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(54) Title: CATALYTIC HYDROGEN PRODUCTION

(57) Abstract: The present disclosure provides a method of producing hydrogen. The method includes heating a mixture comprising a metal component exhibiting a nanostructured surface, water, and carbon dioxide.

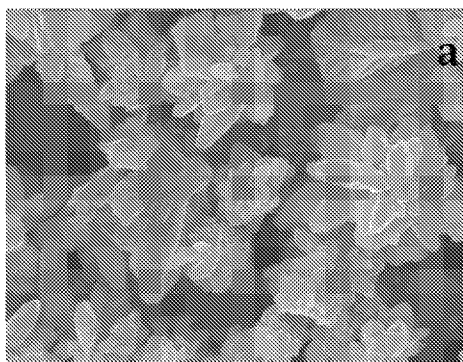


FIG. 1A



CATALYTIC HYDROGEN PRODUCTION

PRIORITY APPLICATION

5 **[0001]** This application claims priority to U. S. Provisional Application Serial Number 62/473,756, filed March 20, 2017, the disclosure of which is incorporated herein in its entirety by reference.

BACKGROUND

10 **[0002]** Hydrogen is considered to present opportunities for environmentally friendly energy production. One of the challenges associated with using hydrogen as an energy carrier is the efficient production of hydrogen. It would be desirable to establish simple protocols for the production of acceptably pure hydrogen.

SUMMARY OF THE DISCLOSURE

15 **[0003]** The present disclosure provides a method of producing hydrogen. The method includes heating a mixture comprising a metal component exhibiting a nanostructured surface, water, and carbon dioxide or carbonate.

20 **[0004]** The present disclosure further provides a kit for producing hydrogen. The kit includes a mixture having a metal component exhibiting a nanostructured surface, a quantity of water, and a quantity of carbon dioxide.

25 **[0005]** There are several advantages associated with various embodiments of the method and kit of the present disclosure, some of which are unexpected. For example, according to various embodiments of the present disclosure, hydrogen gas of high purity can be obtained. Additionally, according to various embodiments of the present disclosure, a metal or metal compound with a synthesized nanostructured surface can be an important component for hydrogen production. According to various embodiments of the present disclosure, the metal or metal compound with a synthesized nanostructured surface can help to produce hydrogen of a higher purity than a corresponding metal component that has a nanostructured surface formed from acid, base, or laser etching. For example, according to 30 various embodiments of the present disclosure a purity of the hydrogen produced ranges from about 20% (V/V) to about 98% (V/V). Other advantages, according to various embodiments of the present disclosure include a total lack of, or any significant amount of, carbon monoxide (CO) produced that might act as a poison if the hydrogen is used in fuel cells.

According to various embodiments of the present disclosure, there is potential for continuous production of hydrogen with a flow through reactor. According to various embodiments of the present disclosure, a method or system including the metal employs commonly available feedstocks (e.g., water, carbon dioxide, and cobalt) and is substantially free of highly toxic materials and does not produce toxic waste materials. According to various embodiments of the present disclosure, systems and methods using the metal do not require high temperatures or pressures. According to various embodiments of the present disclosure cobalt can be recycled for reuse in the reaction system.

BRIEF DESCRIPTION OF THE FIGURES

[0006] The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments discussed in the present document.

[0007] FIGs. 1A-1D are SEM images of synthesized nanostructured cobalt particles at four different magnifications: (a) 20,000 X, (b) 15,000 X, (c) 8,000 X, and (d) 2,200 X.

[0008] FIG. 2 is a graph showing amounts of produced H_2 with different gases at different pressures.

[0009] FIG. 3 is a graph showing amounts of H_2 produced with different gases at different pH values.

[0010] FIG. 4 is a graph showing amounts of produced H_2 at different reaction times.

[0011] FIG. 5 is a graph showing amounts of produced H_2 at different NaOH concentrations.

DETAILED DESCRIPTION

[0012] Reference will now be made in detail to certain embodiments of the disclosed subject matter, examples of which are illustrated in part in the accompanying drawings. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that the exemplified subject matter is not intended to limit the claims to the disclosed subject matter.

[0013] Throughout this document, values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of “about 0.1% to about 5%” or “about 0.1% to 5%” should be

interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement “about X to Y” has the same meaning as “about X to about Y,” unless indicated otherwise. Likewise, the statement “about X, Y, or about Z” has the same meaning as “about X, about Y, or about Z,” unless indicated otherwise.

[0014] In this document, the terms “a,” “an,” or “the” are used to include one or more than one unless the context clearly dictates otherwise. The term “or” is used to refer to a nonexclusive “or” unless otherwise indicated. The statement “at least one of A and B” has the same meaning as “A, B, or A and B.” In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section.

[0015] In the methods described herein, the acts can be carried out in any order without departing from the principles of the disclosure, except when a temporal or operational sequence is explicitly recited. Furthermore, specified acts can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed act of doing X and a claimed act of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

[0016] The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range, and includes the exact stated value or range.

[0017] The term “substantially” as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more, or 100%.

[0018] In the search for sustainable cleaner energy carrier, hydrogen is considered as an intriguing future energy carrier, overcoming the environmental impact and sustainability issues associated with fossil fuels. Photocatalytic splitting of water has drawn major attention in the low-cost production of hydrogen with the use of sunlight as the energy source. One way to accomplish the photocatalytic splitting of water is with a TiO₂ based photocatalyst. The band gap of TiO₂ (3.2 eV) requires the use of ultraviolet (UV) light in the photodissociation of water, even though the energy required to dissociate water (1.23 V) can

be provided by infrared (IR) radiation. Photocatalysts developed in recent decades show greater efficiency with UV light compared to the photocatalysts developed for work under visible light. Because solar radiation contains only about 4 % UV light, recent research has paid much attention to the development of photocatalysts that harness visible light, which has a 43 % solar radiation contribution.

[0019] This disclosure can provide a system or method for producing higher hydrogen purity levels. As described further herein, the gaseous phase in the reactors used for hydrogen production was internally monitored in the identification of various gaseous intermediates and products. In some examples, the amount of H₂ produced in the reactions was about 30.5 % (v/v) of H₂ or even 98.4 %. Hence, the disclosed reaction setup was useful for generating hydrogen to feed a fuel cell for the production of cleaner energy with a sustainable energy source. The absence or limited amount of CO production with produced H₂ can be beneficial since even a small amount of CO present in the H₂ stream (few parts per million) can lead to the poisoning of Pt anodes in fuel cells causing a large loss of efficiency. As disclosed herein, the production of H₂ can proceed free of irradiation.

[0020] According to various embodiments of the present disclosure, a method of producing hydrogen includes disposing a metal component exhibiting a nanostructured surface, a quantity of carbon dioxide, and water in a reaction vessel. Once the components are disposed in the reaction vessel, the pH of the vessel is brought to basic conditions the temperature of the reaction vessel is increased. The reaction vessel can be a stainless steel or glass container that is configured to allow or block the transmission of light into the reaction vessel.

