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(71) Applicant: **THE UNIVERSITY OF SYDNEY** [AU/AU];  
Parramatta Road, Sydney, New South Wales 2006 (AU).

(72) Inventors: **ARAB, Mobin**; 3/86 Houston Road, Kingsford, NSW 2032 (AU). **MINETT, Andrew, I**; 42 Owen Street, Bulli, NSW 2516 (AU). **CHURCH, Tamara, Lynne**; 17 Reserve Street, Beaconsfield NSW 2015 (AU). **LI, Xiaobo**; A 807/35 Arncliffe Street, Wollli Creek, NSW 2205 (AU). **MASCHMEYER, Thomas**; 47 Ivey Street, Lindfield, NSW 2070 (AU). **NOORBEHESHT, Nikan**; 26/9 Bay Drive, Meadowbank, NSW 2114 (AU). **HARRIS, Andrew, T.**; c/o The University of Sydney, Parramatta Road, Sydney, NSW 2006 (AU). **FAISAL, Shaikh,**

**Nayem**; 13/602 Punchbowl Road, Lakemba, NSW 2195 (AU). **HUSIN, Agus**; 11/169 Avoca Street, Randwick, NSW 2031 (AU).

(74) Agent: **SPRUSON & FERGUSON**; GPO Box 3898, Sydney, New South Wales 2001 (AU).

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(54) Title: ELECTROCATALYSTS AND ELECTROCHEMICAL CELLS

(57) Abstract: A nanocomposite comprising heteroatom-doped graphene and heteroatom-doped carbon nanotubes (CNTs), wherein the nanocomposite has a heteroatom content of at least about 1 wt%.



## ELECTROCATALYSTS AND ELECTROCHEMICAL CELLS

### Field of the Invention

[0001] The present invention relates to a nanocomposite and uses thereof as a catalyst, proton conductive material, and electrochemical cells (e.g. photoelectrochemical cells) comprising said nanocomposite and/or proton conductive material.

### Background

[0002] Any discussion of the background art throughout the specification should in no way be considered as an admission that such background art is prior art, nor that such background art is widely known or forms part of the common general knowledge in the field.

[0003] Sustainable energy production is a major challenge faced by the world today. A growing population with an ever-increasing demand for energy coupled with rapid depletion of fossil fuels has led to an increased need for sustainable and clean energy technologies.

[0004] Water splitting (electrolysis) is one the most promising sustainable technologies for meeting increasing energy demand and reducing fossil fuel emissions. Splitting of water is a reaction in which water ( $H_2O$ ) is separated into oxygen ( $O_2$ ) and hydrogen ( $H_2$ ). One aim of water splitting is to produce sustainable hydrogen to be used as an energy source, for example, in fuel cell vehicles and other industries such as aerospace, refining, welding and metal fabrication. Water splitting is also a key step in photosynthesis, providing electrons to power the electron transport chain in photosystem II and thereby resulting in evolution of oxygen. Thus, another aim of water splitting is to provide a sustainable source of oxygen and/or assist in artificial photosynthesis.

[0005] Splitting of water requires large amounts of energy, typically generated from fossil fuels. In efforts to alleviate the environmental toll of fossil fuel consumption, precious and nondurable materials like platinum (Pt), e.g., as Pt/C, and other noble metals are commonly used as catalysts for water splitting due to their intrinsic catalytic activity. In addition to the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), the key steps in the splitting of water, Pt catalysts are also used in electrochemical reactions such as oxygen reduction reaction (ORR) and the reduction of carbon dioxide. However, there are significant drawbacks arising from using precious metals as catalysts including high costs due to their low abundance in nature, and low durability/stability due to loss of catalytic activity after a relatively

low number of catalytic cycles. This in turn is detrimental to the efficiency and cost of electrochemical cells that utilise precious metals as water-splitting catalysts.

[0006] Accordingly, there is a need for new catalysts for electrochemical reactions, such as the splitting of water, which remove or at least ameliorate one or more of the disadvantages associated with existing catalysts. There is also a need for improved electrochemical cells comprising these catalysts such as, for example, fuel cells, photoelectrochemical cells and batteries.

[0007] In addition to deficiencies arising from the use of existing catalysts for electrochemical reactions (e.g., water-splitting catalysts), current electrochemical cells suffer from additional drawbacks. For example, photoelectrochemical cells (PEC) are reaction units in which light energy is utilised through a combination of electrochemical processes and photochemical process to convert a reactant feed stream to reaction products. Conventional photochemical cells typically comprise two separate compartments: a first compartment containing an anode and a second compartment containing a cathode. The anode side is utilised for oxidation of a proton source (e.g., water), while the cathode side is utilised for reduction of a reactant feed stream (e.g., carbon dioxide). Connecting the two compartments is an electron conductor, typically in the form of a metal wire, and a proton conductor.

[0008] In some photochemical cells, the proton conductor is a polymer (e.g., Nafion®) membrane. Such membranes have low proton conductivity in the absence of water. Therefore, at least one of the compartments must be in a liquid phase. As films of such proton-conducting polymers inhibit the passage of reactants from one compartment to the other, they are used to separate the first and second compartments. This places limitations on the configuration available for such photoelectrochemical cells. Furthermore, ion migration from the liquid compartment to the gas compartment, or vice versa, may occur. This reduces the performance of the cathode side or the anode side of the cell, depending on the direction of migration, which reduces the overall performance of the cell.

