

Description

Electrocatalyst for Hydrogen Production

Cross-Reference to Related Applications

- 5 This application claims the benefit of priority of Singapore patent application No. 10201402950V, filed 5 June 2014, the contents of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

- The present invention relates to an electrocatalyst for hydrogen production, methods
10 and systems for using the same and methods for its fabrication.

Background Art

- There is an increasing need to develop renewable energy sources in light of depleting fossil fuels. Hydrogen production technology is regarded as one of the promising green technologies. At present, hydrogen production consists primarily of
15 steam reforming of hydrocarbons, such as methane, at high temperatures up to 1000 °C, followed by a water-gas shift reaction. The apparent drawback is that this process generates one carbon dioxide (CO₂) molecule for every four hydrogen molecules (H₂) produced. The emission of CO₂ poses environmental concerns as it is an undesirable greenhouse gas.
- 20 Electrolytic water splitting represents a prospective approach to producing hydrogen as carbon-neutral fuel. Compared to steam reforming, this approach entails numerous advantages. For instance, electrolytic water splitting can be performed at low temperatures, yields high purity hydrogen, is a relatively simple process, and does not emit CO₂. Additionally, hydrogen is a sustainable fuel source.
- 25 In general, electrolytic water splitting involves water oxidation on an electroanode to produce oxygen and proton reduction on the cathode:

Anode reaction: $[2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^-]$ ----- Reaction (1)

Cathode reaction: $[2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})]$ ----- Reaction (2)

Reaction 1, i.e. water oxidation, is rate limiting because it has a comparatively higher energy barrier. On the counter electrocathode, Reaction (2), i.e. proton reduction, proceeds easier because it has a much lower energy barrier. Without an efficient catalyst, a significant overpotential is required for water oxidation, resulting in low efficiency.

Extensive efforts have been made to develop efficient electrocatalysts for water oxidation. Known catalysts include cobalt-based, cobalt and manganese oxide clusters, ruthenium oxide, iridium oxide and nickel oxide electrocatalysts. However, the electrocatalytic efficiencies of these known catalysts are not promising enough to be considered economically viable for scale up operations.

Accordingly, there is a need to provide an alternative electrocatalyst for the electrolytic generation of hydrogen that overcomes or ameliorates the deficiencies discussed hereinabove.

Summary

In a first aspect, the present disclosure relates to an electrocatalyst consisting of amorphous Ru nanoparticles.

In another aspect, there is provided an electrode, when used in electrolytic water oxidation, said electrode consisting of amorphous Ru nanoparticles.

In another aspect, there is provided a method of generating hydrogen, the method comprising applying a voltage to an anode and a cathode in an electrolyte, wherein said anode consists of amorphous Ru nanoparticles.

In the present disclosure, there is provided a method of producing hydrogen, the method comprising: applying a voltage to an anode and a cathode in an electrolyte, wherein said anode consists of amorphous Ru nanoparticles disposed on a conductive support. In one embodiment, the electrolyte comprises water and the disclosed method comprises oxidizing water at the anode to yield oxygen and protons. In a particular embodiment, the electrolyte consists essentially of water. Advantageously, the disclosed method is capable of producing hydrogen in a water:hydrogen molar ratio of 1:1.

In still another aspect, there is provided a system for producing hydrogen, the system comprising a cathode and an anode electrically communicated with an electrolyte, a voltage source coupled to said cathode and anode; and wherein said
5 anode consists of amorphous Ru nanoparticles.

Advantageously, it has been found that the amorphous Ru nanoparticles act as effective catalysts for the anode reaction of water oxidation, even when the Ru nanoparticles loading at/on the anode is in relatively low concentrations of about 10 - 30 $\mu\text{g per cm}^2$ of the anode surface. In particular, the disclosed electrocatalyst is
10 capable of reducing or completely eliminating over-potential to the electrodes in order to facilitate the water splitting redox reactions. In particular embodiments, the disclosed method is capable of effecting the redox reactions under a potential difference of about 1.2 V – 1.5 V. Advantageously, in particular embodiments, the calculated Faradaic efficiency of the disclosed method for producing hydrogen from
15 water is demonstrably close to about 95% to 100%, or about 99% -100%.