[0021] Various components used in conjunction with the method can account for different quantities of the composition in the reaction vessel. For example, the quantity of the metal component in the reaction vessel can be in a range from about 0.3 g to about 100 kg. However, the amount of the metal component can be any suitable amount for production of different quantities of H₂. The metal component can include an elemental metal or alloy thereof. In some examples the metal component can include a metal oxide. The elemental metal or alloy thereof can be in a range from about 0.01 wt% to about 100 wt% of the metal component, about 80 wt% to about 100 wt%, 95 wt% to about 100 wt%, or less than, equal to, or greater than about 0.01 wt%, 0.5, 1, 10, 20, 30, 40, 50, 60, 70, 75, 80, 85, 90, 95, or 100 wt%.

[0022] The metal component can include one or more metals or alloys thereof. For example, the metal component can include at least one of the elements Co, Ti, Ru, Rh, Pd, Os, Ir, La, Ce, Fe, Cu, and Ni or an alloy thereof. In various embodiments the metal component can include substantially 100 wt% cobalt or an alloy thereof.

5 **[0023]** The metal component can act to initiate and maintain the formation of the hydrogen in some embodiments. Without intending to be bound to any theories, the inventors believe that the formation of the nanostructured surface on the metal component contributes to the formation of the hydrogen. The nanostructured surface can have a plurality of features having any suitable configuration. As shown in FIGs. 1A-1D, each of the plurality of features
10 of the nanostructured surface has a nanoleaf configuration. Each of the features can have different nanoscale dimensions. For example, each of the nanostructures can have the following dimensions: about 1 nm to about 1,000 nm in length, about 1 nm to about 1,000 nm in height, and about 1 nm to about 1,000 nm in thickness.

[0024] The metal component is synthesized through a chemical process. This is a so
15 called “bottom up” approach in that the nanostructured surface is formed through a chemical process building nanomaterials from molecules, ions or metal atoms. This is directly contradictory to other examples of metal components, which include nanostructured surfaces formed through chemical or laser etching techniques—so called “top down” approaches. Examples of metal components made through top-down approaches are described in United
20 States Published Patent Application No. 2012/0097521 to (“Shen”).

[0025] The nanostructured surface of the metal component formed through a top-down approach is different than those of a metal component formed from a bottom-up approach. As can be seen in FIGs. 1A-1D, the nanostructured surface of the metal components have a nanoleaf structure. In contrast, the nanostructured surface of the metal
25 components of Shen, formed by acid, base, or laser etching have a nanospike or nanoflake structure.

[0026] The nanostructured surface of the metal component of the instant disclosure is formed by reacting a metal salt with a reducing agent. The metal can be any one of the metals described herein. The anion can be any suitable anion such as chloride, bromide, iodide,
30 fluoride, nitrate, sulfide, sulfate, perchlorate and the like. In examples where the metal is cobalt, the salt can be at least one of CoCl_2 , $\text{Co}(\text{NO}_3)_2$, CoSO_4 , and mixtures thereof. The reducing agent can be one of many suitable reducing agents such as N_2H_4 , $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, NaBH_4 ,

sodium dithionite, sodium hypophosphite, lithium aluminum hydride, tin (II) salts, hydrogen, and mixtures thereof.

[0027] After the nanostructured surface of the metal component is formed, the metal component can be “aged” for a period of time before use in the hydrogen producing reaction.

5 The metal component can be aged for any suitable amount of time. For example, the metal component can be aged for a time ranging from about 1 day to 15 days, 2 days to 10 days, less than, equal to, or greater than 1 day, 2, 3, 4, 5, 6, 7, 8, 9, or 10 days. The metal component can be aged for example in an oven under vacuum or in the presence or absence of oxygen.

10 **[0028]** The amount of each component in the reaction vessel can be selected from many suitable amounts. Generally, the amount of each component can depend on the size of the reaction vessel or the amount of hydrogen to be produced.

[0029] The carbon dioxide is supplied to the reaction vessel as a gas. The pressure of the carbon dioxide in the reaction vessel can be in a range from about atmospheric pressure or
15 0 psi above ambient to about 250 psi, about 15 psi to about 50 psi, about 20 psi to about 40 psi, less than, equal to, or greater than about, 10 psi, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 200, 205, 210, 215, 220, 225, 230, 235, 240, 245, or 250 psi.

[0030] The amount of water in the reaction vessel can be any appropriate amount.
20 While not so limited, the quantity of the water in the reaction vessel can range from about 200 μL to about 5000 μL , about 500 μL to about 1000 μL , less than, equal to, or greater than about 200 μL , 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350, 1400, 1450, 1500, 1550, 1600, 1650, 1700, 1750, 1800, 1850, 1900, 1950, 2000, 2050, 2100, 2150, 2200, 2250, 2300, 2350, 2400,
25 2450, 1500, 2550, 2600, 2650, 2700, 2750, 2800, 2850, 2900, 2950, 3000, 3050, 3100, 3150, 3200, 3250, 3300, 3350, 3400, 3450, 3500, 3550, 3600, 3650, 3700, 3750, 3800, 3850, 3900, 3950, 4000, 4050, 4100, 4150, 4200, 4250, 4300, 4350, 4400, 4450, 4500, 4550, 4600, 4650, 4700, 4750, 4800, 4850, 4900, 4950, or 5000 μL . The wt% of the water relative to the other components can range from about 0.01 wt% to about 60 wt%. Additionally, the water can be
30 continuously introduced in the reaction vessel.

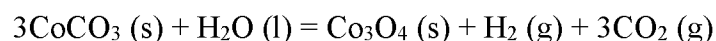
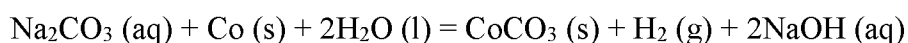
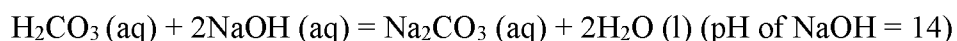
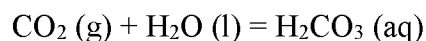
[0031] In addition to the components described herein, other components can be added to the reaction vessel. It can be desirable to keep the pH within the reaction vessel above 7.

[0032] Once the components are in the reaction vessel, the temperature of the vessel is increased. The temperature of the reaction vessel can be increased to a temperature ranging from about 100 °C to about 350 °C, about 130 °C to about 170 °C, less than, equal to, or greater than 100 °C, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 225, 230, 235, 240, 245, 250, 255, 260, 265, 270, 275, 280, 285, 290, 295, 300, 305, 310, 315, 320, 325, 330, 335, 340, 345, or 350 °C.

