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RONDINONE et al.(10) **Pub. No.: US 2019/0127866 A1**(43) **Pub. Date: May 2, 2019**(54) **ELECTROCHEMICAL CATALYST FOR
CONVERSION OF CO₂ TO ETHANOL**(30) **Foreign Application Priority Data**

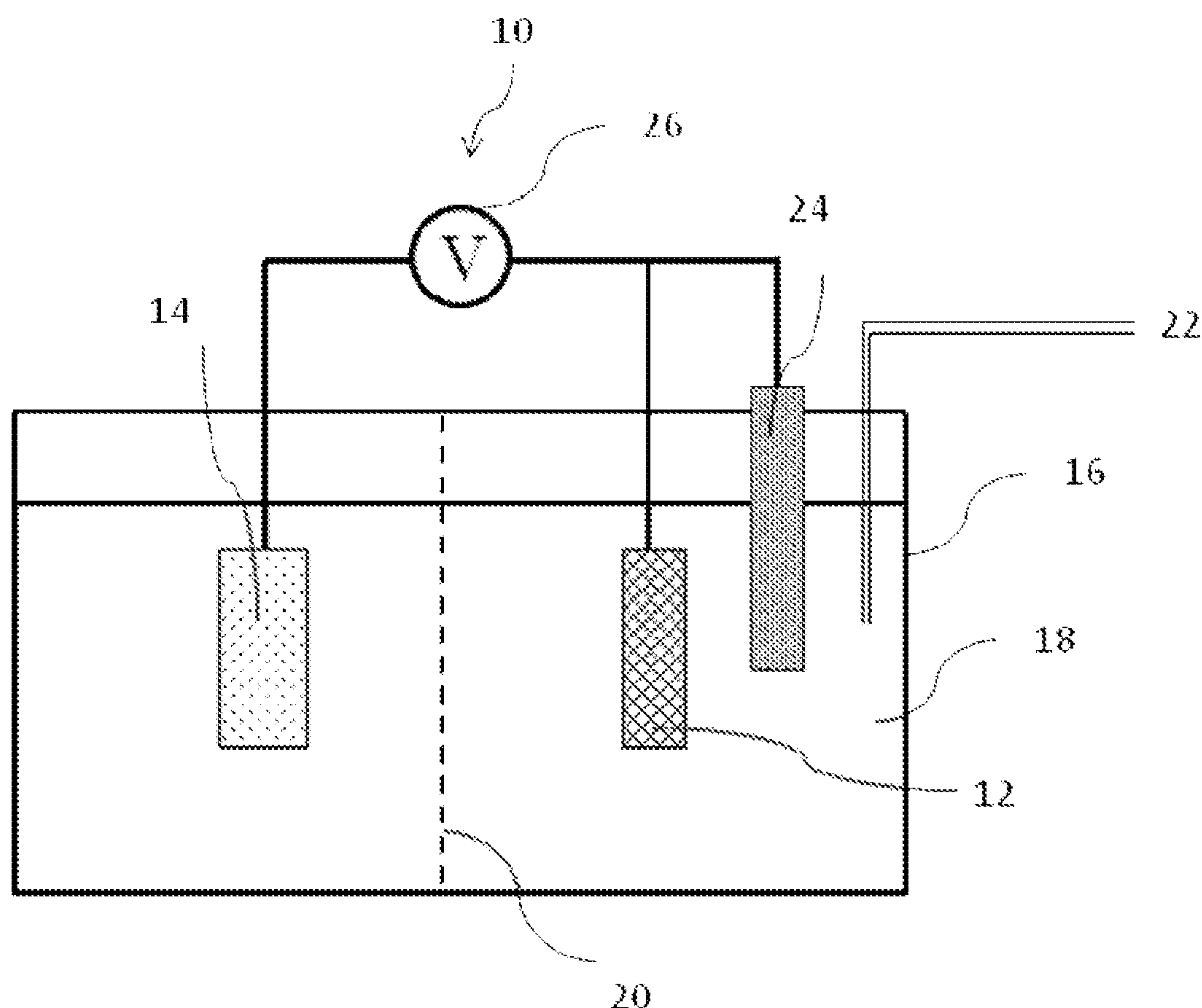
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(2) Date: **Nov. 1, 2018**(57) **ABSTRACT**

An electrocatalyst comprising (i) carbon nanospikes and (ii) copper-containing nanoparticles residing on and/or embedded between said carbon nanospikes. The carbon nanospikes are doped with a dopant selected from the group consisting of nitrogen, boron, and phosphorous. Also disclosed herein is a method of producing the electrocatalyst and a method for converting carbon dioxide into ethanol by use of the above-described electrocatalyst.