[0009] Accordingly, there is also a need for new proton conductors that address one or more of the deficiencies of existing proton conductors. There is also a need for photoelectrochemical devices comprising those proton conductors.

**Summary of the Invention**

[0010] According to a first aspect of the present invention, there is provided a nanocomposite comprising heteroatom-doped carbon nanostructures, wherein the nanocomposite has a heteroatom content of at least about 1 wt%.

[0011] The following options may be used in combination with the above aspect, either individually or in any suitable combination.

[0012] The heteroatom-doped nanostructures may comprise any two or more of heteroatom-doped graphene, heteroatom-doped carbon nanotubes (CNTs) and heteroatom-doped fullerenes. The heteroatom-doped nanostructures may comprise heteroatom-doped graphene and heteroatom-doped CNTs. They may comprise heteroatom-doped graphene and heteroatom-doped fullerenes. They may comprise heteroatom-doped CNTs and heteroatom-doped fullerenes. They may comprise heteroatom-doped graphene, heteroatom-doped carbon nanotubes (CNTs) and heteroatom-doped fullerenes. The CNTs may be single walled CNTs, multi-walled CNTs or a combination thereof.

[0013] The nanocomposite may comprise heteroatom-doped graphene and heteroatom-doped carbon nanotubes (CNTs), wherein the nanocomposite has a heteroatom content of at least about 1 wt%.

[0014] The heteroatom-doped CNTs may be multi-walled carbon nanotubes. The heteroatom-doped graphene may comprise an amount of heteroatom in the range of about 1 wt% to about 10 wt%. The heteroatom-doped CNTs may comprise an amount of heteroatom in the range of about 1 wt% to about 10 wt%. The heteroatom-doped graphene and heteroatom-doped CNTs may be present in a ratio between about 10:1 and about 1:10. The heteroatom-doped CNTs may be adsorbed onto the surface and/or between layers of the heteroatom-doped graphene.

[0015] The nanocomposite may be in the form of a dispersion. It may be in the form of a solid. The N-graphene may not form agglomerates of more than about ten layers.

[0016] The heteroatom may be selected from the group consisting of nitrogen, sulfur, phosphorus, boron, silicon, aluminium and combinations thereof. The heteroatom may be nitrogen. The nitrogen may be introduced into the N-graphene or N-CNTs using a nitrogen source selected from the group consisting of an amino acid (e.g., L-arginine), ammonia, aniline, benzylamine, N-benzylmethylaniline, butylamine, diethylamine, N,N-

dimethylacetamide, N,N-dimethylformamide, ethylenediamine, formamide, hexamethylenediamine, hydrazine, isopropylamine, melamine, 1-methylpiperazine, N-methylenediamine pyridine, pyrrole, quinoline, trimethylenediamine, urea, uric acid and combinations thereof. The nitrogen source may be selected from the group consisting of an amino acid, urea, uric acid and combinations thereof. The nitrogen source may be uric acid. The nitrogen source may ethylenediamine. The nitrogen source may not be ammonia.

[0017] The N-graphene and/or the N-CNTs may further comprise a co-dopant. The co-dopant may be selected from the group consisting of sulfur, phosphorus, boron, silicon, aluminium and combinations thereof.

[0018] The nanocomposite may have an equivalent spherical diameter in the range of about 1 nm to about 1 mm. The nanocomposite may have a mean equivalent spherical diameter in the range of about 1 nm to about 1 mm. The nanocomposite may have a mean equivalent spherical diameter in the range of about 1 nm to about 1  $\mu$ m.

[0019] The nanocomposite may not be supported on a hydroxide support. It may not be formed on a solid support.

[0020] According to a second aspect of the present invention, there is provided a process for producing a nanocomposite of the first aspect of the invention, said process comprising: a) providing heteroatom-doped graphene; b) providing heteroatom-doped CNTs; and c) combining the heteroatom-doped graphene and heteroatom-doped CNTs in solution to form the nanocomposite.

[0021] The following options may be used in combination with the above aspect, either individually or in any suitable combination.

[0022] Step c) may comprise heating the solution to facilitate formation of the nanocomposite.

[0023] The solution may be heated to a temperature between about 30 °C to about 150 °C.

[0024] The process may further comprise: d) drying the nanocomposite produced in step c) to form a solid.

[0025] The process may further comprise producing the heteroatom-doped graphene provided in step (a). The production of heteroatom-doped graphene may comprise: a) mixing graphene

oxide with a heteroatom source in solution to produce heteroatom-doped graphene oxide; and b) reduction of heteroatom-doped graphene oxide to heteroatom-doped graphene. Steps a) and b) may be performed simultaneously. The heteroatom source may be a reducing agent. The ratio of graphene oxide to heteroatom source in step a) may be in the range of about 1:1 to about 1:20. The process may further comprise: c) drying the heteroatom-doped graphene produced in step b) to form a solid. The process may further comprise: d) heating the solid formed in step c). The solid may be heated to a temperature between about 100°C and about 2000 °C. The process may further comprise a step of producing the graphene oxide. The graphene oxide may be produced by exfoliation of graphite.

[0026] The process may further comprise a step of producing the heteroatom-doped CNTs. The production of heteroatom-doped CNTs may comprise chemical vapour deposition.