Furthermore, by using the disclosed electrocatalyst, the generation of hydrogen may be advantageously performed under room temperature and atmospheric pressure.

In addition, it has been found that the amorphous Ru nanoparticles can be advantageously prepared by methods that do not require costly equipment
20 associated with RF magnetron sputtering, vapor deposition methods, electro-deposition, chemical or hydrothermal synthesis methods. Thus, the disclosed Ru electrocatalysts are cost-effective to produce and hence can be economically viable in operations. Accordingly, the present disclosure further provides a method for preparing the amorphous Ru nanoparticles and the fabrication of a Ru nanoparticle-
25 coated electrode for use in the above disclosed electrolytic method/system of producing hydrogen.

The present disclosure further envisions applications and uses of the electrocatalyst, including but not limited to, in fuel cells and solar-powered hydrogen generators.

Brief description of drawings

The invention would be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

- 5 [Fig. 1a] is a Transmission Electron Microscope (TEM) image of the synthesized Ru nanoparticles at 270 °C.

[Fig. 1b] shows the XRD patterns of the h.c.p. Ru phase, the synthesized Ru particles and Ru particles annealed at temperatures from 150 °C to 700 °C.

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[Figs. 2a, 2c, 2e] are potential/current graphs charting the electrochemical performance of 1-layer, 3-layer and 5-layer ruthenium nanoparticles thin films annealed at varying temperatures under argon gas. The linear voltammetry experiments were conducted on a FTO substrate (1 cm²) in sodium sulfate solution (0.1 M, pH 6) at a scan rate of 0.05 V/s. The insets show the enlarged region at potential of 1.2 V (vs. reference electrode Ag/AgCl).

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[Figs. 2b, 2d, 2f] are bar charts comparing the current densities of 1, 3, or 5-layer ruthenium nanoparticles thin films at 1.2 V (vs. Ag/AgCl). The Ru thin films were prepared by annealing the Ru nanoparticles at various temperatures under argon gas.

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[Fig. 3] is bar chart comparing current densities of ruthenium nanoparticles thin films at 1.2 V (vs. Ag/AgCl), wherein the Ru films are prepared by annealing at varying temperatures under argon and comprise either (a) 1-layer; (b) 3-layer or (c) 5-layer. Linear voltammetry experiments were conducted on a FTO substrate (1 cm²) in sodium sulfate solution (0.1 M, pH 6) at a scan rate of 0.05 V/s.

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[Fig. 4] is a graph depicting hydrogen evolution of 1, 3, 5-layer ruthenium nanoparticles thin films annealed at 250 °C under argon atmosphere. The experiments were recorded at 1.2 V (vs. Ag/AgCl) on a FTO substrate (1 cm²) in sodium sulfate solution (0.1 M, pH 6).

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[Fig. 5a] is a schematic of an experimental setup showing an exemplary embodiment of the disclosed system for hydrogen production. The system comprises a solar/photovoltaic module with dimensions 110×60 mm, which
5 used to drive/power the electrolysis reaction in sodium sulfate solution (0.1 M, pH 6). A two-electrode configuration system was used with a Pt sheet as the counter electrode, and Ru/FTO electrodes as the working electrodes.

[Fig. 5b] charts the hydrogen evolution of a 5-layer ruthenium nanoparticles thin
10 film annealed at $250\text{ }^{\circ}\text{C}$ under argon atmosphere. Three, 8-hour cycles of experiments were performed and the power source was provided by a photovoltaic module under solar illumination.

Description of Embodiments

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In a first aspect, the present invention relates to an electrocatalyst comprising amorphous Ru nanoparticles. Description of the amorphous Ru nanoparticles and the methods for their fabrication will be discussed in the sections that follow.

The present invention also relates to a method of producing hydrogen, the method
20 comprising: applying a voltage to an anode and a cathode in an electrolyte, wherein said anode comprises amorphous Ru nanoparticles disposed on the anode. During electrolysis, the oxidation of water molecules may be catalyzed by the active sites present in the Ru nanoparticles.