[0033] With all the components present and the temperature increased, the reaction begins. The reaction can be allowed to proceed continuously or for any suitable finite amount of time. For example, a quantity of the metal component can be placed in a reactor. Water and carbon dioxide can be continuously supplied to the reactor. The continuous supply of water and carbon dioxide to the metal component in the reactor can produce a stream of H₂. This process can be configured to run for any suitable amount of time. For example, the reaction can run for a time period ranging from about 0.5 hours to about 100 hours, about 20 hours to about 94 hours, about 60 hours to about 80 hours, less than, equal to, or greater than 0.5 hours, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 100 hours. Additionally, longer times are contemplated within the scope of this disclosure.

[0034] Without intending to be bound to any theory, the inventors believe that the production of hydrogen is driven by the thermal decomposition of water with the oxidation of the metal component having the nanostructured surface as catalyzed by the carbon dioxide.

The production of hydrogen may be explained by the reactions below in which the metal component includes cobalt:



[0035] A purity of the hydrogen produced from the reaction ranges from about 20% (v/v) to about 99% (v/v), 25% (v/v) to about 35% (v/v), less than, equal to, or greater than 20 % (v/v), 25, 30, 35, 40, 45 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or 99 % (v/v). The inventors have found that the purity of the hydrogen produced by the methods described herein, using the metal component including the nanostructured surface formed from the bottom-up procedures is greater than that of hydrogen produced according to a corresponding method

wherein the metal component exhibiting a nanostructured surface is produced by acid etching, base etching, or laser etching, or no etching.

[0036] The methods described herein can be carried out by individually adding each component to the reaction vessel. In further embodiments, however, a kit including the metal component, water, and carbon dioxide can be produced and the reaction can be triggered by increasing the temperature of the kit.

Examples

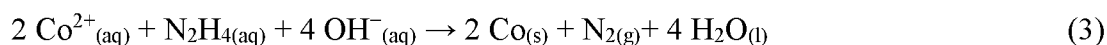
[0037] Various embodiments of the present disclosure can be better understood by reference to the following Examples which are offered by way of illustration. The present disclosure is not limited to the Examples given herein.

Example 1.1 Materials

[0038] In the synthesis of the nanostructured cobalt metal component, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (J.T. Baker), hydrazine monohydrate, 98+% (Alfa Aesar) and NaOH were used. Deionized water (18.2 MΩ, Elga, Purelab-Option Q) was used in all the synthesis steps. Except where noted, all chemicals were analytical reagent grade and used without further purification.

Experiment 1.2 Synthesis of nanostructured cobalt particles

[0039] The synthesis was an aqueous phase reduction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with excess hydrazine hydrate in a basic medium. The stoichiometric reaction in the reduction of Co^{2+} to Co metal with hydrazine is given below.



[0040] In order to obtain nanostructures on the synthesized Co particles, excess hydrazine and NaOH were used by modifying the above stoichiometric ratio as shown below.



[0041] Dissolved $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ in water is reddish pink in color. After introducing excess hydrazine and NaOH, a vigorous reaction occurs overflowing the reaction vessel.

[0042] In the synthesis of the nanostructured cobalt, a mixture of NaOH and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was prepared with concentrations of 5.44 M and 17.01 M, respectively. A 25.0 mL portion of the NaOH/ N_2H_4 mixture was added to 50 mL of 0.34 M Co^{2+} solution while stirring the reaction mixture at 400 rpm and maintaining the temperature at 80 °C. After about 45 minutes, the cobalt particles were collected by holding a magnet on the outside wall of the reaction flask and pouring off the reaction mixture. This was followed by washing the cobalt particles with deionized water. The cobalt particles were dried in a vacuum oven overnight at 70 °C before conducting experiments.

10 Example 2.1 Characterization of nanostructured cobalt particles

Example 2.2 SEM characterization

[0043] Scanning Electron Microscopy (SEM) images of the synthesized catalyst were taken using a JEOL JSM-7401F Field Emission Scanning Electron Microscope at 10.0-15.0 kV. Sharp features/nanostructures on the surface of the cobalt particles could be observed as shown in FIGs. 1A-1D.

Example 2.2 TEM characterization

[0044] TEM characterization of the synthesized cobalt particles was done using a Philips EM400T transmission electron microscope at 100 kV. According to the TEM images, it could be observed that the bulk of the cobalt particles were irregular in shape and the size was in the micrometer range. The crystalline structure of the particles could be observed from the electron diffraction pattern.

25 Example 3.1 Hydrogen production experiments

[0045] In the experiments, the nature of the H_2 production reaction (photochemical or thermal), the effect of CO_2 and its pressure, the effect of pH in the reaction medium and other reaction parameters were studied for the optimum production of H_2 .

[0046] The stainless steel reactor is basically a hollow metal cylinder, which is capped with a threaded plug at one end. The other end of the cylinder is sealed with a stainless steel threaded nut fitted with stainless steel tubing, which is connected to a pressure gauge. A T-connector in the stainless steel tubing allows pressurizing the reactor with a desired gas and sampling the gaseous products through a septum. Heating tape wrapped

around the cylinder and connected to a controller, which regulates heating of the reactor to a desired temperature. The exact temperature of the reactor was measured with a thermocouple placed against the outside wall of the cylinder under the heating tape. After about 18 hours of reaction time, the gaseous phase of the reactor was analyzed by injecting 1 mL of gaseous sample into the Peak Performer-1 H₂ and CO analyzer.

[0047] Dilutions of the injected samples were performed as necessary to stay within the calibration range.

Example 3.2 Optimization of reaction parameters

[0048] Reaction parameters (i.e. amount of water, CO₂ pressure, reaction time and pH of the reaction medium) were optimized to obtain higher conversion efficiencies for the production of H₂. The role of CO₂ in the production of H₂ was studied by carrying out experiments with Ultra High Purity (UHP) He and atmospheric gases as the pressurizing gas instead of CO₂.

[0049] Even though the production of H₂ was first detected when the reactors were pressurized with CO₂, the role of CO₂ in the final product of interest here (e.g., H₂) was not clear. Hence, the importance of CO₂ and its pressure in the reactor were evaluated. Four different experiments were carried out by changing the type of gas and its pressure as given in Table 1.

Table 1: Experimental conditions used in determining the role of CO₂ in H₂ production.

Type of gas used	Pressure	Amount of water (μL)	Mass of catalyst (g)	Reaction time (hours)	Final temp (°C)
CO ₂	40 psi	700	0.6012	19	116.5
UHP He	40 psi	700	0.6080	19	116.5
Air	40 psi	700	0.6061	19	116.5
Air	1 atm	700	0.6081	19	116.5

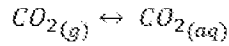
[0050] The amounts of H₂ produced in each experiment listed in Table 1 are given in FIG. 2. According to FIG. 2, it can clearly be seen that CO₂ and elevated pressure in the system play a major role in the production of H₂. When CO₂ was present in the system, the production of H₂ was the highest. The amounts of produced H₂ were higher at elevated pressure (air at 40 psi) compared to the lower pressure (air at 1 atm) in the system.

