] Also described herein are methods to make a catalyst. In some embodiments, the catalyst may be an exfoliated graphene, wherein the graphene is surface functionalized with at least one poly(ionic liquid), and wherein at least one metallic nanoparticle is disposed on the functionalized graphene surface. The catalyst may be used as an electrode in a photoelectrochemical cell, electrochemical cell, or a fuel cell. In some embodiments, the exfoliated graphene catalyst may be a plurality of exfoliated graphene nanosheets. In some embodiments, the graphene nanosheet may have a thickness of about 0.2 nanometer to about 100 nanometers, about 0.2 nanometer to about 50 nanometers, about 0.2 nanometer to about 10 nanometers, or about 0.2 nanometer to about 1 nanometer, and ranges between any two of these values. In some embodiments, the poly(ionic) liquid may be 3-ethyl-1-vinylimidazolium tetrafluoroborate, 1-methyl-3-vinylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-vinyl-3-methylimidazolium tetrafluoroborate, 1-isobutenyl-3-methylimidazolium tetrafluoroborate, 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, 1-allyl-3-methylimidazolium bromide, 1,3-bis(cyanomethyl)imidazolium bis(trifluoromethylsulfonyl)imide, or any combination thereof. Further, any ionic liquid with back-bones, including imidazolium, ammonium, phosphonium and sulfonium, and with polymerizable side chains, such as vinyl, or allyl can be used. Further, the metallic nanoparticle that may be disposed on the poly(ionic) liquid functionalized carbon material surface may be Au, Ag, Pd, Co, Cu, Pt, Ni, Fe, Mn, Cr, V, Ti, Sc, Ce, or any combination thereof. For example, the catalyst may be an exfoliated graphene surface functionalized with 1-vinyl-3-methylimidazolium tetrafluoroborate, and platinum nanoparticles disposed on the functionalized surface.

[0032] In some embodiments, a method of preparing a catalyst may include oxidizing graphite to form graphite oxide, exfoliating graphite oxide to form one or more graphene nanosheets, contacting the one or more graphene nanosheets with a poly(ionic) liquid to form one or more coated graphene nanosheets, and contacting a metal compound with the one or more coated graphene nanosheets.

[0033] In some embodiments, the graphite may be oxidized by Hummers method as described in the art. For example, the powdered graphite may be contacted with a mixture of an acid, sodium nitrate, and an oxidizing agent. In some embodiments, the oxidizing agent may be a permanganate compound, a persulfate compound, a nitrate compound, or any combination thereof. The acid may be sulfuric acid or nitric acid. In some embodiments, the powdered graphite and the mixture are heated to a temperature of about 0° C. to about 90° C., about 0° C. to about 70° C., about 0° C. to about 50° C., or about 0° C. to about 30° C. Specific examples include about 0° C., about 10° C., about 20° C., about 40° C., about

60° C., about 90° C., and ranges between any two of these values. The heating may be carried out for about 30 minutes to about 6 hours, about 30 minutes to about 4 hours, about 30 minutes to about 3 hours, or about 30 minutes to about 2 hours. Specific examples include about 30 minutes, about 1 hour, about 2 hours, about 3 hours, about 4 hours, about 6 hours, and ranges between any two of these values. In some embodiments, the reaction may be performed in step-wise process, the first step comprising heating the reactants at temperatures below 10° C. for 30 minutes, and the second step comprising heating at temperatures between 60° C. and 90° C. for 1 hour.

[0034] In some embodiments, the graphite oxide prepared by the method described herein may be exfoliated by a thermal process. For example, the graphite oxide may be heated to a temperature of about 150° C. to about 400° C., about 150° C. to about 300° C., or about 150° C. to about 200° C. in the presence of hydrogen (H₂). Other exfoliation techniques that may be used are solar exfoliation, vacuum exfoliation, microwave exfoliation, electrochemical exfoliation, ultrasonic exfoliation, and the like.

[0035] In some embodiments, contacting the graphene nanosheets with a poly(ionic) liquid involves refluxing the graphene nanosheets with a poly(ionic) liquid and an initiator. Non-limiting examples of the poly(ionic) liquid include 3-ethyl-1-vinylimidazolium tetrafluoroborate, 1-methyl-3-vinylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-tetrafluoroborate, 1-allyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide, 1-allyl-3-methylimidazolium bromide, 1,3-bis(cyanomethyl)-imidazolium bis(trifluoromethyl-sulfonyl)imide, or any combination thereof. In some embodiments, the initiator may be an azo compound, a peroxide, or any combination thereof.