[0027] The heteroatom may be selected from the group consisting of nitrogen, sulfur, phosphorus, boron, silicon, aluminium and combinations thereof. The heteroatom may be nitrogen. The nitrogen source may be a reducing agent. The nitrogen may be introduced into the N-graphene or N-CNTs using a nitrogen source selected from the group consisting of an amino acid (e.g., L-arginine), ammonia, aniline, benzylamine, N-benzylmethylamine, butylamine, diethylamine, N,N-dimethylacetamide, N,N-dimethylformamide, ethylenediamine, formamide, hexamethylenediamine, isopropylamine, melamine, 1-methylpiperazine, N-methylenediamine pyridine, pyrrole, quinoline, trimethylenediamine, urea, uric acid and combinations thereof. The nitrogen source may be selected from the group consisting of an amino acid, urea, uric acid and combinations thereof. The nitrogen source may be uric acid. The nitrogen source may be ethylenediamine. The nitrogen source may not be ammonia.

[0028] The process may further comprise co-doping the N-graphene and/or the N-CNTs with a co-dopant. The co-dopant may be selected from the group consisting of sulfur, phosphorus, boron, silicon, aluminium and combinations thereof.

[0029] According to a third aspect of the present invention, there is provided an electrode comprising a nanocomposite of the first aspect of the invention.

[0030] According to a fourth aspect of the present invention, there is provided an electrochemical cell comprising a nanocomposite of the first aspect of the invention.

[0031] The following options may be used in combination with the above aspect, either individually or in any suitable combination.

[0032] The electrochemical cell may comprise a cathode comprising the nanocomposite of the first aspect of the invention. The electrochemical cell may comprise an anode comprising the nanocomposite of the first aspect of the invention. The electrochemical cell may be selected from the group consisting of a fuel cell, water electrolyser, a photoelectrochemical cell and a battery. It may be a hydrogen-fuel cell. It may be a battery. The battery may be a lithium battery.

[0033] According to a fifth aspect of the present invention, there is provided use of the nanocomposite of the first aspect of the invention as a catalyst for a reduction reaction.

[0034] The following options may be used in combination with the above aspect, either individually or in any suitable combination.

[0035] The reduction reaction may be a hydrogen evolution reaction (HER). It may be an oxygen reduction reaction (ORR). It may be reduction of carbon dioxide (CO<sub>2</sub>).

[0036] According to a sixth aspect of the present invention, there is provided use of the nanocomposite of the first aspect of the invention as a catalyst for an oxidation reaction.

[0037] The oxidation reaction may be an oxygen evolution reaction (OER).

[0038] According to a seventh aspect of the present invention, there is provided use of the nanocomposite of the first aspect of the invention as a catalyst for splitting water.

[0039] According to an eighth aspect of the present invention, there is provided use of an electrochemical cell according to the third aspect of the invention for splitting water.

[0040] According to a ninth aspect of the present invention, there is provided a photoelectrochemical cell comprising: (a) an anode comprising at least one oxidation catalyst; (b) a cathode comprising at least one reduction catalyst, wherein the cathode is in electrical communication with the anode; and (c) a proton conductor having a porous structure, wherein the proton conductor connects the anode and the cathode, thereby allowing transfer of protons between the anode and the cathode.

[0041] The following options may be used in combination with the above aspect, either individually or in any suitable combination.

[0042] The porous structure of the proton conductor may be provided by bonded or non-bonded nano-fibres. The proton conductor may comprise a polymeric material. The polymeric material may be gas-permeable. The polymeric material may comprise perfluorosulfonic acid. The porous structure of the proton conductor may be formed by electrospinning the polymeric material. The proton conductor may be at least partially transparent to electromagnetic (EM) radiation. The proton conductor may be at least partially transparent to EM radiation having a wavelength in the range of about 350 to about 850 nm.

[0043] The photoelectrochemical cell may further comprise an electrically conductive substrate. The anode and cathode may each be disposed on a surface of the electrically conductive substrate, thereby providing the electrical communication. The anode and cathode may each be disposed on different surfaces of the electrically conductive substrate. The electrically conductive substrate may form a layer between the anode and cathode. The anode and cathode may be disposed on the same surface of the electrically conductive substrate, such that the electrically conductive substrate forms a first layer and the anode and cathode form a second layer. The electrically conductive substrate may comprise one or more materials selected from the group consisting of stainless steel, copper, nickel, iron and gold. The electrically conductive substrate may comprise two or more layers. Each of the two or more layers of the electrically conductive substrate may be individually selected from a mesh or sheet.

[0044] The anode may comprise a photovoltaic cell. The photovoltaic cell may be a multi-junction photovoltaic cell. The multi-junction photovoltaic cell may be a triple-junction amorphous silicon-based photovoltaic cell. The oxidation catalyst may be disposed on or adjacent to a *p*-side of the photovoltaic cell.

[0045] The at least one oxidation catalyst may be a water-oxidising catalyst. The at least one oxidation catalyst may be selected from the group consisting of cobalt oxides, manganese oxides, nickel oxides, iron oxides, nanocomposites and combinations thereof. The at least one oxidation catalyst may be cobalt (II,III) oxide. The at least one oxidation catalyst may be in the form of nanoparticles. The oxidation catalyst nanoparticles may have an equivalent spherical diameter in the range 5 nm to 70 nm. The oxidation catalyst nanoparticles may have a mean equivalent spherical diameter in the range 20 nm to 35 nm. The at least one oxidation catalyst may be the nanocomposite of the first aspect of the invention.