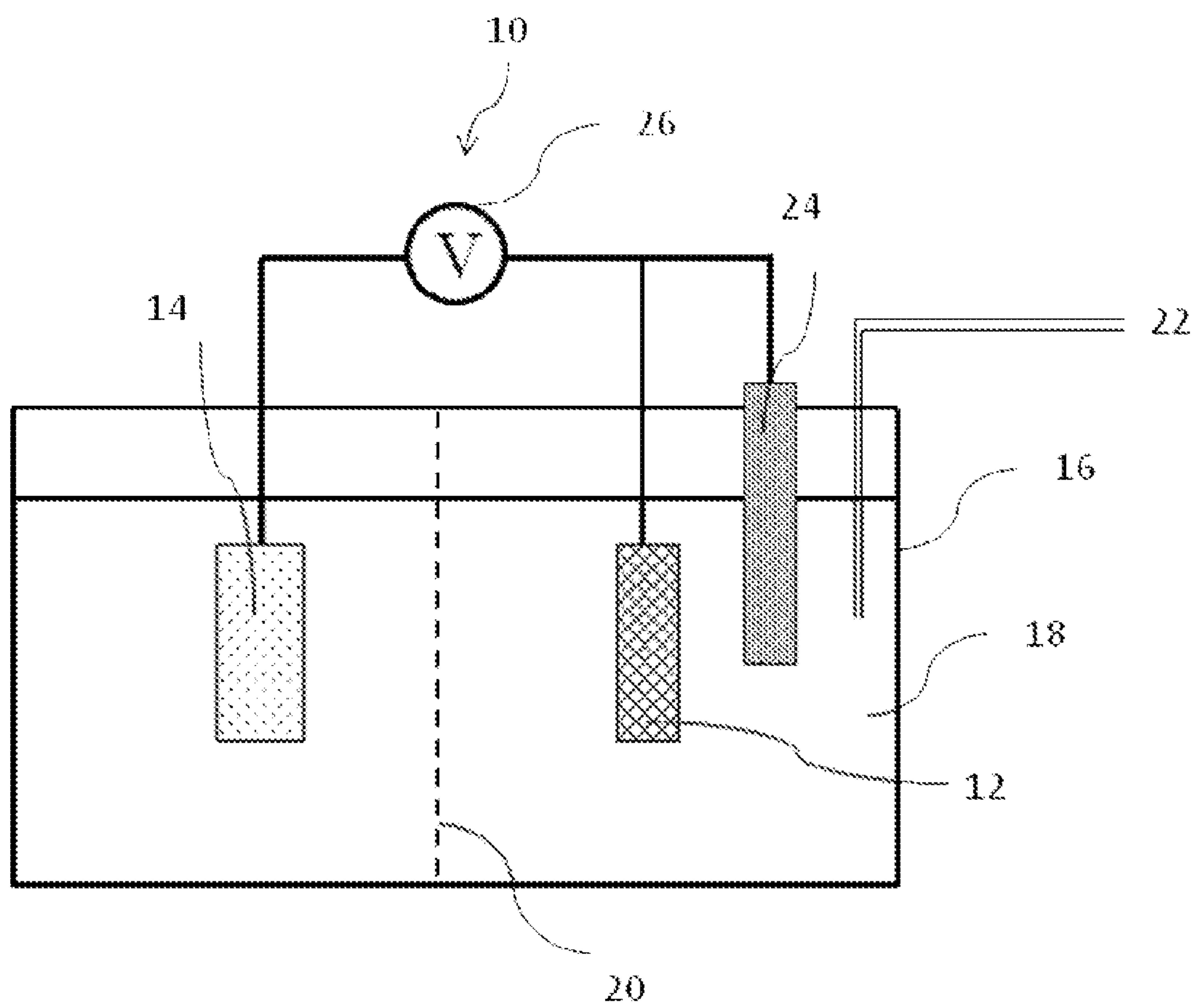


FIG. 1

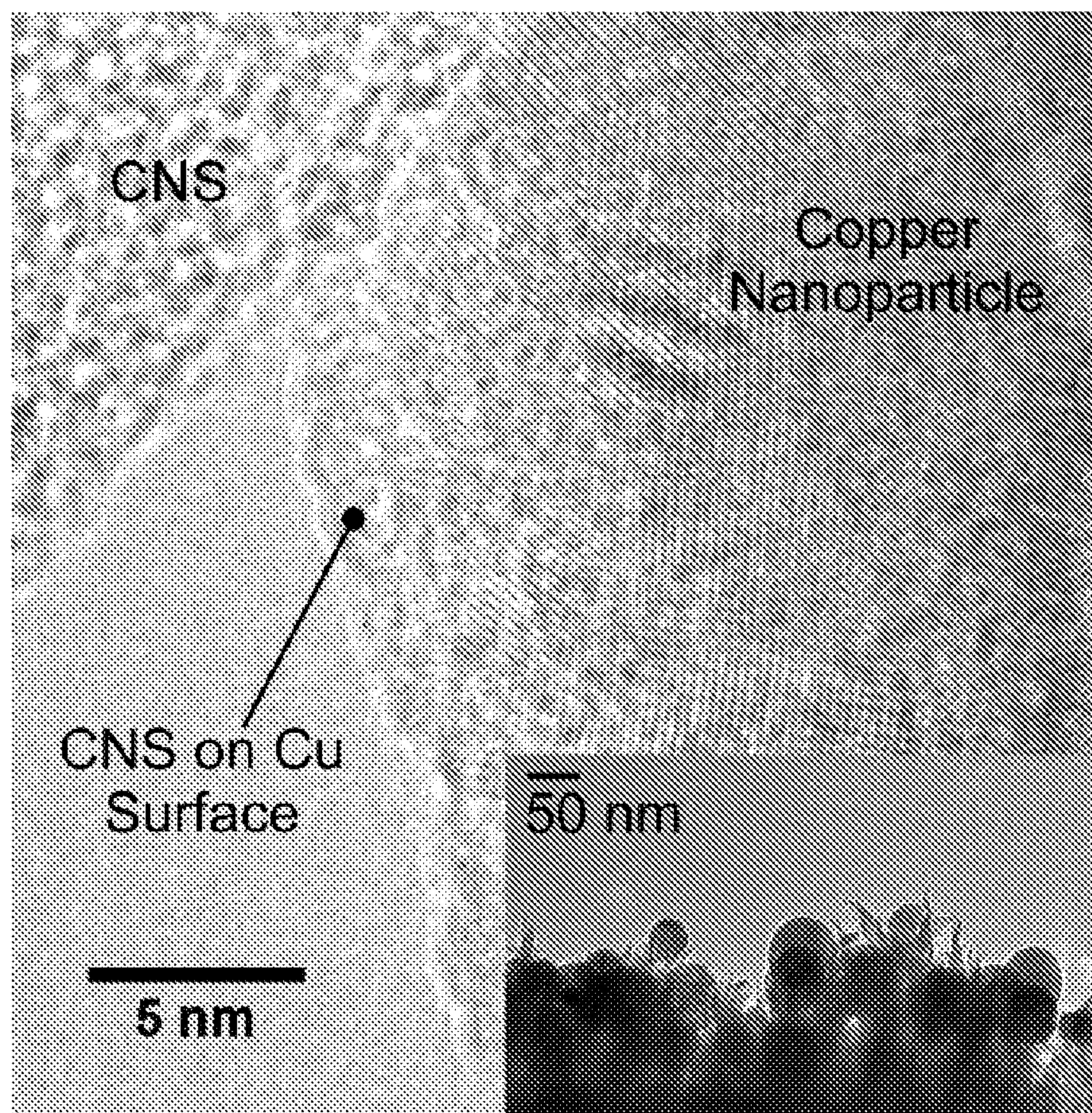
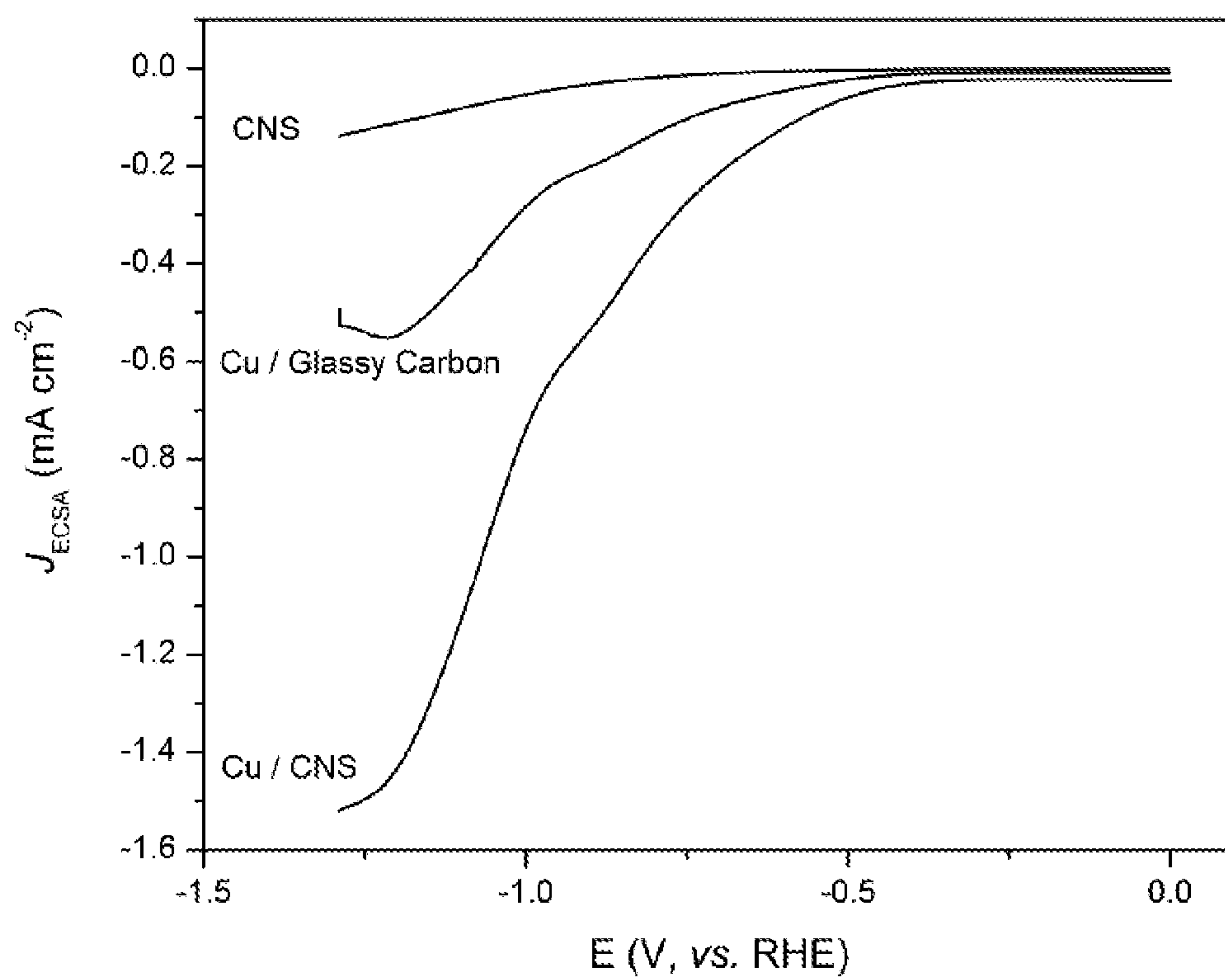


FIG. 2

**FIG. 3**

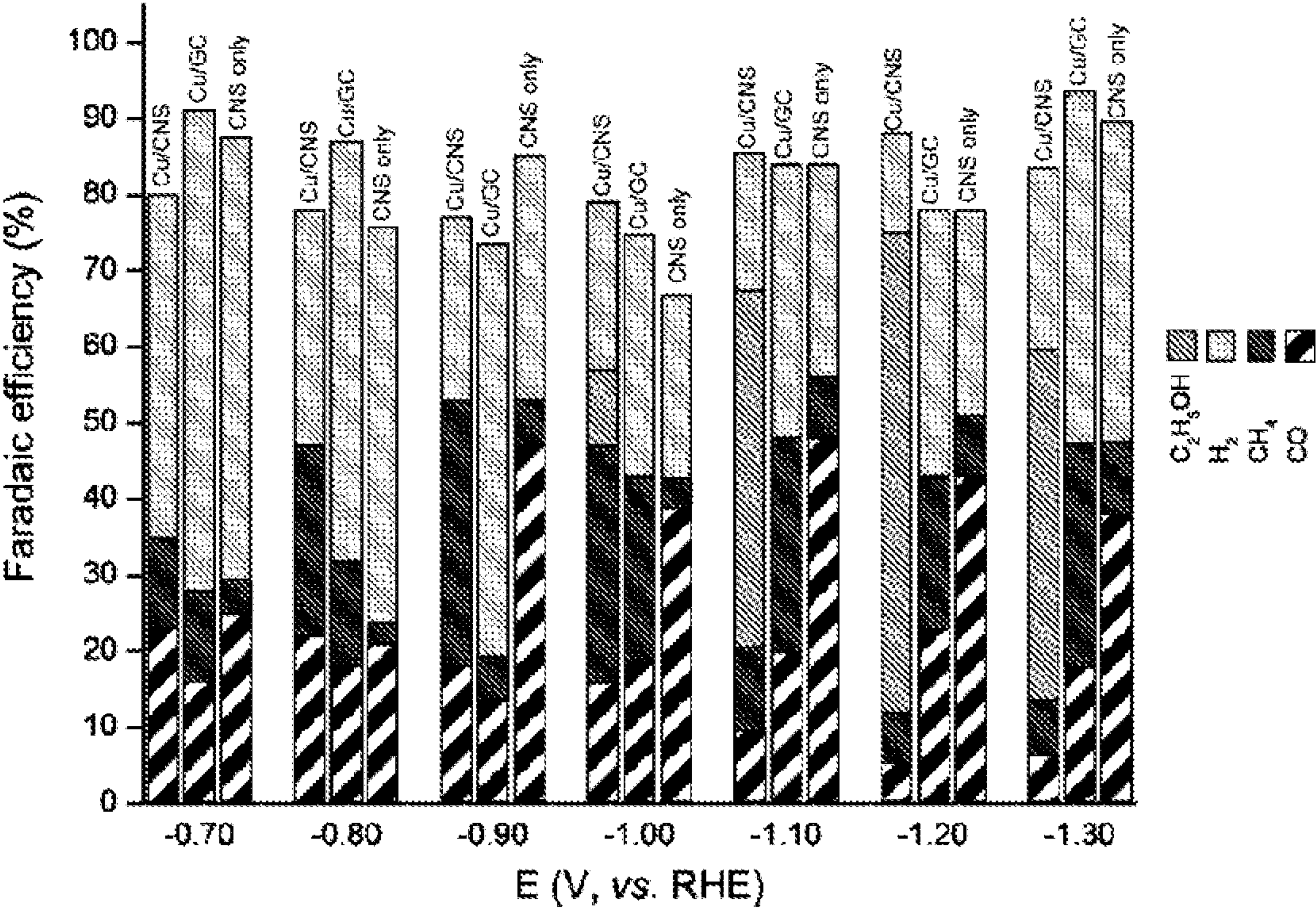
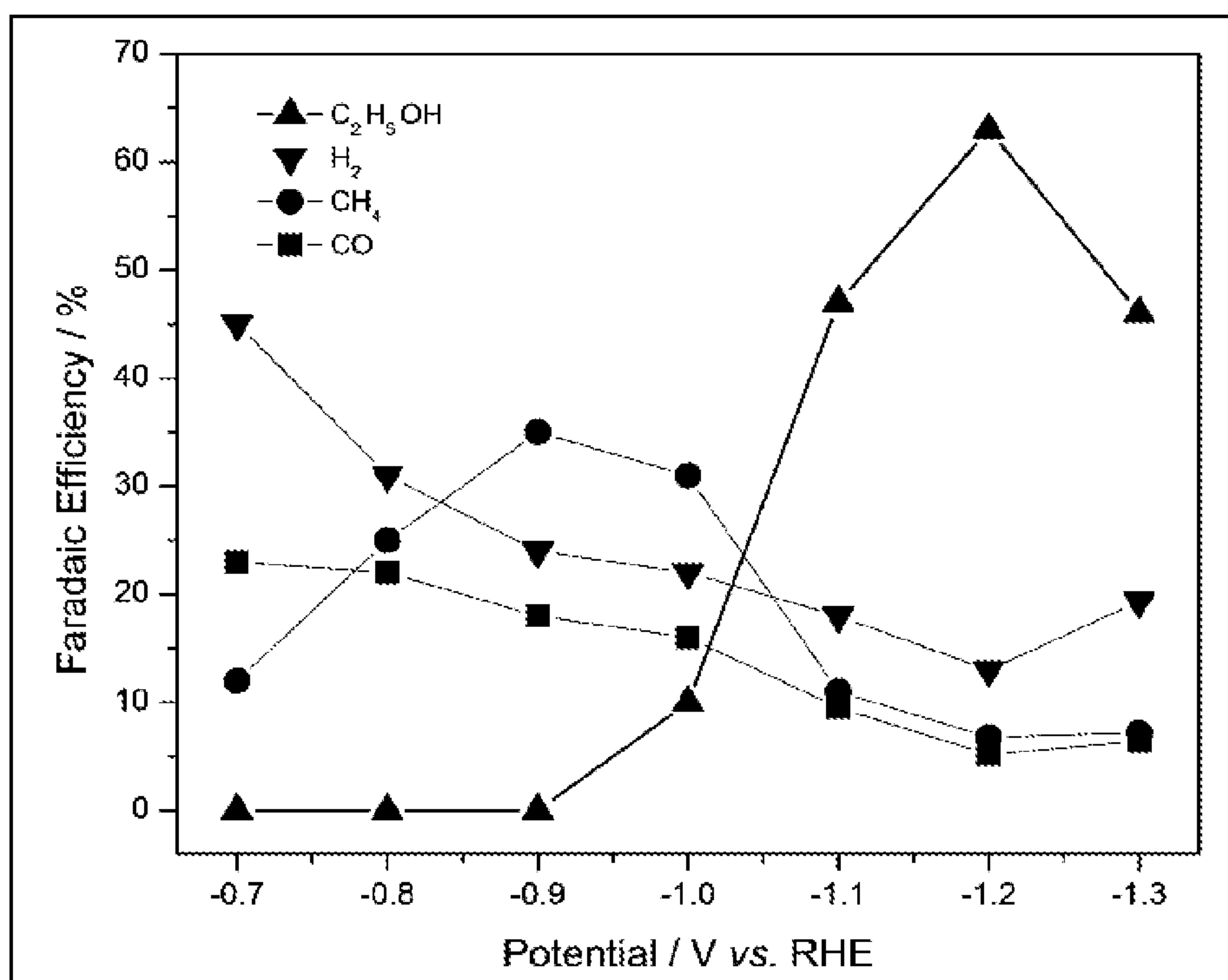