The Ru nanoparticles may be synthesized prior to deposition or impregnation onto a
25 surface of the anode. The anode surface may be partially or fully doped with the amorphous Ru nanoparticles.

Prior to being deposited onto the anode, the Ru nanoparticles may be synthesized by oxygen-free techniques under an inert gas (e.g., Argon) blanket. In a particular
30 embodiment, ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) is mixed with oleylamine and 1-octadecene to form a solution. The solution is dried and degassed at 90°C under argon atmosphere. The solution is further heated at $270\text{ }^{\circ}\text{C}$ and maintained for

about 30 minutes. After which, the solution is allowed to cool to ambient or room temperature. The crude solution of Ru nanoparticles is then diluted with hexane and precipitated with ethanol. Crude Ru nanoparticles may be isolated or recovered by appropriate means, e.g., centrifugation or filtration. The isolated Ru nanoparticles
5 can be dispersed in a suitable organic solvent (e.g., hexane) and optionally subjected to one or more purification steps.

Other ruthenium salts or hydrates may be used as precursor or starting material for nanoparticle synthesis. Suitable ruthenium precursors may be selected from, but are not limited to, ruthenium oxides and halides.

10 Advantageously, the use of oleylamine with an appropriate amount of a co-solvent (e.g., octadecene) may lead to substantially monodisperse Ru nanoparticles. The oleylamine may be mixed with the co-solvent in a volume ratio of from about 1:10 to about 3:10. In a particular embodiment, the volume ratio of oleylamine and the co-solvent may be about 2:10. Advantageously, it has been found that these volume
15 ratios provide optimized synthesis conditions to yield substantially monodisperse nanoparticles. Furthermore, the co-solvent may be optionally selected from the group consisting of: octadecene, n-octyl ether, dioctyl ether, docosane, and mixtures thereof.

The degassing step may be undertaken at temperatures of from about 50 °C to
20 about 140 °C. In non-limiting embodiments, the degassing step may be undertaken at temperatures selected from 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, or 140 °C. The degassing step can be performed with an ascending / descending temperature profile having temperature limits selected from any two temperature values disclosed above. In other embodiments, the degassing step may
25 be performed at constant temperature.

The subsequent reaction heating step may be undertaken at temperatures of from about 200 °C to about 340 °C. In non-limiting embodiments, the heating step may be undertaken at temperatures selected from 200 °C, 210 °C, 220 °C, 230 °C, 240 °C, 250 °C, 260 °C, 270 °C, 280 °C, 290 °C, 300 °C, 310 °C, 320 °C, 330 °C or 340 °C.
30 The heating step may be performed at a temperature range with limits selected from

any two temperature values disclosed hereinabove. The heating step may also be performed at constant temperature.

The heating step may be undertaken for any duration necessary to substantially or completely metastasize the Ru particles from the Ru complexes, which may have
5 formed by reaction with oleylamine and/or other solvents or surfactants present in the mixture. In a particular embodiment, performing the degassing step at 90 °C and subsequently reacting the mixture at 270 °C for around 30 minutes is advantageously observed to provide substantially monodisperse Ru nanoparticles having the properties and physical characteristics as disclosed herein.

10 The object of the synthesis is to provide Ru nanoparticles having an average particle size/diameter selected from 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 nm. In particular embodiments, the average nanoparticle size is from 1 to 8 nm, or 1 to 6 nm, 1 to 4 nm, or 1 to 2 nm. In embodiments, the Ru nanoparticles may be substantially monodisperse and exhibit a homogeneous, average particle size of about 2 nm. The
15 nanoparticles may also be substantially spherical in shape. Where the nanoparticles are not spherical in shape, the above disclosed average particle size shall apply to its equivalent spherical diameter.

The disclosed method may comprise coating the Ru nanoparticles onto a surface of an electroanode or anode. Prior to coating, the Ru nanoparticles may be dispersed
20 in an organic solvent (e.g., hexane) to obtain a Ru nanoparticle/solvent dispersion. The dispersion may be applied to the anode surface to coat a layer or a thin film of Ru nanoparticles thereon.