[0046] The at least one reduction catalyst may be a carbon dioxide-reducing catalyst. The at least one reduction catalyst may be a proton-reducing catalyst. The at least one reduction

catalyst may be copper (I) oxide. The at least one reduction catalyst may be in the form of nanoparticles. The reduction catalyst nanoparticles may have an equivalent spherical diameter in the range of about 5 nm to about 70 nm. The nanoparticles may have a mean equivalent spherical diameter in the range of about 20 nm to about 35 nm. The at least one reduction catalyst may be the nanocomposite of the first aspect of the invention.

[0047] The proton conductor may partially or completely envelop the anode, the cathode or both. The photoelectrochemical cell may further comprise means of providing one or more gaseous feed streams to the photoelectrochemical cell, such that the gaseous feed stream(s) contacts the oxidation catalyst, the reduction catalyst or both. The photoelectrochemical cell may be for reducing a humid carbon dioxide (CO<sub>2</sub>) gas stream to CO<sub>2</sub> reduction products. The CO<sub>2</sub> reduction products may include water, carbon, carbon monoxide, alcohols, ketones, carboxylic acids, aldehydes, heterocycles and C<sub>1-10</sub> hydrocarbons.

[0048] According to a tenth aspect of the present invention, there is provided a photoelectrochemical cell comprising: (a) an anode comprising an oxidation catalyst disposed on a surface of a photovoltaic cell; (b) a cathode comprising a reduction catalyst; (c) a proton conductor having a porous structure, wherein the proton conductor connects the anode and the cathode; and (d) an electrically conductive substrate, wherein the anode and cathode are each disposed on a surface of the electrically conductive substrate, thereby providing electrical communication between the anode and the cathode; and wherein the proton conductor comprises a gas-permeable polymeric material, which is at least partially transparent to electromagnetic (EM) radiation, the proton conductor at least partially enveloping the anode, cathode and electrically conductive substrate.

[0049] According to an eleventh aspect of the present invention, there is provided a proton conductor having a porous structure, wherein said porous structure allows permeation of a gas through said proton conductor.

[0050] The following options may be used in combination with the above aspect, either individually or in any suitable combination.

[0051] The porous structure of the proton conductor may be provided by bonded or non-bonded nano-fibres. The proton conductor may comprise a polymeric material. The polymeric material may be gas-permeable. The polymeric material may comprise perfluorosulfonic acid. The porous structure of the proton conductor may be formed by electrospinning the polymeric material. The proton conductor may be at least partially transparent to electromagnetic (EM) radiation. The proton conductor may be at least partially transparent to EM radiation having a

wavelength in the range of about 350 to about 850 nm. The porous structure of the proton conductor may allow permeation of a liquid through the proton conductor.

[0052] According to a twelfth aspect of the present invention, there is provided a process for preparing a porous proton conductor comprising the steps of: (i) providing a proton-conducting polymeric material; and (ii) electrospinning the polymeric material, thereby producing a porous proton conductor. The porous proton conductor prepared according to the twelfth aspect of the invention may be a proton conductor of the eleventh aspect of the present invention.

[0053] According to a thirteenth aspect of the present invention, there is provided a porous proton conductor prepared by the process of the twelfth aspect of the present invention.

[0054] According to a fourteenth aspect of the present invention, there is provided a method of reducing carbon dioxide ( $\text{CO}_2$ ) to  $\text{CO}_2$ -reduction products, the method comprising the steps of: (i) providing water vapour and  $\text{CO}_2$  gas stream to the photoelectrochemical cell of the ninth or tenth aspect of the present invention, whereby the water vapour contacts the oxidation catalyst and the  $\text{CO}_2$  gas contacts the reduction catalyst; (ii) exposing the anode to an electromagnetic (EM) radiation source, thereby converting the water vapour to oxygen gas, protons and/or electrons; (iii) transporting the protons and electrons to the cathode via the proton conductor; and (iv) exposing the cathode to the electromagnetic (EM) radiation source, thereby reducing the  $\text{CO}_2$  gas in the presence of the protons and electrons to  $\text{CO}_2$  reduction products.

[0055] The following options may be used in combination with the above aspect, either individually or in any suitable combination.

[0056] The water vapour and  $\text{CO}_2$  gas may be provided in a single gaseous feed stream. The gaseous feed stream may have a relative humidity of between 50% and 100%. The  $\text{CO}_2$ -reduction products may be selected from the group consisting of water, carbon, carbon monoxide, alcohols, ketones, carboxylic acids, aldehydes, heterocycles and  $\text{C}_{1-10}$  hydrocarbons. The method may further comprise the step of: (iv) collecting the  $\text{CO}_2$  reduction products.

[0057] According to a fifteenth aspect of the present invention, there are provided  $\text{CO}_2$  reduction products produced by the method of the fourteenth aspect of the present invention.

[0058] According to a sixteenth aspect of the present invention, there is provided use of the photoelectrochemical cell of the ninth or tenth aspect of the present invention for converting  $\text{CO}_2$  to  $\text{CO}_2$  reduction products.