FIG. 4

**FIG. 5**

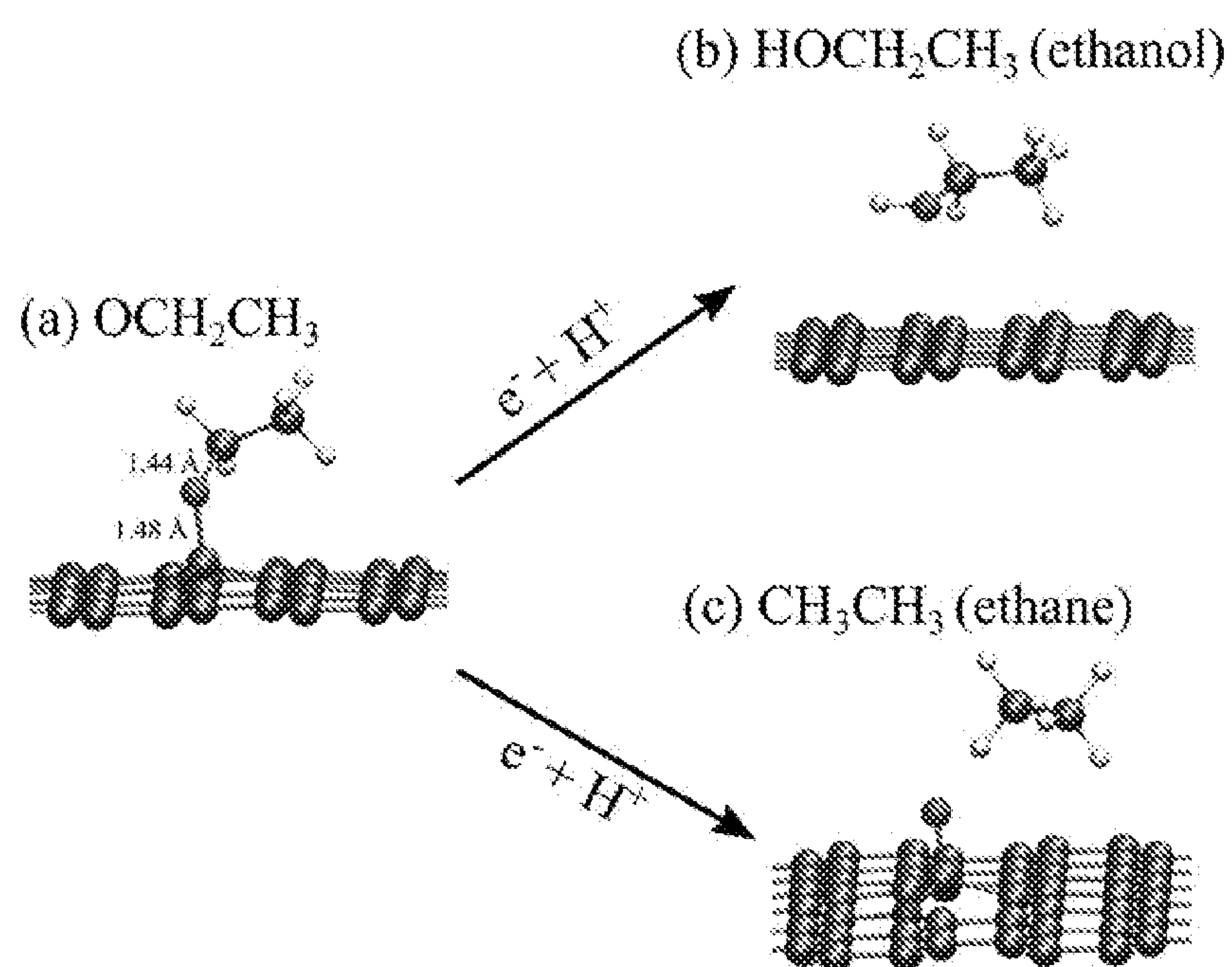


FIG. 6

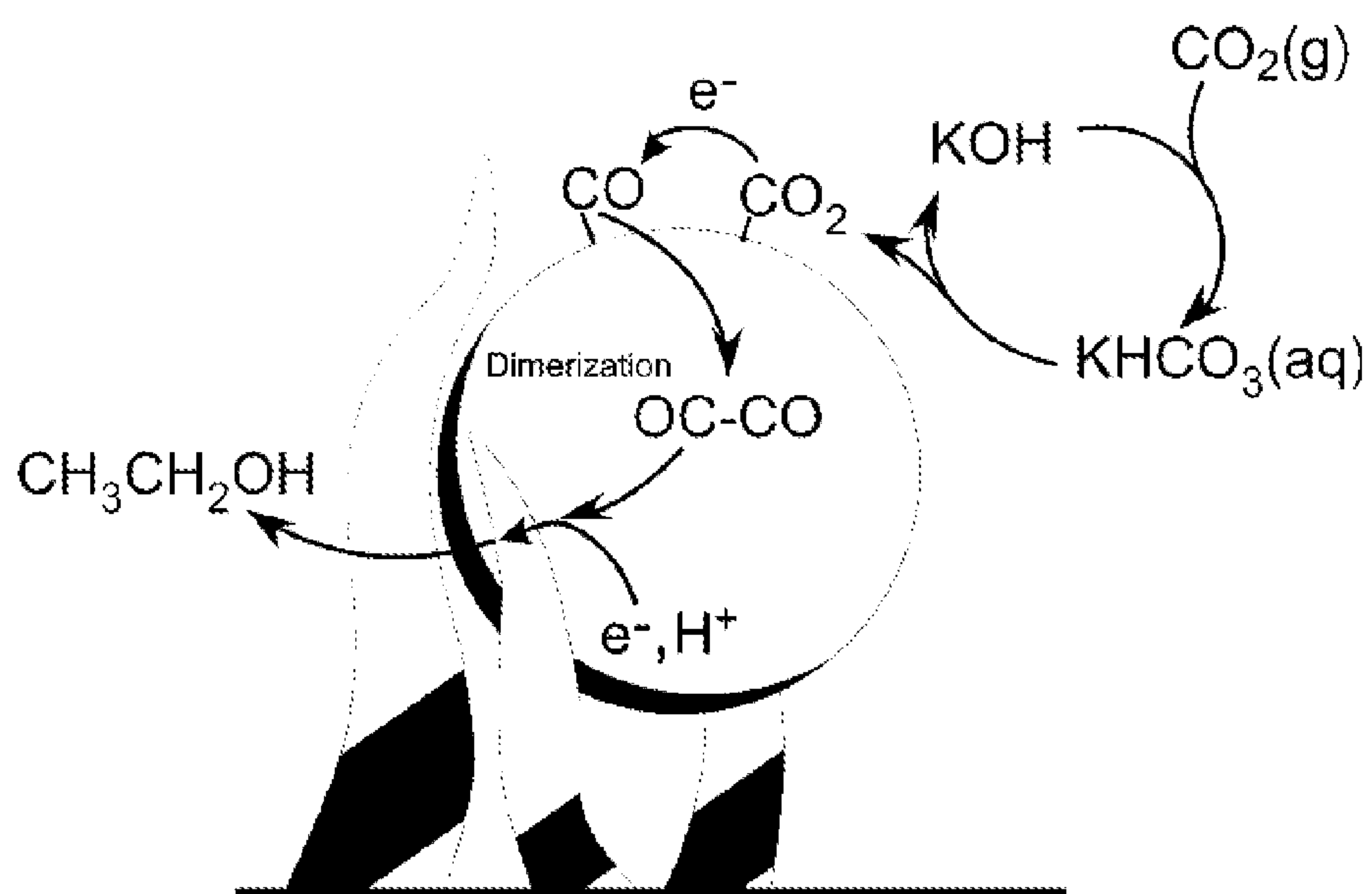


FIG. 7

ELECTROCHEMICAL CATALYST FOR CONVERSION OF CO₂ TO ETHANOL

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0001] This invention was made with government support under Prime Contract No. DE-AC05-00OR22725 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

CROSS REFERENCE TO RELATED APPLICATION

[0002] The present application claims benefit of U.S. application Ser. No. 15/143,651, filed on May 2, 2016, all of the contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0003] This invention generally relates to the field of electrocatalysis and to methods for converting carbon dioxide into useful products. The invention relates, more particularly, to electrocatalysts for converting carbon dioxide to ethanol.

BACKGROUND OF THE INVENTION

[0004] A low cost, easily implemented and widely distributable means to mitigate or eliminate carbon dioxide (CO₂) emissions will be necessary to meaningfully address climate change. Closing the carbon cycle by utilizing CO₂ as a feedstock for currently used commodities, in order to replace a fossil fuel feedstock, is an important intermediate step towards a carbon-neutral future.

[0005] There has been significant interest in the electrochemical conversion of CO₂ to liquid hydrocarbon fuels as a means to close the carbon cycle, and to store and transport energy in a manner that could meet the demands of existing internal combustion engines. Metal-based catalysts, such as copper, platinum, iron, silver, and gold have been investigated for CO₂ reduction, with high Faradaic efficiencies achieved for methane conversion.