[0051] It is understood that the production of H_2 from water by the oxidation of zero valent iron particles under mild hydrothermal conditions is possible. In those instances, the CO_2 acts as a catalyst in the process for the production of H_2 .

[0052] The formation of $CoCO_3$ in the reaction chambers could be visually noticed after about 18 hours with the appearance of pink islands on the black catalytic bed. The formation of $CoCO_3$ was further demonstrated by Thermo Gravimetric Analysis (TGA) by analyzing $CoCO_3$ standards and the cobalt catalyst before and after the thermal decomposition reaction.

[0053] According to the TGA data, the loss of weight at around 250 °C in the cobalt catalyst obtained after the reaction can be correlated with the loss of the weight in the $CoCO_3$ standard. The weight gain after about 300 °C in the cobalt catalyst used in the H_2 production can be correlated to the weight gain obtained with the freshly prepared cobalt catalyst. The weight gain of the cobalt catalyst at elevated temperatures may be due to the oxidation of the catalyst with trace amounts of O_2 present in the carrier gas as a contaminant. Hence, it is possible that some of the cobalt catalyst has converted to $CoCO_3$ in the H_2 production process. Since the two TGA curves obtained with $CoCO_3$ standards and with the cobalt catalyst used in the H_2 production process show different patterns of weight loss and temperature changes, further confirmation is necessary for the formation of $CoCO_3$.

[0054] The necessity of CO_2 in the production of H_2 was further confirmed by carrying out reactions at different pH values. The pH of water due to the dissolution of H_2CO_3 formed from water and CO_2 at 40 psi pressure was calculated as described below:



Applying Henry's Law

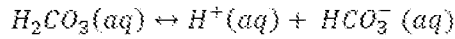
$$P_{CO_2} \times K_H = [CO_{2(aq)}]$$

$$\begin{aligned} P_{CO_2} \text{ in the system} &= 40 \text{ psi} - 14.70 \text{ psi} \\ &= 25.29 \text{ psi} \\ &= 1.72 \text{ atm} \end{aligned}$$

$$1.72 \text{ atm} \times 3.4 \times 10^{-2} M/\text{atm} = [CO_{2(aq)}]$$

$$[CO_{2(aq)}] = 5.848 \times 10^{-2} M$$

Assuming all the $CO_{2(aq)}$ is in the form of H_2CO_3 .



$$K_a = \frac{[H^+(aq)] \times [HCO_3^-(aq)]}{[H_2CO_3(aq)]}$$

$$2.65 \times 10^{-7} = \frac{[H^+(aq)]^2}{5.848 \times 10^{-2} - [H^+(aq)]}$$

$$[H^+(aq)] = 1.243 \times 10^{-4} M$$

$$\text{pH} = 3.90$$

[0055] Hence, the pH of water in the reactor reached around 3.90 due to the dissolution of CO_2 at 40 psi of CO_2 pressure. If the production of H_2 in the system is due to the low pH achieved with the dissolution of CO_2 and not due to the formation of $CoCO_3$, an experimental setup with pH adjusted to 3.9 should be able to produce the same amount of H_2 in the absence of CO_2 . Hence, an experiment was carried out with the pH of the water adjusted to 3.91 and the system pressurized with ultra-high purity helium (UHP He) instead of CO_2 . Two control experiments were carried out with water without adjusting the pH and pressurizing them with CO_2 and UHP He. The reaction conditions used in the three reactions are given in Table 2.

Table 2: Reaction conditions used for experiments to determine the role of CO_2 on the pH of the system.

Type of gas used	Pressure	Amount of water (μL)	pH of water	Reaction time (hours)	Final temp ($^{\circ}\text{C}$)
UHP He	40 psi	700	3.915	17.5	86
CO_2	40 psi	700	6.043	17.5	86
UHP He	40 psi	700	6.043	17.5	86

[0056] The amounts of produced hydrogen for each experimental condition are shown in FIG. 3. According to FIG. 3, it can be noted that the low pH without CO₂ does not produce high amounts of H₂ as when CO₂ is present in the system. Hence, the role of CO₂ in the system is not merely lowering the pH, but rather CO₂ is participating in the reaction as an active reactant or catalyst for the production of H₂.

[0057] The production of H₂ at 30.5 % (V/V) in reactors was first observed with a 120 hours reaction time. Hence, the optimization of reaction time for the production of H₂ was crucial. Four different experiments were carried out at 20 h, 44 h, 68 h and 94 h time durations and the produced H₂ was measured for each experimental setup (FIG. 4).

According to FIG. 4, the production of H₂ seems to reach a maximum around 27 % (V/V) in 44 to 68 h timeframe. Hence, the production of H₂ was then optimized by changing the amount of base in the reaction medium.

[0058] It was noted above that lower pH did not favor the production of H₂ in the reactors over near neutral pH. The production of H₂ with basic pH was then tested since basic pH promotes the dissolution of acidic CO₂ and favors the formation of CoCO₃. Five experiments were carried out at different NaOH concentrations and the production of H₂ was monitored over 20 h (Table 3). Produced H₂ at each experimental condition is shown in FIG. 5.

Table 3: Experimental conditions used in the optimization of amount of base for the production of H₂.

CO ₂ Pressure	NaOH concentration	Amount of NaOH (μL)	Mass of catalyst (g)	Reaction time (hours)	Final temp (°C)
40 psi	0	-	0.6120	20	101.1
40 psi	1.25	700	0.6152	20	101.1
40 psi	2.5	700	0.6159	20	101.1
40 psi	3.75	700	0.6052	20	101.1
40 psi	6.25	700	0.6190	20	101.1

[0059] According to the FIG. 5, it can be noticed that the highest amount of H₂ production was obtained with 3.75 M NaOH in 20 hours. Production of 27.5 % (V/V) of H₂ at neutral pH took about 68 h of reaction time. Hence, the reaction time can be shortened by one third to obtain the same or even higher H₂ production with the introduction of a basic medium.

[0060] The decrease in the production of H₂ at higher NaOH concentrations (6.25 M) may be due to the dissolution of all the CO₂ in the reactor and lowering the pressure in the system. With previous experiments, it was demonstrated that elevated pressure was necessary for the production of H₂.

5

Example 3.3 Further optimization of reaction parameters

[0061] In further examples hydrogen was produced using a system substantially in line with that described in Example 3.1. Reagents included cobalt, NaOH, and CO₂. The reagents were heated to a set temperature and the amount of hydrogen produced was determined. The amount of hydrogen produced by varying the temperature or reagent parameters was studied and the results are presented in the Tables 4-11 herein.