## Brief Description of Figures

[0059] Embodiments of the present invention will now be described, by way of example only, with reference to the accompanying figures wherein:

[0060] Figure 1 is a schematic illustration of an exemplary process for preparation of a nanocomposite as described herein (N-CNT-N-RGO).

[0061] Figure 2 shows (a) a scanning electron microscopy (SEM) image; (b) a high resolution scanning electron microscopy (HRSEM) image; (c) a transmission electron microscopy (TEM) image; (d) a high resolution transmission electron microscopy (HRTEM) image of a N-CNT-N-RGO composite; (e) an X-ray diffraction pattern of nitrogen doped graphene (N-RGO) in a N-CNT-N-RGO composite; and (f) an HRTEM of nitrogen doped carbon nanotube (N-CNT) in a N-CNT-N-RGO composite.

[0062] Figure 3 shows (a) an electron energy loss spectroscopy EELS and (b) high-resolution transmission electron microscopy energy dispersive X-ray (HRTEM-EDX) images, of a N-CNT-N-RGO composite.

[0063] Figure 4 shows (a) an X-ray photoelectron spectroscopy (XPS) survey spectrum of a N-CNT-N-RGO; and (b) a high-resolution N1s XPS spectra of a N-CNT-N-RGO.

[0064] Figure 5 is an exemplary schematic structure showing the binding conditions of nitrogen in graphene plane.

[0065] Figures 6 shows Raman spectra of: (a) a N-CNT-N-RGO; and (b) a CNT-RGO composite.

[0066] Figure 7 is a rotating disk electrode (RDE) voltammogram in O<sub>2</sub> saturated 0.1 M KOH solution at room temperature (rotation speed 1600 rpm, sweep rate 20 mV s<sup>-1</sup>) for the CNT, N-CNT, RGO, N-RGO, N-CNT-N-RGO and Pt/C.

[0067] Figure 8 shows (a) cyclic voltammograms (CV) of N-CNT-N-RGO and Pt/C electrodes in O<sub>2</sub> saturated 0.1M KOH before (solid line) and after (dash line) a continuous potentiodynamic swept for 5000 cycles at room temperature (25 °C), scan rate: 0.1 V/s; and (b) RDE voltammograms for the ORR in O<sub>2</sub> saturated 0.1 M KOH of N-CNT-N-RGO and Pt/C

electrodes before (solid line) and after (dash line) a continuous potentiodynamic swept for 5000 cycles at room temperature (25 °C), scan rate: 0.1 V/s, electrode rotating rate: 1600 rpm.

[0068] Figure 9 shows the performance of a N-CNT-N-RGO catalyst in the oxygen evolution reaction (OER) by a linear sweep voltammogram (LSV) curves of the NCNT-N-RGO and Pt/C electrodes in Ar-saturated 0.1 M KOH (a) and 0.5 H<sub>2</sub>SO<sub>4</sub> (b) at 5mV/s.

[0069] Figure 10 shows the performance of a N-CNT-N-RGO catalyst in the OER by Tafel plots of the NCNT-N-RGO and Pt/C electrodes in Ar-saturated 0.1 M KOH (a) and 0.5 H<sub>2</sub>SO<sub>4</sub> (b) at 2mV/s.

[0070] Figure 11 shows the performance of a N-CNT-N-RGO catalyst in the hydrogen evolution reaction (HER) by LSV curves of the N-CNT-N-RGO and Pt/C electrodes in Ar-saturated 0.1 M KOH (a) and 0.5 H<sub>2</sub>SO<sub>4</sub> (b) at 5mV/s.

[0071] Figure 12 shows the performance of a N-CNT-N-RGO catalyst in the HER by Tafel plots of the N-CNT-N-RGO and Pt/C electrodes in Ar-saturated 0.1 M KOH (a) and 0.5 H<sub>2</sub>SO<sub>4</sub> (b) at 2mV/s.

[0072] Figures 13(a) and (b) are schematic diagrams showing two different configurations of anodes and cathodes disposed on an electrically conductive substrate;

[0073] Figure 14 is a schematic diagram of a photoelectrochemical cell comprising a porous proton conductor;

[0074] Figures 15(a) and (b) are scanning electron micrograph images of a nano-fibrous proton conductor;

[0075] Figure 16 is a photograph of a photoelectrochemical cell comprising a porous proton conductor;

[0076] Figure 17 is a schematic diagram showing the experimental set-up used for measuring the current produced by a photoelectrochemical cell; and

[0077] Figure 18 shows the current produced by the photoelectrochemical cell of Fig. 16, measured using a potentiostat, when illuminated and when dark in the presence of (a) CO<sub>2</sub> and H<sub>2</sub>O, (b) Ar and H<sub>2</sub>O, (c) CO<sub>2</sub> and (d) CO<sub>2</sub> and H<sub>2</sub>O;

[0078] Figure 19 is a photograph of a photoelectrochemical cell comprising a porous proton conductor;

[0079] Figure 20 shows the current produced by a photoelectrochemical cell of Fig. 19, measured using a potentiostat, when illuminated and when dark in the presence of a humid Ar feed stream and a humid CO<sub>2</sub> feed stream; and

[0080] Figure 21 shows the current produced by a photoelectrochemical cell (a) without a thermal sink and (b) with a thermal sink.