[0036] In some embodiments, refluxing the graphene nanosheets with a poly(ionic) liquid and an initiator may be performed at an elevated temperature, such as a temperature of about 60° C. to about 90° C., about 60° C. to about 80° C., about 60° C. to about 70° C., or about 60° C. to about 65° C. Specific examples include about 60° C., about 65° C., about 70° C., about 80° C., about 90° C., and ranges between any two of these values. In some embodiments, the refluxing may be performed for a variety of times, such as for about 10 hours to about 24 hours, about 10 hours to about 24 hours, about 10 hours to about 24 hours, or about 10 hours to about 24 hours. Specific examples include about 10 hours, about 12 hours, about 15 hours, about 18 hours, about 24 hours, and ranges between any two of these values. The method may further include the steps of filtering, washing, and drying the graphene nanosheets coated with poly(ionic) liquid.

[0037] In some embodiments, the poly(ionic) liquid coated graphene nanosheets may be contacted with a metal compound by mixing them in a solvent to form a solution, and dielectrically heating the solution. Non-limiting examples of the metal compound that may be used are compounds or salts of Au, Ag, Pd, Co, Cu, Pt, Ni, Fe, Mn, Cr, V, Ti, Sc, Ce, or any combination thereof. Suitable solvent that may be used include ethylene glycol, propylene glycol, dimethylformamide, or any combination thereof. When mixed, the solution may have a pH of about 7 to about 10, about 7 to about 9, or about 7 to about 8. Specific examples include about pH 7, about pH 8, about pH 9, about pH 10, and ranges between any two of these values.

[0038] In some embodiments, the method further includes dielectrically heating the solution by a radio frequency energy

having a frequency of about 300 MHz to about 300 GHz. For example, the dielectrically heating step may involve heating by a microwave energy having a frequency of about 300 MHz to about 300 GHz, about 600 MHz to about 300 GHz, about 1 GHz to about 300 GHz, about 30 GHz to about 300 GHz, or about 100 GHz to about 300 GHz. Specific examples include, but are not limited to, about 300 MHz, about 5 GHz, about 100 GHz, about 200 GHz, about 300 GHz, and ranges between any two of these values (including their endpoints). The dielectric heating may be performed by any device known in the art, such as an oven.

[0039] In some embodiments, the dielectrically heating step may be performed for generally any duration of time, for example, for about 10 seconds to about 60 minutes, about 1 minute to about 60 minutes, about 10 minutes to about 60 minutes, or about 30 minutes to about 60 minutes. Specific examples include, but are not limited to, about 10 seconds, about 1 minute, about 5 minutes, about 10 minutes, about 30 minutes, about 60 minutes, and ranges between any two of these values (including their endpoints). In some embodiments, the method may further include washing the coated graphene nanosheets disposed with metal nanoparticles, and filtering the coated graphene nanosheets disposed with metal nanoparticles.

EXAMPLES

Example 1

Preparation of PT/Graphene Catalyst

[0040] Graphitic oxide was prepared by Hummers method. Briefly, about 100 grams of powdered flake graphite and 50 grams of sodium nitrate were mixed with 2.3 liters of sulfuric acid. The ingredients were mixed in a 15-liter battery jar that had been cooled to 0° C. in an ice-bath. While maintaining vigorous agitation, about 300 grams of potassium permanganate was added to the suspension. The rate of addition was controlled carefully to prevent the temperature of the suspension from exceeding 20° C. The ice-bath was then removed and the temperature of the suspension was brought to 35° C., where it was maintained for 30 minutes. About 4.6 liters of water was slowly stirred into the paste, causing violent effervescence and an increase in temperature to 98° C. The diluted suspension, brown in color, was maintained at this temperature for 15 minutes. The suspension was then further diluted to approximately 14 liters with warm water and treated with 37% hydrogen peroxide to reduce the residual permanganate and manganese dioxide. Upon treatment with the peroxide, the suspension turned bright yellow. The suspension was filtered resulting in a yellow-brown filter cake. After washing the yellowish-brown filter cake three times with a total of 14 liters of warm water, the graphite oxide residue was dispersed in 32 liters of water. The remaining salt impurities were removed by treating with resinous anion and cation exchangers. The dry form of graphite oxide was obtained by centrifugation followed by dehydration at 40° C. over phosphorus pentoxide under vacuum.