This coating step may involve physical deposition or chemical deposition. In embodiments, the Ru nanoparticles may be deposited onto the surface of the anode
25 by one or more methods selected from the group consisting of: sputtering, spraying, spin-coating and dipping. In a particular embodiment, the Ru nanoparticles are dispersed in hexane and thereafter spin-coated onto the electroanode to thereby form a Ru-nanoparticle thin film / layer thereon. The spin coating may be performed at a speed of 1,000 rpm for 30 seconds. The speed and duration of the spin-coating
30 step are not particularly limited. One or more layers of the Ru nanoparticles may be

applied or coated as necessary to achieve a desired Ru loading on the anode or a desired thickness of the deposited catalyst layer.

Advantageously, it has been found that the Faradaic electrolytic efficiency can be as high as 95 to 100% or 99 to 100% or even 99.5 to 100%, despite a comparatively
5 low concentration (by weight) of the electrocatalyst. In embodiments, the efficiency of the water to hydrogen conversion may be from about 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9% or 100%, with a variance of about $\pm 0.5\%$. The method of calculating efficiency using Faraday's First Law is fully described in the Examples contained herein.

10 For instance, the total concentration of Ru in the Ru-coated anode may be from about 5 to about 200 μg per cm^2 anode. All weight concentrations disclosed herein in relation to the Ru electrocatalyst loading refer to the weight of Ru per unit area (cm^2) of the surface of the anode to which the Ru nanoparticles has been applied. The average loading of Ru may be selected from 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55,
15 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, 195 or 200 μg per cm^2 . All recited catalyst loading values may be subject to a variance of ± 1 , ± 2 , ± 3 , or ± 4 μg per cm^2 . The average weight loading of the Ru catalyst may also be in a range selected from any two recited values. Where more than one layer of nanoparticles is applied onto the
20 anode, each layer may independently comprise an average weight loading of about 5, 10, 20, 25, 30, 35, 40, 45 or about 50 μg Ru cm^{-2} anode. Each Ru nanoparticle thin film may independently comprise the same or different catalyst weight loading.

The disclosed method may further comprise heating the Ru-coated anode under conditions to form amorphous Ru nanoparticles. The heating may comprise
25 annealing. It has been found that, in order to provide thermodynamically efficient or near 100% efficient catalytic activity, it is preferable for the Ru nanoparticles to exhibit an amorphous structure after the heating step.

The heating conditions may comprise annealing the Ru-coated anode at temperatures of between 150 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$. In embodiments, the annealing step
30 may be performed at temperatures of around 150 $^{\circ}\text{C}$, 175 $^{\circ}\text{C}$, 200 $^{\circ}\text{C}$, 225 $^{\circ}\text{C}$, 250 $^{\circ}\text{C}$, 275 $^{\circ}\text{C}$, 300 $^{\circ}\text{C}$, 325 $^{\circ}\text{C}$, 350 $^{\circ}\text{C}$, 375 $^{\circ}\text{C}$, or 400 $^{\circ}\text{C}$. The disclosed annealing

temperatures may be subject to variance of about ± 1 °C to ± 24 °C. In embodiments, the annealing step may be undertaken at a range of temperatures selected from any two distinct temperatures disclosed herein. In particular embodiments, the Ru-coated anode is annealed at temperatures of from 150 to 400 °C. In other embodiments, the Ru-coated anode is annealed at temperatures of from 250 to 300 °C. In still other embodiments, the Ru-coated anode is annealed at temperatures of from 150 to 250 °C. In other embodiments, the annealing step is maintained at a specific temperature e.g., 250°C. Annealing at the disclosed temperature ranges may result in Ru nanoparticles having a substantially amorphous or essentially amorphous phase. Advantageously, a catalyst loading of about 150 – 200 $\mu\text{g Ru cm}^{-2}$ anode and annealed at temperatures of from about 200 °C to 250 °C may provide optimal catalytic activity.