### Definitions

[0081] As used in this application, the singular form "a", "an" and "the" include plural references unless the context clearly dictates otherwise. For example, the phrase "a catalyst" also includes a plurality of catalysts.

[0082] As used herein, the term "comprising" means "including." Variations of the word "comprising", such as "comprise" and "comprises," have correspondingly varied meanings. Thus, for example, a photochemical cell "comprising" nanocomposite A may contain only nanocomposite A or may include one or more additional nanocomposites (e.g., nanocomposite A and nanocomposite B).

[0083] It will be understood that use of the term "about" herein in reference to a recited numerical value (e.g., a temperature or pressure) includes the recited numerical value and numerical values within plus or minus ten percent of the recited value.

[0084] Any description of a prior art document herein, or a statement herein derived from or based on that document, is not an admission that the document or derived statement is a part of the common general knowledge of the relevant art.

[0085] For the purposes of description all documents referred to herein are incorporated by reference in their entirety unless otherwise stated.

[0086] As used herein, the term "heteroatom-doped" or "heteroatom-doping" refers to the intercalation and/or incorporation of heteroatoms into a carbon framework. Heteroatoms include, but are not limited to, nitrogen, sulfur, phosphorous, boron, silicon and aluminium.

[0087] As used herein, the term "graphene" includes pristine graphene and reduced graphene oxide (RGO).

[0088] As used herein, the term "nanocomposite" refers to a structure comprising two or more components, in which one of the components has at least one dimension between about 1 nm and about 100 nm.

[0089] As used herein, the term "carbon nanostructure" refers to a structure consisting of carbon atoms having at least one dimension between about 1 nm and about 100 nm.

### **Description of Embodiments**

[0090] Certain aspects of the present invention relate to nanocomposites which are suitable for use as catalysts in electrochemical cells. The nanocomposites may be used in a variety of applications. For example, the nanocomposites may be used as catalysts for splitting of water to produce sustainable hydrogen to be used, for example, as an energy source in a hydrogen fuel cell. Additionally or alternatively, they may be used as catalysts for oxygen evolution reactions (OER), oxygen reduction reactions (ORR), and/or reduction of carbon dioxide.

[0091] The nanocomposites described herein comprise heteroatom-doped carbon nanostructures, e.g., graphene, fullerenes and/or carbon nanotubes, which may confer improved electromagnetic, physiochemical, optical, and/or structural properties. Non-limiting examples of suitable heteroatoms for doping the carbon nanostructures include, but are not limited to, nitrogen, sulfur, phosphorus, boron, silicon, aluminium or combinations thereof.

[0092] In some embodiments, the nanocomposites comprise heteroatom-doped graphene (e.g., N-graphene). In some embodiments, heteroatom combinations may be incorporated into the carbon structure of graphene. The heteroatom combination may comprise any two or more of nitrogen, sulfur, phosphorus boron, silicon or aluminium.

[0093] As known to the skilled addressee, graphene is intrinsically non-flat and forms random corrugations which may cause undesirable properties for use in various applications.

Graphene also has a tendency to agglomerate (or re-stack) due to strong van der Waals interactions between neighbouring sheets, resulting in a loss of effective surface area and reduced electrical conductivity. Introducing heteroatoms into graphene may alter the local electron density and result in modified and/or enhanced physico-chemical properties of the graphene and/or may reduce the tendency of the graphene to agglomerate. Agglomeration

may also be ameliorated using nano-spacers between layers of graphene. Suitable nano-spacers include, but are not limited to, CNTs and fullerenes.

[0094] For example, introducing heteroatoms into the graphene may, for example, enhance the electrical conductivity of the graphene. The heteroatoms may donate one or more free electrons to the graphene, causing free electron mobility and thereby increasing the electron conductivity of the graphene. Heteroatom doping of graphene may reduce the band gap and increase the chemical potential of the graphene. By way of example, nitrogen may be incorporated into the carbon structure of graphene by, for example, replacing a carbon atom to form 6-membered or 5-membered rings. For example, nitrogen may be incorporated into the graphene to form 6-membered pyridinic rings by replacing a carbon in a 6-membered ring at an edge of the graphene structure. Pyridinic-nitrogen contributes one p-electron to one aromatic  $\pi$ -system while having a lone electron pair. Additionally or alternatively, a quaternary nitrogen may replace a carbon atom in the 6-membered ring graphitic framework which contributes three p-electrons, i.e., one electron to each of the three aromatic  $\pi$ -systems into which the nitrogen is incorporated. Additionally or alternatively, nitrogen may be incorporated as a pyrrolic-nitrogen, wherein the nitrogen can replace a carbon in a 5-membered ring or a carbon bonded to hydrogen in a 6-membered ring at the edge of the graphene structure. Nitrogen may be incorporated into the graphene to form any combination of functionalities, for example, combinations of pyridinic, quaternary and/or pyrrolic nitrogen. The position of nitrogen in the graphene may affect the physico-chemical properties of the N-graphene. For example, it has been postulated that quaternary nitrogen has the most effective catalytic activity as it is able to contribute more electrons into the graphene than pyridinic or pyrrolic nitrogen. The position of nitrogen in the graphene structure may be influenced by controlling the nitrogen source and/or temperature at which nitrogen doping is carried out. For example, it has been postulated that use of a high affinity nitrogen source at high temperature tends to form quaternary nitrogen.