[0041] The above obtained graphite oxide was thermally exfoliated at 200° C. under hydrogen (H₂) atmosphere in a tubular furnace. The graphene obtained by hydrogen exfoliation technique had wrinkled structure due to the rapid removal of oxygen containing functional groups.

[0042] The hydrogen exfoliated graphene (HEG) obtained above was surface functionalized with a poly(ionic) liquid.

Graphene (HEG) (100 milligrams) was dispersed in methanol (25 mL) by ultrasonication, followed by the addition of 200 milligrams of 1-vinyl-3-methylimidazolium tetrafluoroborate $[(\text{VMIM})\text{BF}_4]$ and 7 milligrams of 2,2'-azobisisobutyronitrile (AIBN) under stirring. The mixture was transferred to a 50 mL round-bottomed flask equipped with a condenser and refluxed for 16 hours at 80°C . under vigorous stirring and N_2 protection. Further, about 100 mL of double-distilled water was added to the mixture and filtered through a nylon 66 membrane. The filtered material was repeatedly washed with double-distilled water and acetone several times in order to remove physically absorbed polymer and unreacted monomer. The final product was dried in a vacuum oven at 60°C . and labeled as HEG-PIL (hydrogen exfoliated graphene-poly(ionic) liquid).

[0043] The decoration of Pt nanoparticles over the surface of HEG (hydrogen exfoliated graphene) and HEG-PIL was carried out by microwave assisted reduction method. Briefly, 50 milligrams of HEG or HEG-PIL was dispersed in 50 mL ethylene glycol followed by the drop wise addition of 2.77 mL aqueous solution of H_2PtCl_6 (3.6 milligrams Pt in 1 mL solution). The solution was mixed thoroughly by stirring and pH value of the solution was adjusted to 8-9 with 1.0 M NaOH aqueous solution. The mixture was exposed to the microwave irradiation (800 W) for 5 minutes and then diluted with double-distilled water, filtered through a Nylon 66 membrane, and washed with double-distilled water and acetone several times. The product with HEG support was labeled as "Pt/HEG", and with HEG-PIL support was labeled "Pt/HEG-PIL".

Example 2

Characterization of PT/HEG-PIL Catalyst

[0044] The HEG, Pt/HEG, and Pt/HEG-PIL obtained in Example 1 were subjected to high resolution transmission electron microscopy (HRTEM). Images of HEG revealed the disorder induced in graphite structure resulting in the form of sheets by exfoliation (FIG. 2A). The rapid removal of intercalated oxygen containing functional groups and other functional groups during exfoliation resulted in a wrinkled structure of graphene sheets. The HRTEM image showed the presence of wrinkles in the planar graphene sheets. FIG. 2B shows morphology of the poly(ionic) liquid functionalized HEG, where the presence of islands of poly(ionic) liquid were clearly visible. The HRTEM image of platinum nanoparticle dispersed HEG-PIL (FIG. 2C) showed the good dispersion of Pt nanoparticles. In HEG-PIL, the PIL film on the HEG produced an uniform distribution of the imidazole groups that may serve as functional groups for the immobilization of Pt through electrostatic interaction and coordination.

Example 3

Electrochemical Analysis of PT/HEG-PIL

[0045] The electrochemical CO_2 conversion behavior of the prepared electrocatalyst was determined by conventional three electrode system. The three electrode system consisted of a working electrode, a counter electrode, and a reference electrode along with electrolyte solution. Ag/AgCl electrode was used as reference electrode, Pt wire as used as a counter electrode, and CO_2 saturated 0.5 M KHCO_3 as electrolyte. The catalyst was dispersed in isopropanol medium by ultrasonication followed by the addition of 5 wt % Nafion solution

as a binder to form a slurry. Then the glassy carbon electrode was modified with the slurry of electrocatalyst and used as a working electrode in three electrode measurement system. The electrocatalytic reduction potential of Pt/HEG-PIL with carbon dioxide saturated 0.5 M KHCO_3 was evaluated by half-cell measurement using cyclic voltammetry (FIG. 3). The glassy carbon electrode was modified with the electrocatalyst and used as a working electrode in three electrode measurement system. The reduction signals at -0.6 and -0.48 V were observed with respect to saturated Ag/AgCl electrode, for the formation of liquid phase methanol and gas phase methane, respectively.