[0006] However, electrocatalysts that could effectively and efficiently reduce CO₂ into a desirable liquid fuel remain elusive. Although copper (Cu) is a metal catalyst known for its ability to electrochemically reduce CO₂, the resultant products are highly diverse. For example, Cu is capable of reducing CO₂ into more than 30 different products, including carbon monoxide (CO), formic acid (HCOOH), methane (CH₄) and ethane (C₂H₄). As such, by means of the conventional art, the efficiency and selectivity achieved using Cu for producing liquid fuel are too low for practical use. Generally, competing reactions limit the yield of any one liquid product to single-digit percentages. Thus, a more efficient and selective method for converting CO₂ into useful fuel products would represent a significant advance in the art.

SUMMARY OF THE INVENTION

[0007] In one aspect, the present invention is directed to an electrocatalyst that efficiently and selectively converts carbon dioxide into ethanol. The electrocatalyst described herein for achieving this includes carbon nanospikes and copper-containing nanoparticles residing on and/or embed-

ded between the carbon nanospikes. The carbon nanospikes are doped with a dopant selected from nitrogen, boron, or phosphorous.

[0008] In another aspect, the invention is directed to a method for producing the electrocatalyst. The method generally involves growing copper-containing nanoparticles onto the carbon nanospikes, which may more specifically be, for example, on the tip of a carbon nanospike or between carbon nanospikes. In particular, the method includes providing a mat of carbon nanospikes, described above, protruding outwardly from a surface of the mat and forming copper-containing nanoparticles on and/or between the carbon nanospikes.

[0009] In another aspect, the invention is directed to a method of converting carbon dioxide into ethanol. The method entails contacting the electrocatalyst, described above, with carbon dioxide in an aqueous solution, with the carbon dioxide in the form of a bicarbonate salt (e.g., by reaction of the carbon dioxide with a metal hydroxide), while the electrocatalyst is electrically configured as a cathode. Generally, the voltage across the cathode and anode is at least 2 volts, or within 2-4 volts, or 2-3.5 volts. More particularly, the method entails contacting the above-described electrocatalyst with an aqueous solution of a bicarbonate salt while the aqueous solution is in contact with a source of carbon dioxide, which replenishes the bicarbonate salt as the bicarbonate salt decomposes to carbon dioxide and a hydroxide salt at the surface of the electrocatalyst, and the electrocatalyst is electrically powered as a cathode and is in electrical communication with a counter electrode electrically powered as an anode, wherein the voltage across the cathode and anode is at least 2 volts or within a range of 2 to 3.5 volts, to convert the carbon dioxide into ethanol.

BRIEF DESCRIPTION OF THE FIGURES

[0010] FIG. 1. A schematic diagram showing an electrochemical cell for CO₂ reduction.

[0011] FIG. 2. High-resolution transmission electron microscopy (HR-TEM) surface image of an electrocatalyst containing Cu nanoparticles electrodeposited on carbon nanospikes (i.e. Cu/CNS electrocatalyst). Electrodeposited Cu nanoparticles are embedded in N-doped carbon nanospikes, which provides intimate contact between the Cu surface and alpha-carbon reactive sites. Inset is a lower magnification image.

[0012] FIG. 3. Linear sweep voltammetry (LSV) curves in a potential range of 0.00 to -1.35 V vs. RHE for the Cu/CNS electrocatalyst shown in FIG. 2 compared to a Cu/C film control electrode and a bare CNS control electrode.

[0013] FIG. 4. Graph showing the fractional Faradaic efficiencies at various potentials for forming various CO₂ reduction products using the Cu/CNS electrocatalyst shown in FIG. 2 and control electrodes of Cu/Glassy Carbon Film and plain CNS.

[0014] FIG. 5. Graph showing partial current density of CO₂ reduction products from the Cu/CNS electrocatalyst shown in FIG. 2 at various potentials.

[0015] FIG. 6. Reaction scheme showing possible reaction pathways of adsorbed ethoxide (intermediate species). The intermediate species OCH₂CH₃ (a) is chemically adsorbed on N-doped CNS. Two routes for further electroreduction are illustrated: the cleavage of the CNS-oxygen bond to produce ethanol (b), or the cleavage of the C—O bond in OCH₂CH₃ to form ethane (c).

[0016] FIG. 7. Schematic showing a hypothetical reaction mechanism for conversion of CO₂ to ethanol using the Cu/CNS electrocatalyst of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0017] In one aspect, the invention is directed to an electrocatalyst that efficiently and selectively converts carbon dioxide into ethanol. The electrocatalyst includes carbon nanospikes and copper-containing nanoparticles residing on and/or embedded between the carbon nanospikes. The carbon-containing nanoparticles are well-dispersed in the carbon nanospikes. As used herein, the term “nanospikes” are defined as tapered, spike-like features present on a surface of a carbon film.

[0018] The carbon nanospikes in the electrocatalyst can have any length. Generally, the nanospike length may be precisely or about, for example, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, or 90 nm, or within a range bounded by any two of these values. In particular embodiments, the carbon nanospikes have a length of from about 50 to 80 nm.

[0019] At least a portion (e.g. at least 30, 40, 50, 60, 70, 80, or 90%) of the carbon nanospikes in the electrocatalyst is composed of layers of puckered carbon ending in a straight or curled tip. The width of the straight or curled tip may be precisely or about, for example, 0.5, 0.6, 0.7, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, or 2.5 nm, or within a range bounded by any two of these values. In particular embodiments, the straight or curled tip has a width of from about 1.8 to 2.2 nm.

[0020] The carbon nanospikes are doped with a dopant selected from nitrogen, boron, or phosphorous. It is believed that the dopant prevents well-ordered stacking of carbon, thus promoting the formation of disordered nanospike structure. In one embodiment, the carbon nanospikes are doped with nitrogen (N). The amount of the dopant in the carbon nanospikes may be precisely or about, for example, 3, 4, 5, 6, 7, 8, or 9 atomic %, or within a range bounded by any two of these values. In particular embodiments, the dopant concentration is from about 4 to 6 atomic %.

[0021] The carbon nanospikes can be prepared by any method known to those skilled in the art. In one embodiment, the carbon nanospikes can be formed on a substrate by plasma-enhanced chemical vapor deposition (PECVD) with any suitable carbon source and dopant source. In a first embodiment, the substrate is a semiconductive substrate. Some examples of semiconductive substrates include silicon, germanium, silicon germanium, silicon carbide, and silicon germanium carbide. In a second embodiment, the substrate is a metal substrate. Some examples of metal substrates include copper, cobalt, nickel, zinc, palladium, platinum, gold, ruthenium, molybdenum, tantalum, rhodium, stainless steel, and alloys thereof. In a particular embodiment, an arsenic-doped (As-doped) silicon substrate is employed and nitrogen-doped carbon nanospikes are grown on the As-doped silicon substrate using acetylene as the carbon source and ammonia as the dopant source. For additional details on the formation of carbon nanospikes of the present invention, reference is made to Sheridan et al., *J. of Electrochem. Society*, 2014, 161(9): H558-H563, the contents of which are herein incorporated by reference in their entirety.

[0022] The copper-containing nanoparticles are supported on, and/or embedded in the carbon nanospikes. The copper-

containing nanoparticles and carbon nanospikes are thus in close proximity, which permits intimate contact between copper surfaces and carbon reactive sites.

[0023] In one embodiment, the copper-containing nanoparticles are composed solely of elemental copper. In another embodiment, the copper-containing nanoparticles are composed of a copper alloy. The copper alloy may contain one, two, or more elements alloying with the elemental copper. The one or more alloying elements can be any of the elements that form a stable alloy with copper. In particular embodiments, the one or more alloying elements are selected from the transition metals, which may be more particularly selected from a first, second, or third row transition metal. The transition metals refer to any of the metals in Groups 3-12 of the Periodic Table of the Elements. In some embodiments, the alloying transition metals may be more specifically selected from Groups 9-12 of the Periodic Table, e.g., cobalt, nickel, zinc, rhodium, palladium, silver, cadmium, iridium, platinum, and gold. In other embodiments, the one or more alloying metals are selected main group elements in Groups 13-15, or Groups 13 and 14 of the Periodic Table, e.g., aluminum, gallium, indium, silicon, germanium, tin, arsenic, and antimony. In more specific embodiments, the one or more alloying elements are selected from nickel, cobalt, zinc, indium, silver, and tin. The one or more alloying elements can be present in any suitable concentration that retains catalytic activity in the copper-containing nanoparticles. Generally, the copper is present in an amount of at least 40, 50, 60, 70, 80, 90, 95, 97, 98, or 99 wt %, with the remainder being attributed to one or more alloying elements, e.g., 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, or 60 wt % attributed to the one or more alloying elements (or an amount within a range bounded by any two of the foregoing values). In some embodiments, the one or more alloying elements are present in a concentration within a range of about 0.01 to 10 weight %, or within a range of about 0.5 to 2 weight %.

[0024] The term “nanoparticles,” as used herein, generally refers to particles having a size of at least 1, 2, 3, 5, or 10 nm and up to 100, 200, 300, 400, or 500 nm in at least one dimension of the nanoparticles. In different embodiments, the copper-containing nanoparticles can have a size of precisely or about, for example 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 150, 200, 250, 300, 350, 400, 450, or 500 nm, or a size within a range bounded by any two of these values. In particular embodiments, the copper-containing nanoparticles have a size from about 30 to 100 nm.

[0025] The copper-containing nanoparticles can have any of a variety of shapes. In a first embodiment, the copper-containing nanoparticles are substantially spherical or ovoid. In a second embodiment, the copper-containing nanoparticles are substantially elongated, and may be rod-shaped, tubular, or even fibrous. In a third embodiment, the copper-containing nanoparticles are plate-like, with one dimension significantly smaller than the other two. In a fourth embodiment, the copper-containing nanoparticles have a substantially polyhedral shape, such as a pyramidal, cuboidal, rectangular, or prismatic shape.

[0026] The copper-containing nanoparticles can be present on the carbon nanospikes at any suitable density. A suitable density is a density that retains electrocatalyst activity. The density of the copper-containing nanoparticles on the carbon nanospikes may be precisely or about, for

example, 0.1×10^{10} , 0.3×10^{10} , 0.5×10^{10} , 0.8×10^{10} , 0.9×10^{10} , 1.0×10^{10} , 1.2×10^{10} , 1.3×10^{10} , 1.4×10^{10} , 1.5×10^{10} , 1.8×10^{10} , 2.0×10^{10} , 2.5×10^{10} , 3.0×10^{10} , 3.5×10^{10} , 4.0×10^{10} , 4.5×10^{10} , or 5.0×10^{10} particles/cm², or within a range bounded by any two of these values. In particular embodiments, the copper-containing nanoparticles are present on the carbon nanospikes in a density of from about 0.2×10^{10} to 1.2×10^{10} particles/cm².

[0027] The coverage of copper-containing nanoparticles on the carbon nanospikes can be any suitable amount. The coverage of copper-containing nanoparticle on the carbon nanospikes can be precisely or about, for example, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, or 75%, or a coverage within a range bounded by any two of these values. In particular embodiments, the coverage of copper-containing nanoparticles on the carbon nanospikes is about 10-20%, or more particularly, 12, 13, 14, 15, or 16%.