[0095] Suitable sources of heteroatoms for incorporation into the graphene are well known to those of ordinary skill in the art.

[0096] In embodiments where the heteroatoms comprise or consist of nitrogen, any suitable nitrogen source may be used. For example, the source may be an amino acid (e.g., L-arginine), ammonia, aniline, benzylamine, N-benzylmethylamine, butylamine, diethylamine, N,N-dimethylacetamide, N,N-dimethylformamide, ethylenediamine, formamide, hexamethylenediamine, isopropylamine, melamine, 1-methylpiperazine, N-methylenediamine, pyridine, pyrrole, quinoline, trimethylenediamine, urea, uric acid, or any combination thereof. In

some embodiments the nitrogen source may be a non-toxic or low toxicity nitrogen source. For example, it may be an amino acid (e.g., L-arginine), urea, uric acid, or any combination thereof. In some embodiments, the nitrogen source may not be ammonia.

[0097] In some embodiments, the heteroatom (e.g., nitrogen) content of the heteroatom-doped graphene may be in the range of about 0.1 wt% to about 20 wt%. For example, the heteroatom (e.g., nitrogen) content of the heteroatom-doped graphene may be in the range of about 0.1 wt% to about 10 wt%, about 1 wt% to about 10 wt%, about 5 wt% to about 15 wt%, about 2 wt% to about 8 wt%, about 0.5 wt% to about 10 wt%, about 0.5 wt% to about 7 wt%, about 0.2 wt% to about 6 wt%, about 3 wt% to about 7 wt%, about 4 wt% to about 6 wt%, e.g., about 0.1 wt%, 0.2 wt%, 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, 10 wt%, 12 wt%, 15 wt% or 20 wt%.

[0098] Suitable methods for introducing heteroatoms into the carbon structure of graphene are well known to those of ordinary skill in the art. For example, nitrogen may be introduced into the carbon structure of graphene by any suitable method. For example, it may be introduced by mixing graphene oxide (GO) with a nitrogen source in any suitable solvent (e.g., water) to produce nitrogen-doped graphene oxide (N-GO), followed by a reduction step to produce nitrogen-doped reduced graphene oxide (N-RGO). GO may be produced by any suitable method, for example, by exfoliation of graphite. Methods for exfoliating graphite are known in the art, for example, the Hummer's method (W.S. Hummers and R.E. Offeman, *J. Am. Chem. Soc.*, 1958, 80, 1339) and modifications thereof. In some embodiments, insertion of nitrogen and reduction occur simultaneously. In some embodiments, the nitrogen source may act as a reducing agent, e.g., uric acid, urea, ammonia or melamine. In the production of N-RGO, the ratio of graphene oxide to nitrogen source may be in the range of about 1:1 to about 1:20. For example, the ratio of graphene oxide to nitrogen source may be in the range of about 1:1 to about 1:10, about 1:5 to about 1:20, about 1:1 to about 1:5, about 1:5 to about 1:15, about 1:2 to about 1:10, about 1:2 to about 1:12, about 1:2 to about 1:8, about 1:10 to about 1:20, about 1:10 to about 1:15, e.g., about 1:1, about 1:2, about 1:3, about 1:4, about 1:5, about 1:6, about 1:7, about 1:8, about 1:9, about 1:10, about 1:11, about 1:12, about 1:13, about 1:14, about 1:15, about 1:16, about 1:17, about 1:18, about 1:19 or about 1:20. The N-GO may be produced in the form of a dispersion in solvent (e.g., water), or it may be dried to yield solid N-GO, e.g., as flakes, sheets or nanoplatelets. In some embodiments, the solid N-GO may be reduced by heating or annealing at high temperature. High temperatures may also assist with incorporation of nitrogen into the graphene. For example, the solid N-RGO may be heated to a temperature between about 100 °C and about 2000 °C, e.g., about 100 °C, 200 °C, 300 °C,

400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400 °C, 1500 °C, 1600 °C, 1700 °C, 1800 °C, 1900 °C, or 2000 °C.

[0099] The heteroatom-doped graphene (e.g., N-graphene) described herein may be functionalised. Functional groups may be introduced at any suitable time during the process of preparing the heteroatom-doped graphene, e.g., before, during or after heteroatom doping. In some embodiments, functional groups may be covalently bound to the heteroatom-doped graphene by, for example, oxidation, esterification, amidation, halogenation, radical addition, cycloaddition, nucleophilic addition or electrophilic addition. Covalently bound functional groups may be attached onto the graphene. Additionally or alternatively, functional groups may be non-covalently bound to the heteroatom-doped graphene, for example, by van der Waals forces,  $\pi$ - $\pi$  interactions, or adsorption of compounds on the surface of the heteroatom-doped graphene, e.g., polynuclear aromatic compounds, surfactants, polymers or biomolecules. In some embodiments, precious and/or non-precious metals or metal salts may be incorporated into the graphene structure.