The annealing step may be performed under constant inert gas flow. The inert gas may be any noble gas that does not react with the nanoparticles and the electrode substrates, e.g., argon. The annealing step may be undertaken until the Ru nanoparticles display a broad XRD pattern (no peaks), which is indicative of a substantial or an essentially amorphous phase. The annealed Ru nanoparticles may be substantially free of crystalline Ru such as Ru in the hexagonal phase. The annealed and amorphous Ru nanoparticles and may be substantially free of Ruthenium oxide (RuO_2). In specific embodiments, the annealing step may be undertaken in the absence of oxygen gas. In embodiments, the annealed nanoparticles may be characterized by XRD patterns according to Fig. 2, in particular, Fig 2b.

The electrolyte of the disclosed method may be a water-containing electrolyte medium. The electrolyte medium may be an aqueous salt solution. The electrolyte medium may also comprise strong acids or bases. Where a salt solution is used, the electrolyte comprises cations having electrode potentials lower than H^+ . For instance, the electrolyte can be aqueous sodium sulfate. In other embodiments, the electrolyte is composed essentially of water. The electrolyte medium may optionally contain one or more homogenous electrocatalysts including enzymes such as hydrogenase.

The electrodes for use in the disclosed method may be selected from platinum, silver, indium tin oxide, fluorine-doped tin oxide (FTO), graphene or graphite. Any combination of two electrodes may serve as the electrode-counter electrode pair. In one embodiment, the anode is a FTO substrate and the counter electrode is a platinum substrate. In yet another embodiment, the anode is a FTO substrate coated with the disclosed amorphous Ru nanoparticles and the counter electrode is a platinum substrate.

Advantageously, it has been found that the disclosed Ru nanoparticle catalysts are resistant to degradation. That is, the disclosed electrocatalyst may be capable of maintaining catalytic activity even after prolonged usage in electrolytic hydrogen production. In the present Examples, it is demonstrated that the disclosed catalysts do not suffer significant degradation even after three 8-hour cycles of electrolytic hydrogen production. These results suggest that the catalysts could provide an extended or comparable operational shelf life compared to conventional electrocatalysts.

In yet another aspect of the present disclosure, there is provided a system for producing hydrogen, the system comprising a cathode and an anode electrically communicated through an electrolyte medium, a voltage source coupled to the cathode and anode; and wherein said anode comprises amorphous Ru nanoparticles.

The amorphous Ru nanoparticles and electrodes of the disclosed system may be as defined above.

Particularly, in the disclosed system, the anode may be selected from platinum (Pt), silver, indium tin oxide (ITO), fluorine-doped tin oxide (FTO), graphene or graphite. In embodiments, the anode is selected from ITO, FTO and Pt. In a particular embodiment, the anode is FTO.

When the system is in use, the anode or cathode may be in complete or partial contact with the electrolyte. When in operation, the active sites of the amorphous Ru nanoparticles may be brought into contact with water molecules in the electrolyte, thereby catalyzing the oxidation of water into oxygen, and H^+ ions.

The total average weight loading of Ru in the Ru-coated anode may be from about 5 to about 200 μg per cm^2 anode. The average weight loading of Ru may be selected from 5, 10, 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, 195 or 200 μg per cm^2 . All recited catalyst loading values may be subject to a variance of ± 1 , ± 2 , ± 3 , or ± 4 μg per cm^2 . The average weight loading of the Ru catalyst may also be in a range selected from any two recited values.

Each layer of amorphous Ru nanoparticles may comprise an average weight loading of about 5 to about 50 μg Ru per cm^2 anode. Where more than one layer of Ru nanoparticles is coated onto the anode, each Ru nanoparticle layer may independently comprise the same or different catalyst weight loading, provided that the total weight loading is as defined hereinbefore. Applying multiple coats/layers of Ru nanoparticle thin films to achieve a desired catalyst loading may advantageously improve the adhesion of the Ru nanoparticle layers to the anode support or substrate. This may avoid or mitigate the loss of catalysts during operation and handling.

The system may be advantageously integrated with a renewable energy source for supplying the potential difference across the electrodes. In a particular embodiment, the renewable energy source comprises a photovoltaic module, such as a solar cell or a solar panel.