Example 4

Electrochemical Analysis of PT/HEG-PIL

[0046] Chronoamperometric technique, a useful method for the evaluation of the electrocatalysts in fuel cells, was employed to further investigate the electrochemical performance of the prepared electrocatalysts and compare their activity. In this method, the change in current at certain voltage was measured with respect to time, and the results are shown in FIG. 4.

Example 5

Photoelectrochemical Cell

[0047] TiO_2 coated carbon cloth (anode) and Pt/HEG or Pt/HEG-PIL coated carbon cloth (cathode) were hot pressed on either sides of Nafion 117 membrane at 130°C . with 2 ton load for 4 minutes. The cathode dimension was maintained at 11.56 cm^2 with 0.5 mg/cm^2 Pt loading. This membrane-electrode assembly was further equipped with anode and cathode reservoirs to the respective sides. The electrical connections were given by stainless steel plates. Anode reservoir was filled with deionized water, while the cathode reservoir was continuously circulated with carbon dioxide saturated deionized water (68 mM, 3 grams/liter at 1 atmosphere partial pressure). The anode reservoir was exposed to light from a 150 W mercury lamp. The oxygen gas produced under light exposure was removed frequently by anode reservoir outlet. Prior to the experiment, the cell was activated for 4 cycles of 15 minutes light exposure in a short circuit.

[0048] Visible light was irradiated to the anode side of the cell to split water into protons and oxygen molecules. The produced protons migrated to cathode side of the cell through the Nafion membrane. At the cathode, protons reacted with dissolved carbon dioxide molecules to produce hydrocarbons methanol and gas phase methane. The dissolved methanol in deionized water was sampled at various time periods and analyzed by spectroscopic techniques. The Fourier transform infrared (FTIR) spectrum of the cathode solution was similar to that of methanol, and showed the stretching vibrations of C—H at around $2800\text{--}3000\text{ cm}^{-1}$ (FIG. 5). This clearly confirmed the conversion of carbon dioxide into methanol in the cathode chamber.

[0049] The quantification of methanol produced in the cathode chamber was carried out by UV-Vis spectroscopy, using commercial methanol as a reference standard (absorption band at 240 nm, inset in FIG. 6). With reference to this peak, the analyzer was calibrated in the range of 0.5 M to 0.00155 M by serial dilutions. Based on this calibration curve, the concentration of methanol in the cathode solution was determined. The cathode reservoir showed a methanol

concentration of 12.63 mM for Pt/HEG-PIL cathode, while it was 3.08 mM for Pt/HEG cathode, after 250 minutes of reaction (FIG. 6).

[0050] Further, the electricity generated was measured by open circuit potential (OCP) and current at low load. Pt/HEG-PIL and Pt/HEG showed an OCP of 510 mV and 450 mV, respectively. Further, Pt/HEG-PIL cathode generated a current density of 238 $\mu\text{A}/\text{cm}^2$ at 45 mV potential, while Pt/HEG generated a current density of 174 $\mu\text{A}/\text{cm}^2$ at 28 mV. These values clearly indicate the better performance of Pt/HEG-PIL over Pt/HEG in carbon dioxide conversion and electricity production.

[0051] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0052] As used in this document, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term “comprising” means “including, but not limited to.”

[0053] While various compositions, methods, and devices are described in terms of “comprising” various components or steps (interpreted as meaning “including, but not limited to”), the compositions, methods, and devices can also “consist essentially of” or “consist of” the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0054] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0055] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (for example, bodies of the appended claims) are generally intended as “open” terms (for example, the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly

recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases “at least one” and “one or more” to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles “a” or “an” limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases “one or more” or “at least one” and indefinite articles such as “a” or “an” (for example, “a” and/or “an” should be interpreted to mean “at least one” or “one or more”); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (for example, the bare recitation of “two recitations,” without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to “at least one of A, B, and C, etc.” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, “a system having at least one of A, B, and C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to “at least one of A, B, or C, etc.” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, “a system having at least one of A, B, or C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase “A or B” will be understood to include the possibilities of “A” or “B” or “A and B.”