[0028] In another aspect, the invention is directed to methods for producing the electrocatalyst described above. Generally, the method involves depositing copper-containing nanoparticles onto a substrate composed of carbon nanospikes (i.e., CNS substrate). The copper-containing nanoparticles can be deposited on the CNS substrate using any method that results in the copper-containing nanoparticles residing on and remaining affixed to the surface of the CNS substrate after the deposition. More specifically, the process results in the copper-containing nanoparticles residing on and/or being embedded between carbon nanospikes. In some embodiments, at least a portion (e.g., at least 30, 40, 50, 60, 70, 80, or 90%) of the carbon-containing nanoparticles reside at the tips of the carbon nanospikes. In some embodiments, at least a portion (e.g., at least 30, 40, 50, 60, 70, 80, or 90%) of the carbon-containing nanoparticles are embedded between the carbon nanospikes.

[0029] In one embodiment, the method for depositing copper-containing nanoparticles on the carbon nanospikes is by electronucleation, such as by immersing the CNS substrate into an aqueous or non-aqueous solution containing one or more copper salts, and applying a voltage onto the CNS substrate to reduce copper ions in the copper salt(s) to elemental copper, thus forming copper-containing nanoparticles on the carbon nanospikes. Some examples of copper salts that may be used include copper sulfate (CuSO₄), copper chloride (CuCl₂), copper nitrate (Cu(NO₃)₂), copper acetate (Cu(CH₃COO)₂), copper acetylacetonate (Cu(C₅H₇O₂)₂), copper carbonate (CuCO₃), copper stearate, copper ethylenediamine, copper fluoride (CuF₂), copper-ligand complexes, and their hydrates. In some embodiments, the solution may also contain additional metal salts, in appropriate amounts, to form copper alloy nanoparticles.

[0030] The electronucleation conditions, such as temperature, length of the voltage pulse, copper salt concentration, and pH, can be suitably adjusted to select for nanoparticles of a specific size or morphology. In particular, the voltage pulse can be adjusted to select for a specific particle size, with longer pulses generally producing larger nanoparticles. In typical embodiments, the voltage pulse is no more than 10 or 5 seconds, or more particularly, no more than 1 second, or up to or less than 500, 100, or 50 microseconds, or up to or less than 1 microsecond.

[0031] The concentration of the copper salt in the aqueous solution can be any suitable concentration at which the electrochemical process can function to produce nanoparticles. In different embodiments, the concentration of the

copper salt is precisely or about, for example, 10 nM, 50 nM, 100 nM, 500 nM, 1 μ M, 10 μ M, 100 μ M, 500 μ M, 1 mM, 5 mM, 10 mM, 50 mM, 100 mM, 500 mM, 0.1 M, 0.5 M, or 1M, or up to the saturation concentration of the copper salt(s), or the concentration is within a range bounded by any two of the above exemplary values. In particular embodiments, the concentration of the copper salt is from about 1 mM to 0.1 M.

[0032] The method described herein for producing copper-containing nanoparticles is practiced by contacting the copper salt solution with the CNS substrate and subjecting the copper salt solution to a suitable potential that reduces copper ions into elemental copper. The applied potential should be sufficiently cathodic (i.e., negative), and may be precisely or about, for example, -0.05 V, -0.1 V, -0.2 V, -0.3 V, -0.4 V, -0.45 V, -0.5 V, -0.6 V, -0.7 V, -0.8 V, -0.9 V, -1 V, -1.1 V, or -1.2 V vs. a reversible hydrogen electrode (RHE). In particular embodiments, the applied potential is from about 0.5-1.0 V.

[0033] The temperature of the reaction (i.e., of the aqueous solution during the electronucleation process) can be precisely or about, for example, -10° C., -5° C., 0° C., 15° C., 20° C., 25° C., 30° C., 40° C., 45° C., 50° C., 55° C., 60° C., 65° C., 70° C., 75° C., 80° C., 85° C., 90° C., or 100° C., or a temperature within a range bounded by any two of the foregoing exemplary temperatures. In particular embodiments, the process is conducted at room or ambient temperature, which is typically a temperature of from about 18-30° C., more typically from about 20-25° C., or about 22° C.

[0034] The pH of the aqueous solution can also be selected to help facilitate the formation of nanoparticles. The pH of the aqueous solution typically ranges from 1.5 to 6. In particular embodiments, the pH of the aqueous solution is from about 4 to 6. The pH of the aqueous solution can be adjusted by adding pH-adjusting agents (e.g., strong acids such as sulfuric acid (H₂SO₄) or strong base such as sodium hydroxide (NaOH)).

[0035] To minimize side reactions, the electronucleation process that produces the copper-containing nanoparticles is typically conducted under an inert atmosphere. The inert atmosphere may consist of, for example, nitrogen, helium, or argon gas. Generally, the aqueous solution is purged with the inert gas before and/or during the electronucleation process.

[0036] Generally, the electronucleation process does not require a surfactant, as commonly used in the art to control the nanoparticle size and/or shape. The absence of a surfactant can be advantageous since the resulting copper-containing nanoparticles are then free of surfactants, which may interfere with the electrocatalytic ability. Instead of surfactants, the invention relies on the carbon nanospikes as nucleation points for growing copper nanoparticles, and couples this with voltage pulse time to adjust the size of the nanoparticles.

[0037] In another embodiment, the method for depositing copper-containing nanoparticles on the carbon nanospikes is by a vapor deposition method. The vapor deposition method can be, for example, physical vapor deposition (PVD) or chemical vapor deposition (CVD).

[0038] In another embodiment, the method for depositing copper-containing nanoparticles on the carbon nanospikes is by adsorption of a copper-containing complex onto the CNS substrate and subsequent decomposition of the copper-

containing complex. The method includes immersing the CNS substrate into a solution comprising a copper-containing complex, whereby the copper-containing complex is adsorbed on the surface of the CNS substrate. The decomposition of the copper-containing complex produces discrete copper-containing nanoparticles on the carbon nanospikes. The solution typically includes a copper-containing complex comprising a chelating agent (a polydentate ligand that forms two or more coordinate bonds to the metal in the complex). Some copper-containing complexes useful in the present invention include copper tartrate or copper ethylenediaminetetraacetate (EDTA). The copper complex can be formed prior to its addition to the solution, or it can be formed in the solution, for example, by mixing a copper salt and a chelating agent. The copper salt can include copper sulfate, copper acetate or copper nitrate. In some embodiments, the solution is an aqueous solution, typically a basic solution with a pH of 10 to 13. In other embodiments, the solution includes an organic solvent such as, for example, hexane. The solution is optionally heated to a temperature at which the ligand in the copper complex is stable, e.g., to 60-70° C., to increase adsorption. After formation of the nanoparticles and removal of the CNS substrate from the solution, the CNS substrate can be further heated to decompose the copper-containing complex in a reducing atmosphere containing, for example, hydrogen gas and yield elemental copper or copper alloy nanoparticles.

[0039] In another embodiment, the method for depositing copper-containing nanoparticles on the carbon nanospikes is by electroless deposition. The method includes immersing the CNS substrate in an electroless plating solution containing one or more copper sources, a chelating agent, and a reducing agent. As well known in the art of electroless copper plating, copper ions from the plating solution become selectively reduced at the surface of a substrate in the solution. When applied, for the instant purposes, on a mat of carbon nanospikes, the electroless solution deposits elemental copper nanoparticles on the carbon nanospikes. As well known, the chemical reduction reactions occur without the use of external electrical power. In the event that copper alloy nanoparticles are desired, the electroless plating solution may include such other alloying species. The copper source may be any of the known copper sources useful in an electroless process, e.g., copper sulfate, copper nitrate, copper chloride, or copper acetate. Some examples of chelating agents include Rochelle salt, EDTA, and polyols (e.g., Quadrol® (N,N,N',N'-tetrakis (2-hydroxypropyl) ethylene-diamine)). Some examples of reducing agents include hypophosphite, dimethylaminoborane (DMAB), formaldehyde, hydrazine, and borohydride. Additionally, the plating solution may include a buffer (e.g., boric acid or an amine) for controlling pH and various optional additives, such as bath stabilizers (e.g., pyridine, thiourea, or molybdates), surfactants (e.g., a glycol), and wetting agents. In some embodiments and when the nanoparticles are composed of copper alloys, the plating solution also contains one or more alloying metal sources such as salts of alloying metals. The plating solution is typically basic. The pH of the plating solution can be adjusted, for example, by addition of sodium hydroxide (NaOH), to a pH of 10 to 13. The plating solution can be optionally heated, e.g., to a temperature of 60-80° C.

[0040] In yet another embodiment, the method for depositing copper-containing nanoparticles on the carbon nano-

spikes is achieved by first producing the copper nanoparticles ex situ (i.e., when not in contact with the nanospikes), by any of the methods of nanoparticle production known in the art, and the resulting nanoparticles are deposited on the carbon nanospikes. The copper nanoparticles are typically produced in solution, and the solution of copper nanoparticles subsequently contacted with the carbon nanospikes. The copper nanoparticles will attach to the carbon nanospikes by adsorption, i.e., physisorption.

[0041] In another aspect, the invention is directed to a method of converting CO₂ into ethanol using the electrocatalyst of the present invention. The method includes contacting the electrocatalyst, described above, with CO₂ in an aqueous solution, with the CO₂ in the form of a bicarbonate salt (e.g., by reaction of the carbon dioxide with a metal hydroxide), while the electrocatalyst is electrically configured as a cathode. More particularly, the method includes contacting the above-described electrocatalyst with an aqueous solution of a bicarbonate salt while the aqueous solution is in contact with a source of carbon dioxide, which replenishes the bicarbonate salt as the bicarbonate salt decomposes to CO₂ and a hydroxide salt, and the electrocatalyst is electrically powered as a cathode and is in electrical communication with a counter electrode electrically powered as an anode. A voltage is then applied across the anode and the electrocatalytic cathode in order for the electrocatalytic cathode to electrochemically convert the carbon dioxide to ethanol.

[0042] The electrochemical reduction of CO₂ can be carried out in an electrochemical cell **10**, as depicted in FIG. **1**. The electrochemical cell **10** includes a working electrode (cathode) **12** containing the electrocatalyst of the present invention, a counter electrode (anode) **14**, and a vessel **16**. The counter electrode **14** may include a metal such as, for example, platinum or nickel. The vessel **16** contains an aqueous solution of bicarbonate **18** as the electrolyte and a source of CO₂. The working electrode **12** and the counter electrode **14** are electrically connected to each other and in contact with the aqueous solution **18**. As shown in FIG. **1**, the working electrode **12** and the counter electrode **14** can be completely immersed in the aqueous solution **18**, although complete immersion is not required. The working electrode **12** and the counter electrode **14** only need to be placed in contact with the aqueous solution **18**.

[0043] The vessel **16** includes a solid or gel electrolyte membrane (e.g., anionic exchange membrane) **20** disposed between the working electrode **12** and the counter electrode **14**. The solid electrolyte membrane **20** divides the vessel **16** into a working electrode compartment housing the working electrode **12** and a counter electrode compartment housing the counter electrode **14**.