The supplied voltage may not be particularly limited and depends on the scale of the electrolytic system. In embodiments of the present disclosure, voltages as low as 1.2 V to 1.5 V have been observed to effect electrolytic hydrogen production in the presence of the disclosed Ru electrocatalysts. In embodiments, the supplied voltage may be selected from 1.2, 1.25, 1.3, 1.35, 1.4, 1.45 or 1.5 V.

The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been 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 invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification
5 and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also
10 form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of
15 Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

Examples

20 Materials and method

Synthesis of ruthenium nanoparticles:

All experiments were carried out by standard oxygen-free techniques under Argon flow. A mixed solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (1 mmol), 1.7 mL of oleylamine and 10 mL of 1-octadecene was dried and degassed at 90 °C under argon atmosphere in a 25-mL
25 three-neck flask for 30 min with continuous stirring. The reaction mixture was further heated up to 270 °C and kept at that temperature for 30 min. Next, the solution was allowed to cool down to room temperature. The obtained crude solution of ruthenium nanoparticles was diluted with 20 mL hexane followed by precipitation with 80 mL ethanol. The crude product was isolated by centrifugation, then dispersed in hexane,

and subjected to a second round of purification. The obtained ruthenium nanoparticles can be re-dispersed easily in hexane for further characterization.

Preparation of ruthenium thin films:

Fluorine-doped tin oxide (FTO) – coated glass slides of dimension 2.5 cm x 1.5 cm
5 were cleaned by ultrasonication in acetone and water for 10 min each and dried in a nitrogen stream. A thin film of ruthenium nanoparticles was prepared by spin coating a hexane solution of the ruthenium nanoparticles onto FTO substrate at a speed of 1000 rpm for 30 s. The obtained homogenous ruthenium nanoparticles thin film on FTO substrate was used for electrochemical characterization or 1 cm x 1 cm silicon
10 substrate for XRD measurement.

To investigate the effect of the thickness of ruthenium nanoparticle film, thin films were prepared by spin coating 1, 3 and 5 Ru nanoparticle layers with a respective average weight loading of about 27, 100 and 167 $\mu\text{g Ru per cm}^2$ FTO surface (as measured by microbalance, Sartorius).

15 The resultant ruthenium thin films on FTO substrate were annealed at temperatures from 150 to 700 °C for 2 hours in Argon. Thin films of ruthenium nanoparticles supported on silicon substrate were also annealed at the same annealing conditions for XRD measurement. The annealed samples were then used for electrochemical analysis.

20 Results and Discussions

The as-synthesized ruthenium nanoparticles (Fig. 1a) were characterized by TEM, showing monodispersed spherical nanoparticles with an average particle size of 2 nm. The Ru nanoparticles were spin coated into thin films which were subsequently annealed in argon atmosphere at different temperatures ranging from 150 to 700 °C
25 for X-ray diffraction (XRD) characterization.

In Fig. 1b, the as-synthesized ruthenium nanoparticles gave a very broad XRD peak, which is indicative of its amorphous phase. The amorphous phase remained after annealing at 150, 200, 250, 300 and 350 °C. However, at 400 °C, the amorphous phase starts to crystallize as observed from the sharper XRD peaks imposed on the
30 amorphous one.

At 450 °C and above, the Ru phase appears to be fully crystallized. This was indicated and confirmed by intense peaks at 38.4°, 42.3° and 44.0°, corresponding to the (100), (002) and (101) crystal planes of hexagonal phase ruthenium (JCPDS 006-0663), respectively. The results show that the amorphous phase of ruthenium nanoparticles may be stable under the annealing temperature below 400 °C. At a higher temperature, the amorphous phase starts to convert to a hexagonal phase without the formation of RuO₂, as corroborated by the XRD analysis.

Electrolytic Activity

- For the study of electrocatalytic activity, thin films of the as-synthesized ruthenium nanoparticles (before annealing) were prepared by spin coating the Ru nanoparticles/hexane dispersion onto a 2.5 cm x 1.5 cm fluorine doped tin oxide (FTO) substrate. The coated Ru/FTO substrates are then annealed at temperatures ranging from 150 to 700 °C.
- Linear sweep voltammetry was conducted in 0.1 M Na₂SO₄ electrolyte using a three-electrode configuration (Ru/FTO working electrode, Pt counter electrode, and Ag/AgCl reference electrode). After annealing at 150 °C to 350 °C, the amorphous thin films showed enhanced current densities compared to the unannealed samples, as shown in the current density – potential curves in Fig. 2a. An optimum current density of 4.36 mA cm⁻² was obtained from the 300 °C - annealed thin film at 1.2 V (vs Ag/AgCl) (Fig. 2b).