10

Table 4: Hydrogen production under optimized condition (using NaOH solution):

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.7 g	3 M	55 mL	60 psi	238	58.5 %
2.7 g	3 M	55 mL	70 psi	237.7 °C	68.8 %
2.7 g	3 M	55 mL	100 psi	240	98.4 %*

15 * 0.001452 ppm carbon monoxide was produced.

Table 5: Impact on H₂ production by changing the amount of cobalt

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.7 g	1 M	55 mL	60 psi	238	44 %
2 g	1 M	55 mL	60 psi	239	32 %

20 Table 6: Impact on H₂ production by changing the NaOH concentration

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.7 g	1 M	55 mL	60 psi	238	44 %
2.7 g	3 M	55 mL	60 psi	238	58 %

Table 7: Impact on H₂ production by changing the amount of water

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.7 g	3 M	18.5 mL	60 psi	237.8 °C	16 %
2.7 g	3 M	55 mL	60 psi	238	58 %

Table 8: Impact on H₂ production by changing the amount of water and keeping the same millimoles of NaOH (source of hydrogen is water):

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.7 g	1 M	55 mL	60 psi	238	44 %
2.7 g	3 M	18.5 mL	60 psi	237.8 °C	16 %

5 Table 9: Impact on H₂ production by changing the pressure of CO₂ supplied:

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.7 g	1 M	55 mL	40 psi	238	18 %
2.7 g	1 M	55 mL	50 psi	238	33 %
2.7 g	1 M	55 mL	60 psi	238	44 %

Table 10: Impact on H₂ production by changing the final temperature:

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.7 g	1 M	55 mL	60 psi	213	26 %
2.7 g	1 M	55 mL	60 psi	238	44 %

10 Table 11: Optimization of final temperature:

Amount of cobalt	Concentration of NaOH	Volume of NaOH solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂
2.3 g	1 M	40 mL	40 psi	195	9.4 %
2.3 g	1 M	40 mL	40 psi	217	17 %
2.3 g	1 M	40 mL	40 psi	226	18.37 %

Example 3.4 Further optimization of reaction parameters

- 15 **[0062]** In further examples hydrogen was produced using a system substantially in line with that described in Example 3.1. Reagents included cobalt, NaOH, and Na₂CO₃. The reagents were heated to a set temperature and the amount of hydrogen produced was determined. The amount of hydrogen, CO, and CO₂ produced by varying the temperature or reagent parameters was studied and the results are presented in Table 12 herein.

Table 12: Hydrogen production using Na₂CO₃ solution (no CO₂ supplied):

Amount of cobalt	Concentration of Na ₂ CO ₃	Volume of Na ₂ CO ₃ solution	Pressure of CO ₂ supplied	Final Temperature	Percentage of H ₂	Amount of CO ₂ (ppm)	Amount of CO (ppm)
2.7 g	3 M	55 mL	0 psi	240 °C	31.5 %	3860	2.7

[0063] The terms and expressions that have been employed are used as terms of

description and not of limitation, and there is no intention in the use of such terms and

expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the

embodiments of the present disclosure. Thus, it should be understood that although the present disclosure has been specifically disclosed by specific embodiments and optional

features, modification and variation of the concepts herein disclosed may be resorted to by

those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of embodiments of the present disclosure.

Additional Embodiments.

[0064] The following exemplary embodiments are provided, the numbering of which is not to be construed as designating levels of importance:

[0065] Embodiment 1 provides a method of producing hydrogen, the method comprising:

heating a mixture comprising:

a metal component exhibiting a nanostructured surface,

water,

at least one of carbon dioxide and carbonate.

[0066] Embodiment 2 provides the method of producing hydrogen of Embodiment 1, further comprising contacting the metal component, the water, and the carbon dioxide.

[0067] Embodiment 3 provides the method of any one of Embodiments 1-2, wherein the metal component comprises an elemental metal or alloy thereof.

[0068] Embodiment 4 provides the method of Embodiment 3, wherein the elemental metal or alloy thereof ranges from about 1 wt% to about 100 wt% of the metal component.

[0069] Embodiment 5 provides the method of Embodiment 3, wherein the elemental metal or alloy thereof ranges from about 80 wt% to about 100 wt% of the metal component.

[0070] Embodiment 6 provides the method of Embodiment 3, wherein the elemental metal or alloy thereof comprises at least one of Co, Ti, Ru, Rh, Pd, Os, Ir, La, Ce, Fe, Cu, and Ni.

[0071] Embodiment 7 provides the method of Embodiment 6, wherein the elemental metal or alloy thereof is Co.

[0072] Embodiment 8 provides the method of Embodiment 7, wherein the Co is formed by reacting a cobalt salt with a reducing agent.

[0073] Embodiment 9 provides the method of Embodiment 8, wherein the cobalt salt is at least one of perchlorate, CoCl_2 , $\text{Co}(\text{NO}_3)_2$, and CoSO_4 .

[0074] Embodiment 10 provides the method of Embodiment 8, wherein the reducing agent is at least one of N_2H_4 and NaBH_4 , sodium dithionite, sodium hypophosphite, lithium aluminum hydride, tin (II) salts, and hydrogen.

[0075] Embodiment 11 provides the method of any one of Embodiment 3-10, wherein the metal component is magnetic.

[0076] Embodiment 12 provides the method of any one of Embodiments 1-11, wherein a pH of the mixture is above 7.

[0077] Embodiment 13 provides the method of any one of Embodiments 1-12, wherein a pH of the mixture is above 9.

[0078] Embodiment 14 provides the method of any one of Embodiments 1-13, wherein the nanostructured surface comprises a plurality of features each independently having dimensions of about 1 nm to about 1,000 nm in length, about 1 nm to about 1,000 nm in height, and about 1 nm to about 1000 nm in thickness.

[0079] Embodiment 15 provides the method of any one of Embodiment 1-14, wherein the nanostructured surface of the metal component formed by a method free of acid etching, base etching, or laser etching.

[0080] Embodiment 16 provides the method of any one of Embodiment 1-15, wherein a pressure, in an environment of the mixture, ranges from about 0 psi to about 250 psi.

[0081] Embodiment 17 provides the method of any one of Embodiment 1-18, wherein the quantity of the metal component in the mixture ranges from about 0.01 wt% to about 60 wt% of the mixture.

[0082] Embodiment 18 provides the method of any one of Embodiment 1-17, wherein the quantity of the water of the mixture ranges from about 30 wt% to about 99 wt% of the mixture.

[0083] Embodiment 19 provides the method of any one of Embodiment 1-18, wherein a temperature of the reaction vessel is increased to about 350 °C.

[0084] Embodiment 20 provides the method of Embodiment 19, wherein a temperature of the reaction vessel is increased from about 100 °C to about 200 °C.