[0044] The electrochemical cell **10** further includes an inlet **22** through which carbon dioxide gas flows into the aqueous solution **18**. The carbon dioxide gas is made to flow into the aqueous solution **18** at a rate that allows sufficient CO₂ transport to the surface of the working electrode **12** while preventing interference from gas bubbles striking the electrode surface. The flow rate of the CO₂ gas is generally dependent on the size of the working electrode. In some embodiments, the flow rate may be about, at least, or up to, for example, 3, 10, 30, 50, 70, 90, 100, 120, 140, 160, 180, or 200 mL min⁻¹, or within a range bounded by any two of these values. However, for larger scale operations using larger electrodes, the flow rate could be much higher. In

some embodiments, before introducing the CO₂ gas into the vessel 16, the CO₂ gas may be humidified with water by passing the gas through a bubbler to minimize the evaporation of the electrolyte. The carbon dioxide being converted may be produced by any known source of carbon dioxide. The source of carbon dioxide may be, for example, a combustion source (e.g., from burning of fossil fuels in an engine or generator), commercial biomass fermenter, or commercial carbon dioxide-methane separation process for gas wells.

[0045] In some embodiments, the electrochemical cell shown in FIG. 1 is a three-electrode cell that further includes a reference electrode 24 for the measurement of the voltage. In some embodiments, a reference electrode is not included. In a particular embodiment, a silver/silver chloride (Ag/AgCl) or reversible hydrogen electrode (RHE) is used as the reference electrode 24.

[0046] The aqueous solution 18 is formed by dissolving a bicarbonate salt in water. The bicarbonate salt is typically an alkali bicarbonate, such as potassium bicarbonate or sodium bicarbonate. The bicarbonate salt concentration may be precisely or about, for example, 0.05, 0.08, 0.1, 0.2, 0.3, 0.4, 0.5, or 0.6 M, or within a range bounded by any two of these values. In a particular embodiment, the bicarbonate concentration is from 0.1 to 0.5 M. In some embodiments, the bicarbonate salt is not originally present in the aqueous solution 18, but is formed in situ by starting with a hydroxide compound that reacts with carbon dioxide in solution to form the bicarbonate salt, e.g., KOH (in aqueous solution) reacting with CO₂ to form KHCO₃. In some embodiments, the aqueous solution 18 includes a mixture of the metal hydroxide and metal bicarbonate. Notably, at least during the reaction with carbon dioxide, the solution 18 should contain a certain level of metal hydroxide at any given moment, as result of the breakdown of the metal bicarbonate, although the metal hydroxide should quickly react with incoming carbon dioxide to re-form the metal bicarbonate.

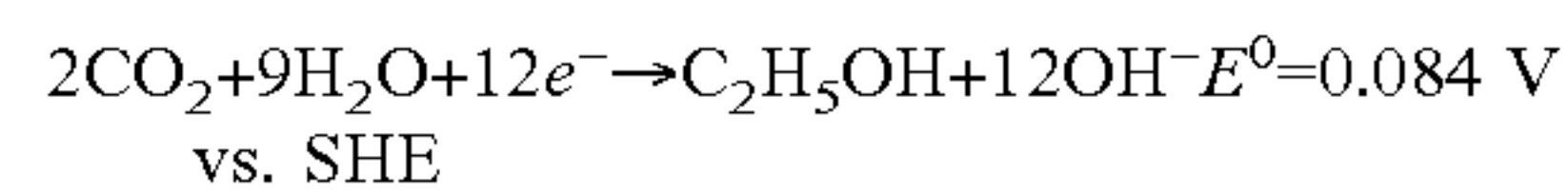
[0047] A negative voltage and a positive voltage are applied to the working electrode 12 and the counter electrode 14, respectively to convert CO₂ to ethanol. Generally, the negative voltage applied to the working electrode 12 may be precisely or about, for example, -0.5, -0.7, -0.9, -1.0, -1.2, -1.4, -1.5, -1.7, -2.0, -2.1, -2.5, -2.7, or -3.0 V with respect to a reversible hydrogen electrode (RHE), or within a range bounded by any two of these values. Generally, the voltage across the working electrode 12 (i.e., cathode) and the counter electrode 14 (i.e. anode) is at least 2 V, or within 2-4 V, or within 2-3.5 V, or within 2-3 V, for converting the CO₂ into ethanol. The voltage can be applied by any method known to those skilled in the art. For example, the voltage can be applied using a potentiostat 26.

[0048] In some embodiments, the CO₂ is converted into a deuterated form of ethanol. The deuterated form of ethanol may contain a portion or all of its hydrogen atoms replaced with deuterium atoms. Some examples of partially deuterated forms of ethanol include CH₃CH₂OD, C₂H₄DOH, and C₂H₃D₂OH, where D represents deuterium. The fully deuterated form of ethanol corresponds to the formula CD₃CD₂OD. Deuterated ethanol can be formed by, for example, dissolving the carbon dioxide in heavy water (deuterium oxide, D₂O which is preferably at least or above 95, 96, 97, 98, 99, 99.5, 99.8, or 99.9 atom % D D₂O) instead

of water (H₂O), and/or using deuterated bicarbonate salts, such as KD₂CO₃ in place of KHCO₃, as needed, in the aqueous solution 18.

[0049] The electrocatalyst of the present invention generally exhibits a higher selectivity for CO₂ electroreduction than H₂ evolution, with a subsequent high Faradaic efficiency in producing ethanol. In the present application, CO₂ is reduced to produce ethanol in primary abundance. Other species, such as hydrogen, methane, and carbon monoxide, may be produced in much lower abundance. Generally, the electrocatalytic process according to the invention advantageously produces ethanol with no ethane or ethylene being produced. The ethanol is generally produced in a yield of at least 60%, 65%, 70%, 75%, or 80% relative to the total products produced, as measured by electron current. Thus, the other species, such as hydrogen, methane, and carbon monoxide, may be produced individually or in sum total amount not exceeding 40%, 35%, 30%, 25%, or 20%.

[0050] Without wishing to be bound by theory, the high efficiency in producing ethanol may result both from an increase in the intrinsic CO₂ reduction activity of copper and from a synergistic interaction between copper-containing nanoparticles and neighboring carbon nanospikes. The major CO₂ reduction product is ethanol, which corresponds to a 12 e⁻ reduction with H₂O as the H⁺ source, where E is the equilibrium potential. The total reaction is:



[0051] The electrocatalyst of the present invention can advantageously operate at room temperature and in water, and can be turned on and off easily. Electrolytic syntheses enabled by the electrocatalyst of the present invention could provide a more direct, rapidly switchable and easily implemented route to distributed liquid fuel production powered by variable renewable energy sources, such as wind and solar.

[0052] Examples have been set forth below for the purpose of illustration and to describe certain specific embodiments of the invention. However, the scope of this invention is not to be in any way limited by the examples set forth herein.

EXAMPLES

Example 1

Preparation of Carbon Nanospikes

[0053] The carbon nanospikes were grown on n-type 4-inch Si wafers {100} with As doping (<0.005Ω) via PECVD in the presence of acetylene (C₂H₂) and ammonia (NH₃) at 650°C for 30 minutes. DC plasma was generated between the wafer (cathode) and the showerhead (anode) in a continuous stream of C₂H₂ and NH₃ gas, flowing at 80 sccm and 100 sccm, respectively. The total pressure was maintained at 6 Torr with a plasma power of 240 W.

[0054] The carbon nanospikes were characterized as a dense nanotextured carbon film terminated by randomly oriented nanospikes approximately 50-80 nm in length, where each nanospike consists of layers of puckered carbon ending in a ~2 nm wide curled tip. Raman spectra indicated that carbon nanospikes have similar structure to disordered, multilayer graphene. XPS indicated nitrogen doping density as 5.1±0.2 atomic %, with proportions of pyridinic, pyrrolic

(or piperidinic) and graphitic nitrogens of 26, 25 and 37% respectively, with the balance being oxidized nitrogen.

Example 2

Preparation of Cu/CNS Electrocatalyst

[0055] Cu nanoparticles were electronucleated from CuSO_4 directly onto carbon nanospikes, and imaged via SEM. These well-dispersed Cu nanoparticles have sizes ranging from about 30 nm to 100 nm with average size of 39 nm, with a density ca. 1.2×10^{10} particles cm^{-2} . According to the average particle size, the coverage of Cu on carbon nanospikes is ca. 14.2%. High-resolution TEM on scraped samples (HR-TEM), as provided in FIG. 2, illustrates the Cu nanoparticle and carbon nanospike interface, which indicates a close proximity between Cu nanoparticles and the carbon nanospikes. A lower magnification TEM image (FIG. 2, inset) confirms the particle size observed via SEM. The lattice spacing of this representative copper nanoparticle was measured as 0.204 nm, which is consistent with copper. A Cu_2O composition with lattice spacing ca. 0.235 nm was present on surfaces of the copper nanoparticles, likely resulting from exposure to air during sample preparation and transportation between measurements. Electronic Energy Loss Spectroscopy (EELS) measurements indicate a graphitic carbon, and confirm the CNS wrapped around the Cu nanoparticles, as shown in FIG. 2.

Example 3

Stability of Cu/CNS Electrocatalyst

[0056] To investigate the short-term stability of the Cu/CNS electrocatalyst, additional HR-TEM images and EELS spectra were taken after a 6-hour CO_2 reduction reaction, and no obvious changes were observed. Likewise, X-ray Photoelectric Spectroscopy (XPS) measurements for Cu $2p_{3/2}$ showed a similar asymmetric peak at 932 eV, which indicates that the Cu nanoparticles were stable after a 6-hour reaction and were mainly comprised of Cu^0 . However, after a 6-hour electroreduction, the fraction of graphitic-N significantly decreased (38.9 to 10.7%), while pyridinic-N and pyrrolic/amine-N increased (14.2 to 24.7% and 39.6 to 54.2%, respectively). While XPS cannot distinguish between pyrrole and amine, electroreduction from pyridinic-N to pyrrolic-N would require removal of a C atom; therefore, the increased pyrrolic/amine-N is likely piperidine, with no increase in pyrrolic fraction. No change in electrochemical activity was observed during this prolonged electroreduction.