After annealing at higher temperatures, the resulting crystalline thin films exhibited a gradual decrease in current densities with increasing annealing temperatures from 400 °C to 700 °C. This result is suggestive of the superior electrocatalytic activity of the amorphous phase relative to its crystalline phase. In comparison, the blank (uncoated) FTO exhibited very low current density (close to 0 mAcm⁻²) upon sweeping from negative to positive potentials (–0.3 to 1.6 V). This confirms that the electrocatalytic activities originated exclusively from the applied ruthenium nanoparticles.

By repeating the spin coating process, more layers of ruthenium nanoparticles were coated on FTO substrate and subsequently annealed at temperatures ranging from 150 to 700 °C. For all the annealing temperatures, both the 3-layer and 5-layer Ru thin films displayed higher electrocatalytic activity compared to the corresponding 1-layer ruthenium thin film (Fig. 2). As shown in Fig. 2c-f, the 1-layer, 3-layer and 5-layer thin films exhibited similar trend of current density as a function of annealing temperature. In particular, the highest current densities were 4.36, 6.20 and 6.79 mA cm⁻² achieved at 1.2 V for the 1-layer, 3-layer and 5-layer amorphous thin films, which were annealed at 300, 250 and 250 °C, respectively.

Fig. 3 then summarizes the current densities of 1, 3, and 5-layer ruthenium thin films at different annealing temperatures. Apart from the phase effect, the annealing step performed on the thin films may also have improved the adhesiveness of ruthenium nanoparticles on the FTO substrate, thus enhancing the electrocatalytic properties significantly.

Upon annealed at the optimized temperature, the ruthenium thin film was evaluated for electrolytic water splitting for hydrogen generation under an external bias of 1.2 V. As shown in Fig. 4, the amount of hydrogen evolved from the 1, 3 and 5-layer thin films was determined to be 44.3, 62.1 and 79.1 μmol h⁻¹, respectively. Using Faraday's First Law, the efficiency from electrical current to hydrogen was calculated to be close to 100%:

Theoretical volume of hydrogen produced (m³) in 8 hours was calculated using Faraday's First Law:

$$V_{\text{theoretical}} = (RITt) / (Fpz),$$

where R is 8.314 Joule mol⁻¹ K⁻¹,

I is averaged current in Amperes,

T is the temperature (in K),

t is time in seconds,

F is Faraday's constant = 96485 Coulombs per mol,

p is ambient pressure = about 1x10⁵ pascals (one pascal = 1 Joule / m³), and

z is number of 'excess' electrons = 2 (for hydrogen, H₂).

Therefore,

$$V_{\text{theoretical}} = [(8.314 \text{ Joule per mol Kelvin}) \times (298 \text{ Kelvins}) \times (0.00387 \text{ amps}) \times (28800 \text{ seconds})] / [(96485 \text{ Coulombs per mol}) \times (1 \times 10^5 \text{ pascals}) \times 2] = 1.431 \times 10^{-5} \text{ m}^3 =$$

5 **14.31 mL.**

Using the 5-layer Ru thin film (annealed at 250°C) as a working electrode, H₂ generated in 8 hours was measured to be 14.20 mL. Accordingly, hydrogen generation efficiency (%) can be calculated as: 100% x (14.20 / 14.31) = 99.23%
10 (demonstrably close to 100% efficiency).

In order to make the hydrogen generation from a renewable energy source, the external bias was replaced by a conventional solar module to generate electricity from sunlight (Fig. 5a).

15 The hydrogen generation experiment was repeated with a 5-layer ruthenium thin film at an identical experimental condition coupled with a 110 x 60 mm crystalline silicon solar module. This concept offers several benefits. One of the most important benefits is the use of crystalline solar module that is capable of harvesting a wide range of visible light with high efficiency. Silicon solar modules are well developed
20 and are widely available.