5 [0085] Embodiment 21 provides the method of any one of Embodiments 1-20, wherein the method is conducted in the substantial absence of light.

[0086] Embodiment 22 provides the method of any one of Embodiment 1-21, wherein a purity of the hydrogen produced ranges from about 20% (v/v) to about 99% (v/v).

10 [0087] Embodiment 23 provides the method of Embodiment 22, wherein a purity of the hydrogen produced is about 30% (v/v).

[0088] Embodiment 24 provides the method of Embodiment 22, wherein the purity of the hydrogen is greater than that of hydrogen produced according to a corresponding method wherein the metal component exhibiting a nanostructured surface in a reaction vessel is produced by acid etching, base etching, or laser etching.

15 [0089] Embodiment 25 provides the method of any one of Embodiments 1-24, wherein the metal component is elemental Co and the temperature of the reaction vessel is increased from about 119 °C to about 140 °C.

[0090] Embodiment 26 provides the method of Embodiment 22, wherein the Co is formed by reacting CoCl_2 with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$.

20 [0091] Embodiment 27 provides a kit for performing the method of any one of Embodiment 1-26, the kit comprising a mixture comprising:

the metal component exhibiting a nanostructured surface;

the quantity of water; and

the quantity of carbon dioxide.

25 [0092] Embodiment 28 provides the kit of Embodiment 27, wherein the mixture is sufficient to produce hydrogen upon an increase of a temperature of the kit.

[0093] Embodiment 29 provides the kit of Embodiment 28 wherein a purity of the hydrogen produced ranges from about 20% (v/v) to about 99% (v/v).

CLAIMS

What is claimed is:

1. A method of producing hydrogen, the method comprising:
heating a mixture comprising:
 - 5 a metal component exhibiting a nanostructured surface,
water, and
at least one of carbon dioxide and carbonate.
2. The method of producing hydrogen of claim 1, further comprising contacting the
10 metal component, the water, and the carbon dioxide.
3. The method of claim 1, wherein the metal component comprises an elemental metal
or alloy thereof.
- 15 4. The method of claim 3, wherein the elemental metal or alloy thereof ranges from
about 1 wt% to about 100 wt% of the metal component.
5. The method of claim 3, wherein the elemental metal or alloy thereof ranges from
about 80 wt% to about 100 wt% of the metal component.
20
6. The method of claim 3, wherein the elemental metal or alloy thereof comprises at
least one of Co, Ti, Ru, Rh, Pd, Os, Ir, La, Ce, Fe, Cu, and Ni.
7. The method of claim 6, wherein the elemental metal or alloy thereof is Co.
25
8. The method of claim 7, wherein the Co is formed by reacting a cobalt salt with a
reducing agent.
9. The method of claim 8, wherein the cobalt salt is at least one of perchlorate, CoCl_2 ,
30 $\text{Co}(\text{NO}_3)_2$, and CoSO_4 .

10. The method of claim 8, wherein the reducing agent is at least one of N_2H_4 and NaBH_4 , sodium dithionite, sodium hypophosphite, lithium aluminum hydride, tin (II) salts, and hydrogen.
- 5 11. The method of claim 3, wherein the metal component is magnetic.
12. The method of claim 1, wherein a pH of the mixture is above 7.
13. The method of claim 1, wherein a pH of the mixture is above 9.
- 10 14. The method of claim 1, wherein the nanostructured surface comprises a plurality of features each independently having dimensions of about 1 nm to about 1,000 nm in length, about 1 nm to about 1,000 nm in height, and about 1 nm to about 1000 nm in thickness.
- 15 15. The method of claim 1, wherein the nanostructured surface of the metal component formed by a method free of acid etching, base etching, or laser etching.
16. The method of claim 1, wherein a pressure in an environment of the mixture ranges from about 0 psi to about 250 psi.
- 20 17. The method of claim 1, wherein the quantity of the metal component in the mixture ranges from about 0.01 wt% to about 60 wt% of the mixture.
18. The method of claim 1, wherein the quantity of the water of the mixture ranges from
25 about 30 wt% to about 99 wt% of the mixture.
19. The method of claim 1, wherein a temperature of the reaction vessel is increased to about 350 °C.
- 30 20. The method of claim 19, wherein a temperature of the reaction vessel is increased from about 100 °C to about 350 °C.

21. The method of claim 1, wherein the method is conducted in the substantial absence of light.
22. The method of claim 1, wherein a purity of the hydrogen produced ranges from about
5 20% (v/v) to about 99% (v/v).
23. A kit for performing the method of claim 1, the kit comprising a mixture comprising:
the metal component exhibiting a nanostructured surface;
the quantity of water; and
10 the quantity of carbon dioxide.
24. The kit of claim 23, wherein the mixture is sufficient to produce hydrogen upon an increase of a temperature of the kit.
- 15 25. The kit of claim 24 wherein a purity of the hydrogen produced ranges from about 20% (v/v) to about 99% (v/v).