Example 4

Carbon Dioxide Reduction

[0057] A customized electrochemical cell made from polycarbonate was employed for CO_2 electrolysis experiments. The cell maintained the working electrode parallel to the counter electrode to achieve a uniform voltage. An anion exchange membrane was used to separate the working and counter electrode compartments to prevent the oxidation of reduced CO_2 products. The cell was designed to have a small electrolyte volume (8 mL) in each of the two compartments, along with a gas headspace of approximately 2 mL above the electrolyte on each side of the membrane. CO_2 , regulated by

a mass flow controller at 3 mL min^{-1} , flowed through the cell during electrolysis. CO_2 flow through the cell was used to observe large current efficiencies for CO_2 reduction products, presumably because of mass transport limitations in a quiescent cell. The flow rate of 3 mL min^{-1} was chosen to ensure sufficient CO_2 transport to the surface while preventing interference from gas bubbles

striking the surface. The CO_2 was humidified with water by passing it through a bubbler before it entered the electrolysis cell in order to minimize the evaporation of electrolyte. For each

electrolysis experiment, the cell was assembled with Cu/CNS electrocatalyst as the working electrode (i.e., Cu/CNS electrode) and platinum as the counter electrode. An Ag/AgCl electrode was used as the reference. The distance between the working and reference electrodes was kept ca. 0.5 cm to reduce solution resistance. A 0.1 M solution of KHCO_3 was prepared with 18.2 M Ω -cm deionized water from a Millipore™ system and used as the electrolyte. The pH of the electrolyte purged with CO_2 was 6.8. Electrolysis was carried out with a Biologic VSP potentiostat (VMP3), using the chronoamperometry (CA) method. All electrochemical data was collected vs. an Ag/AgCl reference and converted to a reversible hydrogen electrode (RHE) scale by $V_{\text{vs. RHE}} = V_{\text{measured vs. Ag/AgCl}} + 0.222 + 0.059 \times \text{pH}_{\text{electrolyte}}$. EC-Lab™ software was used to link different techniques without returning to open circuit for each electrolysis experiment. In order to generate detectable amounts of products, the electrolysis potential using a chronoamperometry protocol was applied for 1 hour in a typical experiment and for 6 hours for stability test

Example 5

Electroreduction Activity of Cu/CNS Electrocatalyst

[0058] CO_2 electroreduction activity was first measured by linear sweep voltammetry (LSV) in the potential range -0.00 to -1.30 V vs. RHE in the presence of CO_2 saturated electrolyte, as shown in FIG. 3. Larger current densities were obtained in Cu/CNS electrode than either Cu/C-Film or bare CNS electrodes, and the onset potential for CO_2 reduction for Cu/CNS electrode was $\sim 0.3 \text{ V}$ more positive than CNS without Cu particles. As shown in FIG. 3, two well-defined reduction waves appeared at -0.9 V and -1.20 V vs. RHE in Cu/CNS LSV curves.

[0059] To investigate the mechanism of the electrochemical reaction, 60-minute chronoamperometry (CA) measurements were conducted over a potential range from -0.7 to -1.3 V , which included these two reduction waves. New electrodes were fabricated for each data point. The gaseous and liquid products of each CA run were analyzed by gas chromatography (GC) and NMR (of headspace and electrolyte, respectively) to calculate overall current density and Faradaic efficiency for CO_2 reduction and for each product. The overall sustained current density for CO_2 reduction, $J_{\text{CO}_2 \text{ redn}}$ was increased with more negative potential in all three electrodes consistent with that shown in LSV curves. Cu/CNS electrode had greater propensity for CO_2 reduction than either Cu/C-Film and bare CNS electrodes, for instance, $J_{\text{CO}_2 \text{ redn}}$ from Cu/CNS electrode was 5-fold higher than for bare CNS and 3-fold higher than for Cu/C-Film, at -1.2 V .

[0060] The fractional Faradaic efficiency was computed by dividing the total electrons into each product (determined independently by chemical analysis) by the total electrons passed during the amperometry experiment. Due to experimental losses between the anode and cathode, the total fractions are less than 100%. The fractional Faradaic efficiency is shown in FIG. 4.

[0061] At -0.9 V vs. RHE and more positive potential, only gas phase products H_2 , CO and CH_4 were obtained from all three electrodes. At -1.0 V vs. RHE and more negative potential, ethanol was produced as a liquid, soluble in the aqueous electrolyte. Trace formic acid was occasionally detected by NMR. Remarkably, ethanol is the only liquid phase product from Cu/CNS, and is not detectable from Cu/C-Film and bare CNS control electrodes. Ethanol, as a C2 product, requires carbon-carbon coupling at some point during the reduction reaction. In comparison, neither control electrode produced C2 products, only C1 products CO and CH_4 . Efforts were made to observe other products more commonly produced by copper electroreduction, such as methanol, ethane or ethylene but none were detected by either GC or NMR.

[0062] Examining the breakdown of Faradaic efficiencies for various reactions on Cu/CNS electrode, reveals that at -1.2 V, ethanol conversion exhibited the highest efficiency at 63% (that is, 63% of the electrons passing through the electrode were stored as ethanol). Also at -1.2 V vs. RHE, the Faradaic efficiency of gas phase products methane and CO dropped to 6.8% and 5.2%, respectively. The Faradaic efficiency of CO_2 reduction (competing against water reduction) is 75%. This means that under the best conditions, the overall selectivity of the reduction mechanism for conversion of CO_2 to ethanol is 84%.

[0063] As shown by the plots in FIG. 5, the fraction current density for each product exhibited volcanic shape dependence to the potentials applied on the Cu/CNS electrode. The maximum current density for methane was observed at -1.0 V vs. RHE, and decreased when ethanol generation began. Then the current for ethanol generation increased with more negative potential until reaching a summit at -1.2 V vs. RHE, where Cu/CNS electrode attained the highest overall CO_2 reduction efficiency. At more negative potential, current density for ethanol and other products from CO_2 reduction remained comparable; however, the Faradaic efficiency value of CO_2 to ethanol conversion declined while the value for H_2 evolution increased significantly. The decline of Faradaic efficiency was the result of the catalysts reaching the mass-transport-limited current density for CO_2 reduction and therefore hydrogen evolution via H_2O reduction at unoccupied active sites.

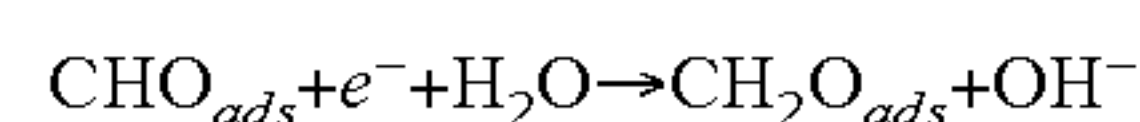
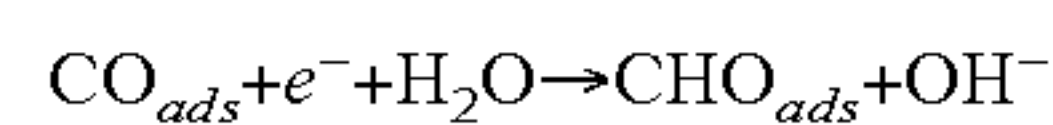
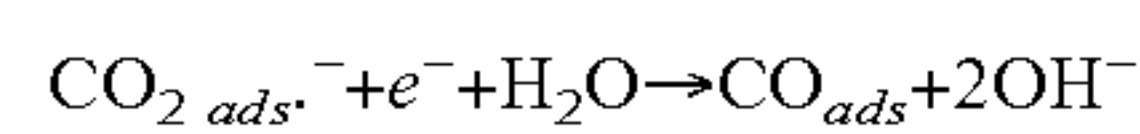
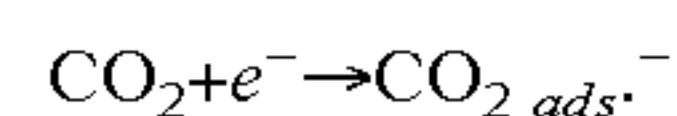
[0064] Previous reports of CO_2 electroreduction on copper have demonstrated a variety of C1 and C2 products, including CO, CH_4 , CH_2O_2 , ethane, ethylene, ethanol. Heavier hydrocarbons have not been reported. C2 products are hypothesized to form through coupling of CO radicals on the surface of the copper, and a high percentage output of C2 products would indicate a rapid coupling of Cu-bound C1 intermediates, or possibly an electron transfer process that is coupled to C—C bond formation between surface-bound C1 intermediates species and a nearby CO in solution. Ordinarily, on bulk copper the coupled C2 would continue to be reduced to ethane or ethylene so long as the product was in contact with the copper electrode. In contrast, with this

experiment, ethanol has been observed as the only C2 product, which indicates the presence of a reaction mechanism that precludes further reduction to ethane.

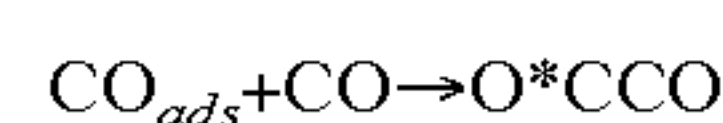
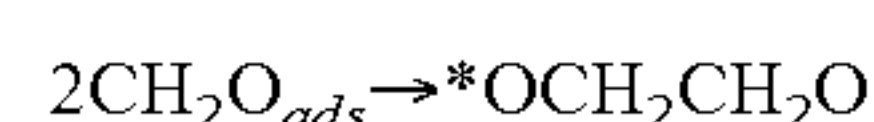
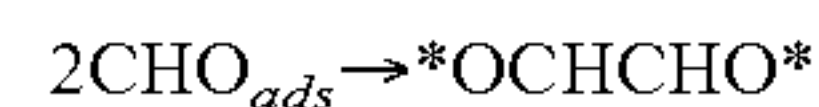
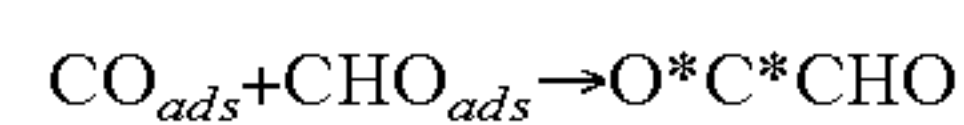
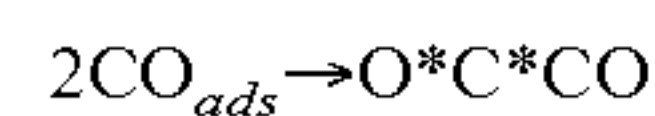
[0065] The hypothesis is that three electrochemically active species are present in Cu/CNS electrocatalysts: (i) Cu nanoparticles, (ii) the various nitrogen dopants present in the carbon nanospikes, and (iii) partially positive-charged carbon atoms immediately adjacent to the nitrogen dopants (termed alpha-C) in the carbon nanospikes. It is predicted that there is a strong interaction between Cu nanoparticle and carbon, and it is expected to extend to carbon nanospikes as well. The strong interaction provides an environment in which a reaction mechanism involving reactive sites on the Cu surface and on the N-doped carbon nanospikes may dominate. In this environment, the close proximity and strong interactions promote transfer of intermediate C2 species from the Cu surface to the N-doped carbon nanospikes. Although measuring the precise distance between Cu nanoparticles and carbon nanospikes was not possible, the contact appears to be direct and intimate according to the HR-TEM images.

[0066] This transfer is important because the electronic structure near the Fermi level of graphene is modified in N-doped carbon nanospikes, where localized π electronic states are reported to form at the neighboring carbon atoms, and propagate anisotropically around the defect due to the perturbation of the π -conjugated system. Due to electron-withdrawing effects in the graphene π -conjugated system, the alpha-C atoms adjacent to nitrogen are positively polarized. This polarization provides an active site for the C2 intermediates to adsorb.