[0056] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0057] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells.

Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0058] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

1. A photoelectrochemical cell comprising:
an anode;
a cathode comprising a carbon material, wherein the carbon material is surface functionalized with at least one poly(ionic) liquid, and wherein at least one metallic nanoparticle is disposed on the functionalized carbon material surface; and
an energy source configured to irradiate the anode.
2. (canceled)
3. The photoelectrochemical cell of claim 1, wherein the anode is in contact with water in a first compartment of the photoelectrochemical cell.
4. The photoelectrochemical cell of claim 3, wherein the anode is configured to oxidize water molecules.
5. (canceled)
6. The photoelectrochemical cell of claim 1, wherein the cathode is in contact with carbon dioxide dissolved in water in a second compartment of the photoelectrochemical cell.
7. The photoelectrochemical cell of claim 6, wherein the cathode is configured to reduce carbon dioxide to at least one hydrocarbon selected from the group consisting of methanol, methane, isopropanol, formic acid, formaldehyde, glyoxal, ethanol, butanol, and any combination thereof.
8. (canceled)
9. The photoelectrochemical cell of claim 1, wherein the at least one metallic nanoparticle comprises Au, Ag, Pd, Co, Cu, Pt, Ni, Fe, Mn, Cr, V, Ti, Sc, Ce, or any combination thereof.
10. The photoelectrochemical cell of claim 1, wherein the at least one poly(ionic) liquid comprises 3-ethyl-1-vinylimidazolium tetrafluoroborate, 1-methyl-3-vinylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-vinyl-3-methylimidazolium tetrafluoroborate, 1-isobutenyl-3-methylimidazolium tetrafluoroborate, 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-allyl-3-methylimidazolium bromide, 1,3-bis(cyanomethyl)imidazolium bis(trifluoromethylsulfonyl)imide, or any combination thereof.
11. The photoelectrochemical cell of claim 1, wherein the carbon material comprises a carbon nanotube, graphene, graphene oxide, or any combination thereof.
- 12-13. (canceled)
14. The photoelectrochemical cell of claim 1, wherein the anode comprises a metal or a semiconductor.
- 15-17. (canceled)
18. The photoelectrochemical cell of claim 1, further comprising an electrolyte in contact with the first compartment and the second compartment, wherein the electrolyte allows movement of protons from the first compartment to the second compartment through a proton exchange membrane.
19. (canceled)
20. The photoelectrochemical cell of claim 1, wherein the energy source comprises UV light, visible light, sunlight, or any combination thereof.
21. A method of reducing carbon dioxide to one or more hydrocarbons, the method comprising:

introducing water to a first compartment of an electrochemical cell, wherein the first compartment includes an anode;

introducing carbon dioxide dissolved in water to a second compartment of the electrochemical cell, wherein the second compartment includes a cathode, wherein the cathode comprises a carbon material that is surface functionalized with at least one poly(ionic) liquid and at least one metallic nanoparticle disposed on the functionalized carbon material surface; and

applying an electrical potential between the anode and the cathode sufficient to reduce carbon dioxide to one or more hydrocarbons.

22. The method of claim 21, wherein applying the electrical potential comprises applying the electrical potential by an external electrical power, irradiation, or any combination thereof.

23. The method of claim 21, wherein introducing water comprises introducing water to the first compartment of the electrochemical cell, wherein the first compartment includes a metal anode or a semiconductor anode.

24. (canceled)

25. The method of claim 21, wherein introducing carbon dioxide dissolved in water comprises introducing carbon dioxide dissolved in water to the second compartment of the electrochemical cell, wherein the second compartment includes the cathode, wherein the cathode is a carbon nanotube, graphene, graphene oxide, or any combination thereof that is surface functionalized with at least one poly(ionic) liquid and at least one metallic nanoparticle disposed on the functionalized surface, and wherein the metallic nanoparticle is selected from Au, Ag, Pd, Co, Cu, Pt, Ni, Fe, Mn, Cr, V, Ti, Sc, Ce, and any combination thereof.