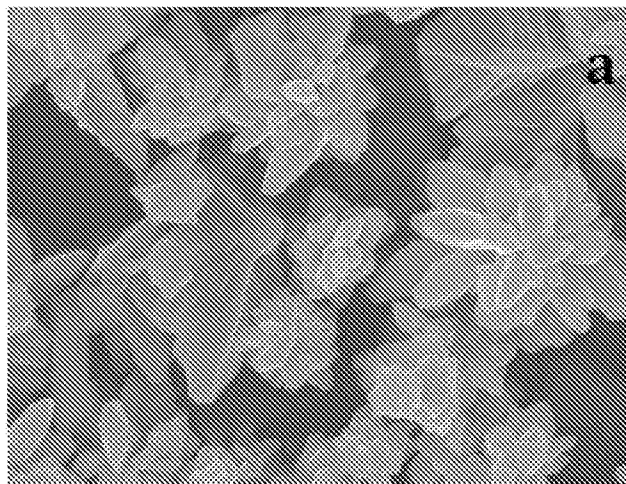


FIG. 1A

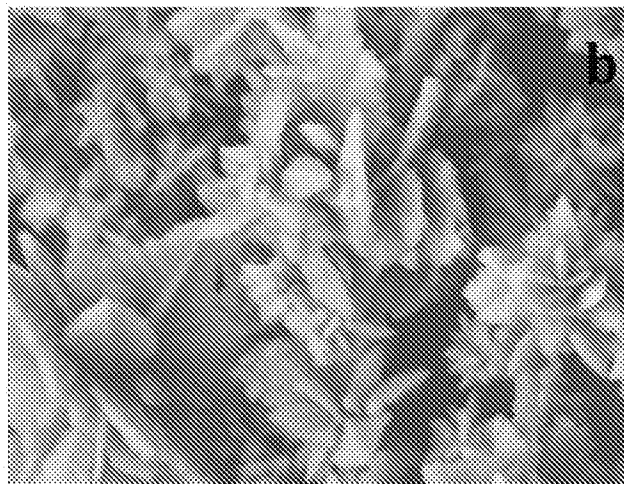


FIG. 1B

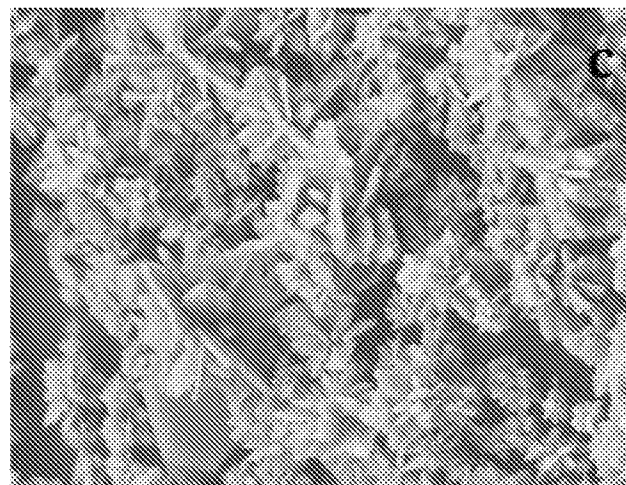


FIG. 1C



FIG. 1D

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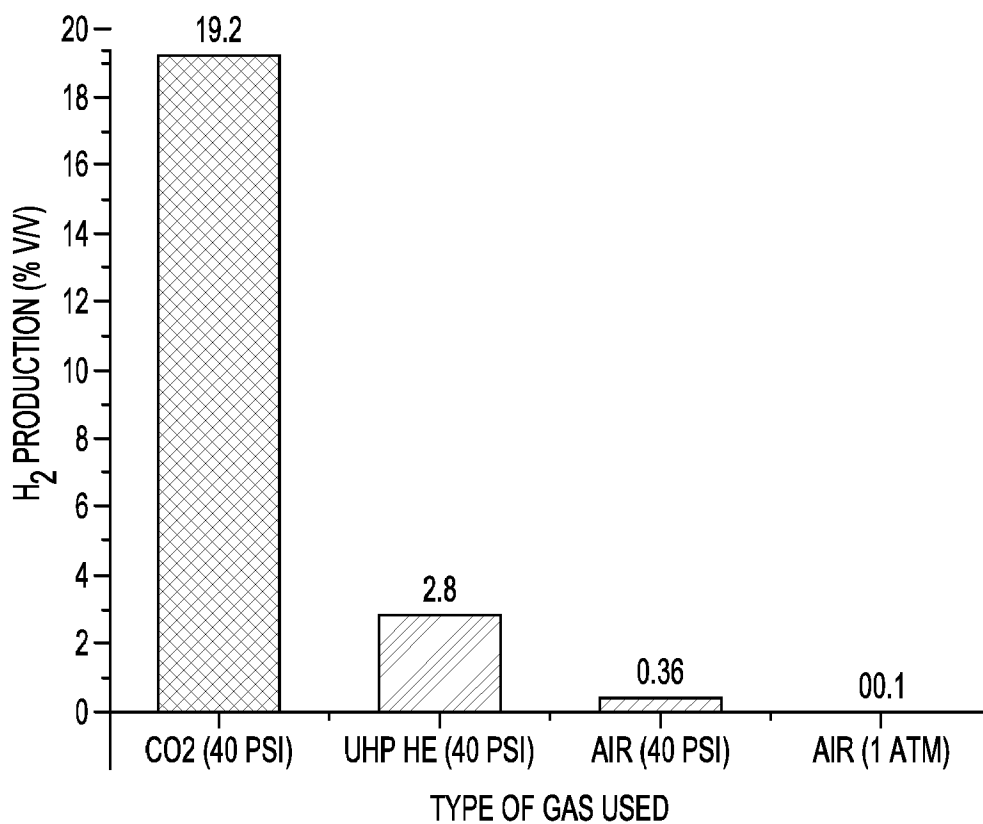