[0067] Concerning the reaction mechanism, following electron transfer to Cu-adsorbed CO_2 to form $CO_2^{ads\cdot-}$, this anionic radical is reduced to CO_{ads} , or other C1 intermediates (CHO_{ads} or CH_2O_{ads}) on the Cu surface:



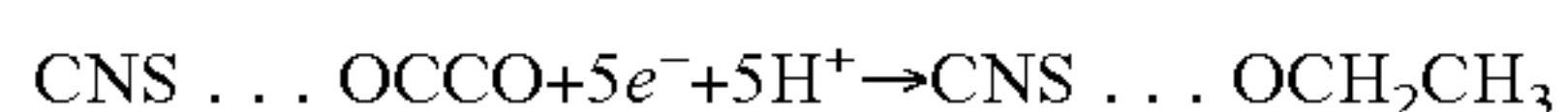
CO and methane will result from further electron transfer to these surface species, whereas C—C coupling may occur among two surface adsorbed intermediates or between a surface species and a CO from solution. At -1.2 V vs RHE, the major product is C2 indicating that at a high enough rate of production of CO radical, C2 coupling is the dominant outcome.



Once coupled C2 products are formed, they reduce only to ethanol. In order for ethanol to be the only C2 product, a mechanism must be available that limits the electroreduction to prevent the formation of ethane.

[0068] To confirm whether nitrogen dopants and the neighboring alpha-C atoms in the carbon nanospikes can effectively adsorb the C2 intermediates, first-principles density functional theory (DFT) calculations were conducted. As carbon nanospikes have similar structure to multilayer graphene, a graphene sheet was adopted to model the interaction between carbon nanospikes and the C2 intermediates (such as OCCO) for simplicity without losing the essence of the physics. For a pristine graphene sheet, the calculations suggest the binding energy between OCCO and graphene is 0.19 eV with a separation distance ~ 2.95 Å. Interestingly, for N-doped graphene, the N dopant and adjacent alpha-C atoms become indeed more active so that the binding energy with OCCO is increased to 0.64 eV with the separation distance shortened to ~ 2.70 Å. The tripling of the binding energy to 0.64 eV clearly indicates that the C2 intermediates can be adsorbed by N-doped carbon nanospikes fairly strongly and may not desorb easily at room temperature. Furthermore, it is significant that the carbon nanospikes are puckered and curled, which indicates local corrugation on the surface. It has been shown that local deformation or buckling could enhance the molecular adsorption on carbon nanotubes and graphene. The buckling of pristine and N-doped graphene were considered when investigating the local curvature effect on OCCO adsorption. Upon buckling, the binding energy between OCCO and the concave of pristine graphene is increased to 0.34 eV, while the binding energy between OCCO and the concave of N-doped graphene is enhanced to 0.74 eV. Therefore, the corrugation and curvature naturally embedded into carbon nanospikes appear to strengthen the binding between carbon nanospikes and the C2 intermediates.

[0069] Consequently, it is expected that the nearby N-dopant and alpha-C in the carbon nanospikes, which is in intimate contact with the Cu surface, adsorbs one of the C2 carbonyls. Further electroreduction then occurs preferentially on the other C2 carbonyl at the Cu surface:



[0070] At this stage, the two carbon atoms in the intermediate species OCH_2CH_3 are saturated, while the oxygen atom becomes non-saturated. As a result, calculations show that the CNS-oxygen bond changes from fairly strong physisorption to much stronger chemisorption, and the separation distance is reduced to 1.48 Å. XPS indicates that some graphitic-N is electrochemically reduced to piperidinic-N during a prolonged electroreduction experiment. According to calculations, the binding energy between OCCO and piperidinic-N doped graphene is ~ 0.62 eV, similar to that between OCCO and graphitic-N doped graphene (~ 0.64 eV). Therefore the reaction mechanism should occur similarly between both sites. Now there are two routes for further reduction: the cleavage of the CNS-oxygen bond to produce ethanol; or the cleavage of the C—O bond in OCH_2CH_3 to form ethane. The former reduction route is much more energetically favorable (more stable by 1.59 eV), consistent with the experiment observation that ethanol is the only C2 product. Hence further reduction cleaves the CNS—oxygen bond on the first carbonyl, producing ethanol.

[0071] FIG. 6 depicts the possible reaction pathways after adsorption of ethoxide (intermediate species) on the electrocatalyst. The intermediate species OCH_2CH_3 (a) is chemically adsorbed on N-doped CNS. Two routes for further electroreduction are illustrated: the cleavage of the

CNS-oxygen bond to produce ethanol (b), or the cleavage of the C—O bond in OCH_2CH_3 to form ethane (c).

[0072] The overall reduction mechanism is illustrated in FIG. 7. In this mechanism, the novel functionality is due primarily to the proximity of multiple reactive sites, which is in turn due to the nanostructured morphology of the electrocatalyst. This demonstrates that the selectivity of a reaction can be tuned solely based on morphology and distance between reactive sites. The change in product output with varying potential also yields some insight into the mechanism. At low potentials, alcohol is not produced nor is any C2 product. This is likely due to the rate limiting step being the first reduction of CO_2 on the Cu surface. At higher overpotential, the concentration of reduced CO species on the Cu surface is increased, yielding a greater likelihood of C2 coupling and subsequent ethanol production. At lower concentrations of CO species, no coupling occurs and the product partially reduces to CO or fully reduces to methane. This reaction mechanism is supported by in situ, electrochemical Raman measurements. Without applied potential, only a CO_3^{2-} stretching band at 1020 cm^{-1} was observed on Cu/CNS electrode (in addition to the broad G band at 1610 cm^{-1} and D band at 1370 cm^{-1} from multilayer graphene in CNS substrate). This observation may correspond to adsorbed CO_3^{2-} on CNS or bicarbonate in the bulk electrolyte. When a negative potential was applied, the peaks at 1460 and 1520 cm^{-1} immediately arose, which indicates that surface intermediates were being generated. These peaks could be assigned to C—H stretching and CH_3 deformation, respectively, in agreement with the electrochemical experiments. At -1.2 V or more negative potential, a new peak arose at 1070 cm^{-1} , which is assigned to alkoxyl or alcohol. This peak appeared immediately as the potential was applied and disappeared when the potential was removed. Hence, the foregoing observation may be a result of surface adsorbed species rather than products diffused into the electrolyte. Considering that ethanol was the only detectable product in solution, the peak at 1070 cm^{-1} may be assigned to ethoxyl C—O stretching in ethanol or its intermediate precursor.

[0073] While there have been shown and described what are at present considered the preferred embodiments of the invention, those skilled in the art may make various changes and modifications which remain within the scope of the invention defined by the appended claims.

What is claimed is:

1. An electrocatalyst comprising (i) carbon nanospikes and (ii) copper-containing nanoparticles residing on and/or embedded between said carbon nanospikes, wherein said carbon nanospikes are doped with a dopant selected from the group consisting of nitrogen, boron, and phosphorous.
2. The electrocatalyst of claim 1, wherein said carbon nanospikes contain layers of puckered carbon.
3. The electrocatalyst of claim 1 wherein at least a portion of the carbon nanospikes contain a straight or curled tip.
4. The electrocatalyst of claim 3, wherein said straight or curled tip has a width ranging from 0.5 nm to 3 nm.
5. The electrocatalyst of claim 1, wherein said carbon nanospikes have a length ranging from 20 nm to 100 nm.
6. The electrocatalyst of claim 1, wherein said electrocatalyst is disposed on a semiconductive substrate or a conductive substrate.
7. The electrocatalyst of claim 1, wherein said electrocatalyst is electrically connected to a counter electrode.

8. The electrocatalyst of claim 1, wherein said copper-containing nanoparticles comprise copper or a copper alloy.

9. The electrocatalyst of claim 1, wherein said copper-containing nanoparticles have a size ranging from 1 nm to 500 nm.

10. The electrocatalyst of claim 1, wherein said copper-containing nanoparticles are present on said carbon nanospikes in a density ranging from 0.5×10^{10} particles/cm² to 3.0×10^{10} particles/cm².

11. The electrocatalyst of claim 1, wherein a concentration of the dopant in said nanospikes is from 3 atomic % to 9 atomic %.

12. A method of producing an electrocatalyst for converting carbon dioxide to ethanol, the method comprising;
providing a mat of carbon nanospikes protruding outwardly from a surface of said mat, wherein said carbon nanospikes are doped with a dopant selected from the group consisting of nitrogen, boron, and phosphorous;
and
forming copper-containing nanoparticles on and/or between said carbon nanospikes.

13. The method of claim 12, wherein said copper-containing nanoparticles are formed by immersing said mat of carbon nanospikes into an aqueous solution containing a copper salt, and applying a reducing voltage onto said mat of carbon nanospikes to reduce copper ions in said copper salt to elemental copper.

14. The method of claim 12, wherein said copper nanoparticles are formed by physical or chemical vapor deposition of copper.

15. The method of claim 12, wherein said copper nanoparticles are formed by electroless deposition of copper from a solution containing a copper salt and a reducing agent, wherein said solution is in contact with said mat of carbon nanospikes.

16. The method of claim 12, wherein said copper nanoparticles are formed ex situ and deposited on said mat of carbon nanospikes.

17. A method of converting carbon dioxide into ethanol, the method comprising contacting an electrocatalyst with an aqueous solution of a bicarbonate salt while said aqueous

solution is in contact with a source of carbon dioxide, which replenishes said bicarbonate salt as said bicarbonate salt decomposes to carbon dioxide and a hydroxide salt at a surface of said electrocatalyst, and said electrocatalyst is electrically powered as a cathode and is in electrical communication with a counter electrode electrically powered as an anode, wherein a voltage across said cathode and said anode is within a range of 2 to 4 volts, to convert said carbon dioxide into ethanol; wherein said electrocatalyst comprises (i) carbon nanospikes and (ii) copper-containing nanoparticles residing on and/or embedded between said carbon nanospikes, wherein said carbon nanospikes are doped with a dopant selected from the group consisting of nitrogen, boron, and phosphorous.

18. The method of claim 17, wherein said ethanol is deuterated ethanol.

19. The method of claim 17, wherein said electrocatalyst is housed in a first compartment of an electrochemical cell, wherein said first compartment contains said aqueous solution in contact with said electrocatalyst; said counter electrode is housed in a second compartment of said electrochemical cell, wherein said second compartment also contains said aqueous solution, and said first compartment and second compartment are separated by a solid electrolyte membrane.

20. The method of claim 17, wherein said bicarbonate salt is KHCO₃ or NaHCO₃.

21. The method of claim 17, wherein said bicarbonate salt has a concentration ranging from 0.1 M to 0.5 M.

22. The method of claim 17, wherein said carbon dioxide is bubbled into said aqueous solution before or during said electrocatalyst is in contact with said aqueous solution.

23. The method of claim 17, wherein said ethanol is produced in a yield of at least 60% relative to total product produced, as measured by electron current.

24. The method of claim 17, wherein no ethane or ethylene is produced.

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