26-28. (canceled)

29. The method of claim 21, wherein applying the electrical potential comprises applying the electrical potential between the anode and the cathode sufficient to reduce carbon dioxide to the one or more hydrocarbons selected from the group consisting of methanol, isopropanol, formic acid, formaldehyde, glyoxal, ethanol, butanol, and any combination thereof.

30-31. (canceled)

32. The method of claim 21, further comprising isolating the one or more hydrocarbons from the second compartment of the electrochemical cell.

33. A catalyst comprising an exfoliated graphene, wherein the exfoliated graphene is surface functionalized with at least one poly(ionic liquid), and wherein at least one metallic nanoparticle is disposed on the functionalized graphene surface.

34. The catalyst of claim 33, wherein the at least one poly(ionic) liquid comprises 3-ethyl-1-vinylimidazolium tetrafluoroborate, 1-methyl-3-vinylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-vinyl-3-methylimidazolium tetrafluoroborate, 1-isobutenyl-3-methylimidazolium tetrafluoroborate, 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-allyl-3-methylimidazolium bromide, 1,3-bis(cyanomethyl)imidazolium bis(trifluoromethylsulfonyl)imide, or any combination thereof.

35-36. (canceled)

37. The catalyst of claim 33, wherein the at least one metallic nanoparticle comprises Au, Ag, Pd, Co, Cu, Pt, Ni, Fe, Mn, Cr, V, Ti, Sc, Ce, or any combination thereof.

38. (canceled)

39. The catalyst of claim **33**, wherein the catalyst is an electrode in a photoelectrochemical cell, electrochemical cell, or a fuel cell.

40. A method of preparing a catalyst, the method comprising:

- oxidizing graphite to form graphite oxide;
- exfoliating graphite oxide to form one or more graphene nanosheets;
- contacting the one or more graphene nanosheets with a poly(ionic) liquid to form one or more coated graphene nanosheets; and
- contacting a metal compound with the one or more coated graphene nanosheets.

41. The method of claim **40**, wherein oxidizing the graphite comprises heating a powdered graphite with a mixture of an acid, sodium nitrate, and an oxidizing agent to a temperature of about 0° C. to about 90° C. for about 30 minutes to about 6 hours.

42-45. (canceled)

46. The method of claim **40**, wherein exfoliating the graphite oxide comprises heating the graphite oxide to a temperature of about 150° C. to about 400° C. in the presence of hydrogen (H₂).

47. (canceled)

48. The method of claim **40**, wherein contacting the one or more graphene nanosheets with the poly(ionic) liquid comprises refluxing the one or more graphene nanosheets with the poly(ionic) liquid and an initiator at a temperature of about 60° C. to about 90° C. for about 10 hours to about 24 hours.

49. The method of claim **48**, wherein refluxing comprises refluxing the one or more graphene nanosheets with the poly

(ionic) liquid selected from the group consisting of 3-ethyl-1-vinylimidazolium tetrafluoroborate, 1-methyl-3-vinylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-vinyl-3-methylimidazolium tetrafluoroborate, 1-isobutenyl-3-methylimidazolium tetrafluoroborate, 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-allyl-3-methylimidazolium bromide, 1,3-bis(cyanomethyl)imidazolium bis(trifluoromethylsulfonyl)imide, and any combination thereof and the initiator.

50-53. (canceled)

54. The method of claim **40**, wherein contacting the metal compound with the one or more coated graphene nanosheets comprises:

- mixing the one or more coated graphene nanosheets with the metal compound in a solvent to form a solution; and
- dielectrically heating the solution.

55. The method of claim **54**, wherein mixing comprises mixing the one or more coated graphene nanosheets with the metal compound selected from the group consisting of a Au compound, a Ag compound, a Pd compound, a Co compound, a Cu compound, a Pt compound, a Ni compound, a Fe compound, a Mn compound, a Cr compound, a V compound, a Ti compound, a Sc compound, a Ce compound, and any combination thereof.

56-57. (canceled)

58. The method of claim **54**, wherein the dielectrically heating the solution comprises heating by a radio frequency energy having a frequency of about 300 MHz to about 300 GHz for about 10 seconds to about 60 minutes.

59-60. (canceled)

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