FIG. 2

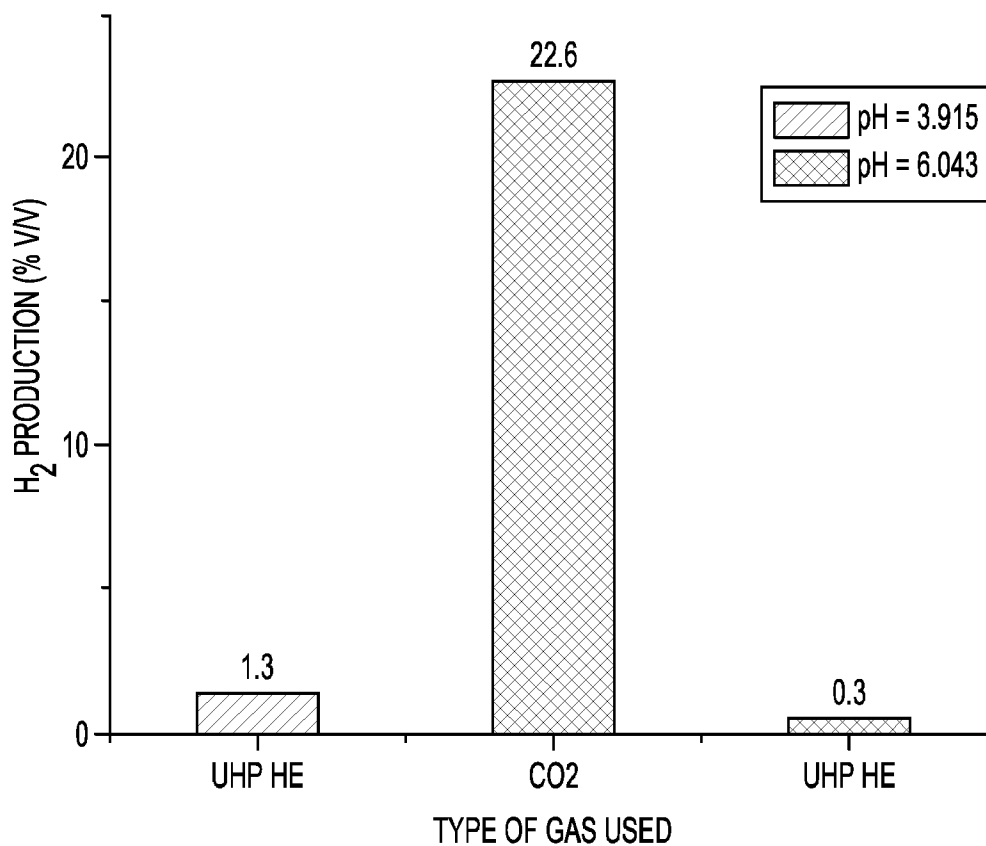


FIG. 3

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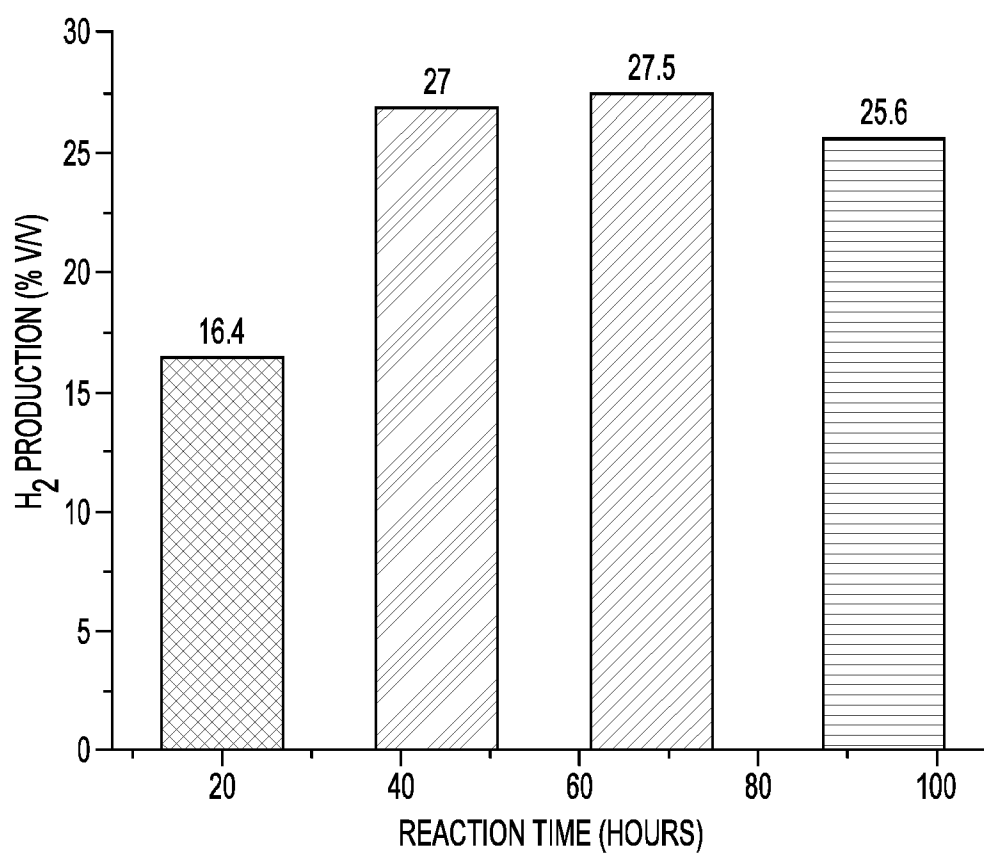


FIG. 4

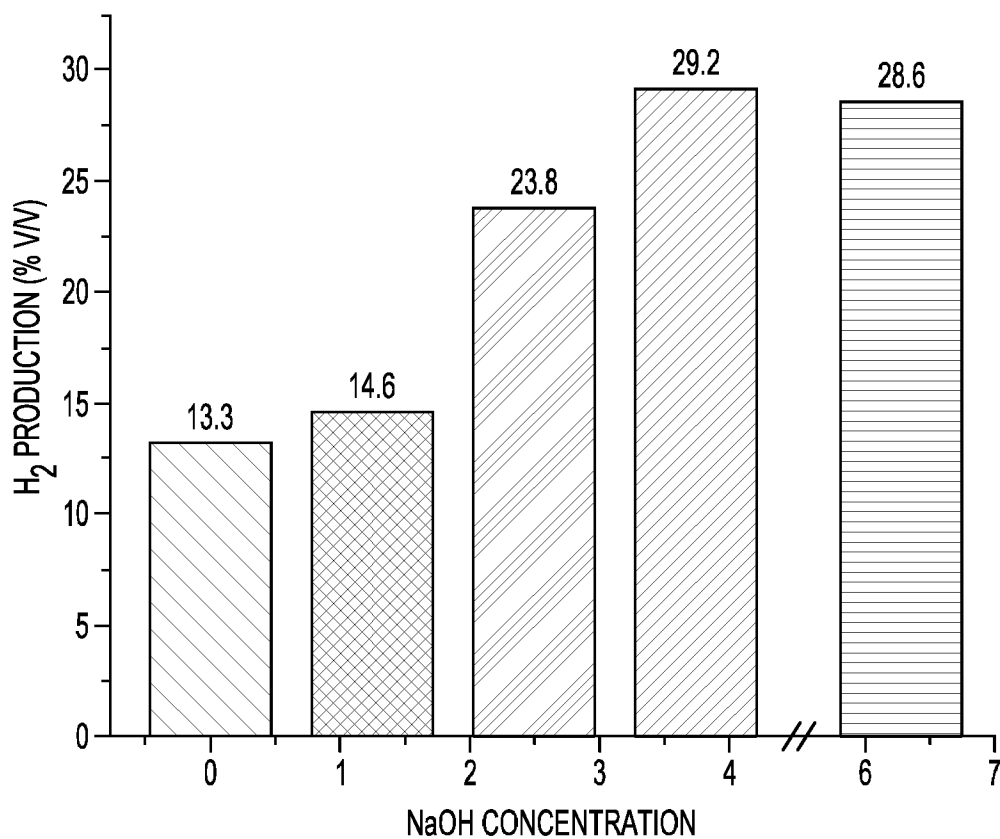


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/023380

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 23/75; C01B 3/08; C01B 3/40; C01G 51/00 (2018.01)

CPC - C01B 3/08; B01J 23/75; C01B 3/40; C01B 2203/1052; C01G 51/00 (2018.05)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

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

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JAYAMANNA, Abiotic photosynthetic production of alkanes using nanostructured Co, Ni and Fe catalysts with CO ₂ and water in the presence of visible light and catalytic production of H ₂ with nanostructured Co particles, University of Massachusetts Lowell, Ph.D. Dissertation November 2016 [retrieved on 11 May 2018]. Retrieved from the Internet: <URL: https://search.proquest.com/docview/1864628684?pq-origsite=gscholar >. Abstract, Pgs. 18-22, 93-107	1-13, 15-18, 21-25
Y		14, 19, 20
Y	US 2013/0153860 A1 (SAMSUNG ELECTRONICS CO LTD) 20 June 2013 (20.06.2013) entire document	14
Y	US 2014/0309102 A1 (L'AIR LIQUIDE SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE) 16 October 2014 (16.10.2014) entire document	19, 20
A	US 3,975,217 A (KUNDA et al) 17 August 1976 (17.08.1976) entire document	1-25
A	US 4,808,233 A (PFANNKUCH) 28 February 1989 (28.02.1989) entire document	1-25

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

14 May 2018

Date of mailing of the international search report

06 JUN 2018

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