The solar module may be separated from the electrolyte so as to prolong lifetime of solar module as well as collection of gas can be done separately at each electrode without the use of sacrificial reagent. Under AM 1.5G illumination on the solar module, a large amount of bubbles has been observed on the surface of Pt counter
25 electrode and the amount of hydrogen evolved was determined to be 0.93 mmol for a period of 8 hours which correspond to a hydrogen generation rate of 115.3 μmol h⁻¹.

The stability of ruthenium thin film was examined by performing another two cycles of hydrogen generation and result revealed that second and third cycle yielded 111.6
30 and 107.5 μmol h⁻¹ (Fig. 5b). These data suggest that no significant degradation of the electrocatalyst was observed even after three cycles of consecutive hydrogen generation. Although ruthenium is a more expensive metal compared to the earth-

abundant metals, the small quantity employed in the current application makes the relative cost effective and the system favors ruthenium metal due to its excellent stability. In addition, the highly stable ruthenium thin film was optimized at 250 °C heat treatment and capable to undergo three cycles of hydrogen generation with retention of high electrolytic activity.

The inventors have for the first time demonstrated the feasibility of amorphous ruthenium nanoparticles as electrocatalysts (anode material). The nanoparticles were synthesized by a non-hydrolytic approach and spin coated on a conductive substrate for electrocatalytic water splitting.

The preparation of ruthenium nanoparticles with uniform size in a facile way is amenable to scale-up operations which are able to efficiently split water molecules into oxygen and hydrogen in stoichiometric amount. In addition to the high catalytic properties, the stability of the ruthenium nanoparticles was remarkable with no significant degradation of electrolytic activity for three consecutive cycles of electrolytic water splitting. Overall, the incorporation of ruthenium nanoparticles as anode material in electrolytic water splitting offer the benefits of high efficiency catalytic properties with excellent chemical stability that renders a long life span, particularly the electrolytic splitting of water is carried out under neutral electrolyte conditions at room temperature and atmospheric pressure.

Claims

1. An electrocatalyst consisting of amorphous Ru nanoparticles.
- 5 2. An electrode, when used in electrolytic water oxidation, said electrode consisting of amorphous Ru nanoparticles.
3. A system for producing hydrogen, said system comprising a cathode and an anode electrically communicated with an electrolyte, a voltage source coupled
10 to said cathode and anode; and wherein said anode consists of amorphous Ru nanoparticles.
4. The system of claim 3, wherein the anode is coated with one or more layers of said amorphous Ru nanoparticles.
- 15 5. The system of claims 3 or 4, wherein the anode has an average Ru loading by weight of about 5 to about 200 μg Ru per cm^2 anode.
6. The system of any one of claims 3 to 5, wherein said electrolyte comprises
20 water.
7. The system of any one of claims 3 to 6, wherein said amorphous Ru nanoparticles have an average particle diameter of about 1 to about 5 nm.
- 25 8. The system of any one of claims 3 to 7, wherein the voltage source comprises a photovoltaic module or solar module.
9. A method of generating hydrogen, the method comprising applying a voltage to an anode and a cathode in an electrolyte, wherein said anode consists of
30 amorphous Ru nanoparticles.
10. The method of claim 9, wherein prior to said applying step, the method comprises a step of providing Ru nanoparticles onto a surface of said anode.

11. The method of claim 10, wherein said providing step comprises coating one or more layers of Ru nanoparticles onto a surface of the anode to form a Ru-coated anode, said one or more layers comprising Ru nanoparticles dispersed in an organic solvent.
12. The method of claim 11, further comprising heating said Ru-coated anode under conditions to form said amorphous Ru nanoparticles.
13. The method of claim 12, wherein said conditions comprises heating said Ru-coated anode at a temperature of from 150 °C to 400 °C.
14. The method of claim 13, said conditions comprising heating said Ru-coated support at a temperature of about 250 °C to about 300 °C in the presence of an inert gas.
15. The method of any one of claims 12 to 14, wherein during said heating step, oxygen is absent.