[00100] The heteroatom-doped graphene may be in the form of nanostructures having any suitable morphology. For example, the heteroatom-doped graphene nanostructures may be in the form of flakes, sheets or nanoplatelets. In some embodiments, the heteroatom-doped graphene does not form agglomerates of more than about 10 layers. For example, the heteroatom-doped graphene may form agglomerates of less than about 10 layers, e.g., less than about 9, 8, 7, 6, 5, 4, 3 or 2 layers. In some embodiments, the heteroatom-doped graphene is present substantially as single layer heteroatom-doped graphene. The heteroatom-doped graphene nanostructures may have any suitable particle size. For example, each of the heteroatom-doped graphene particles may have an equivalent spherical diameter in the range about 1 nm to less than about 1 mm, about 1 nm to about 500  $\mu$ m, about 10 nm to about 500  $\mu$ m, about 100 nm to about 50  $\mu$ m, about 1  $\mu$ m to about 500  $\mu$ m, about 10 nm to about 500 nm, or about 500 nm to about 500  $\mu$ m. The heteroatom-doped graphene particles may have a mean equivalent spherical diameter in the range of about 1 nm to less than about 1 mm, about 1 nm to about 500  $\mu$ m, about 10 nm to about 500  $\mu$ m, about 100 nm to about 50  $\mu$ m, about 1  $\mu$ m to about 500  $\mu$ m, about 10 nm to about 500 nm, or about 500 nm to about 500  $\mu$ m. In some embodiments, the heteroatom-doped graphene may be nanoporous.

[00101] In some embodiments, the nanocomposites described herein comprise heteroatom-doped carbon nanotubes (CNTs), which may confer improved electromagnetic, physiochemical, optical, and/or structural properties. Non-limiting examples of suitable

heteroatoms for doping the CNTs include, but are not limited to, nitrogen, sulfur, phosphorus, boron, silicon, aluminium or combinations thereof.

[00102] As known to the skilled addressee, carbon nanotubes (CNTs) have a tendency to agglomerate, aligning themselves into ropes or bundles held together by van der Waals forces, reducing the amount of effective surface area and electrical conductivity. Introducing heteroatoms into CNTs may alter the local electron density and result in modified and/or enhanced physico-chemical properties of the CNTs and/or may reduce the tendency of the CNTs to agglomerate.

[00103] In some embodiments, the nanocomposites comprise nitrogen-doped carbon nanotubes (N-CNTs). In some embodiments, heteroatom combinations may be incorporated into the carbon structure of the graphitic plane. The heteroatom combination may comprise any two or more of nitrogen, sulfur, phosphorus or boron.

[00104] For example, introducing heteroatoms into the CNTs may, for example, enhance the conductivity of the CNT. The heteroatoms may donate one or more free electrons to the CNTs, causing free electron mobility and thereby increasing the electron conductivity of the CNTs. Heteroatom doping of CNTs may reduce the band gap and increase the chemical potential of the CNTs. By way of example, nitrogen may be incorporated into the carbon structure of CNTs by, for example, replacing a carbon atom to form 6-membered or 5-membered rings. For example, nitrogen may be incorporated into CNTs to form 6-membered pyridinic rings by replacing a carbon in a 6-membered ring at an edge of the CNT structure. Pyridinic-nitrogen contributes one p-electron to one aromatic  $\pi$ -system while having a lone electron pair. Additionally or alternatively, a quaternary nitrogen may replace a carbon atom in the 6-membered ring graphitic framework which contributes three p-electrons to the three aromatic  $\pi$ -systems. Additionally or alternatively, nitrogen may be incorporated as a pyrrolic-nitrogen can replace a carbon in a 5-membered ring or a carbon bonded to hydrogen in a 6-membered ring at the edge of the CNT structure. Nitrogen may be incorporated into the CNTs to form any combination of functionalities, for example, combinations of pyridinic, quaternary and/or pyrrolic nitrogen. The position of nitrogen in the CNTs may affect the physico-chemical properties of the N-CNT. For example, it has been postulated that quaternary nitrogen has the most effective catalytic activity as it is able to contribute more electrons into the CNTs than pyridinic or pyrrolic nitrogen. The position of nitrogen in the CNT structure may be influenced by controlling the nitrogen source and/or temperature at which nitrogen doping is carried out. For example, it has been postulated that use of a high affinity nitrogen source at high temperature tends to form quaternary nitrogen.

[00105] Suitable sources of heteroatoms for incorporation into the CNTs are well known to those of ordinary skill in the art.

[00106] In embodiments where the heteroatoms comprise or consist of nitrogen, any suitable nitrogen source may be used. For example, the source may be an amino acid (e.g., L-arginine), ammonia, aniline, benzylamine, N-benzylmethylamine, butylamine, diethylamine, N,N-dimethylacetamide, N,N-dimethylformamide, ethylenediamine, formamide, hexamethylenediamine, isopropylamine, melamine, 1-methylpiperazine, N-methylenediamine, pyridine, pyrrole, quinoline, trimethylenediamine, urea, uric acid and combinations thereof. In some embodiments the nitrogen source may be a non-toxic or low toxicity nitrogen source. For example, it may be an amino acid, urea, uric acid and combinations thereof. In some embodiments, the nitrogen source may not be ammonia.

[00107] In some embodiments, the heteroatom (e.g., nitrogen) content of the CNTs may be in the range of about 0.1 wt% to about 20 wt%. For example, the heteroatom (e.g., nitrogen) content of the CNTs may be in the range of about 0.1 wt% to about 10 wt%, about 1 wt% to about 10 wt%, about 5 wt% to about 15 wt%, about 2 wt% to about 8 wt%, about 0.5 wt% to about 10 wt%, about 0.5 wt% to about 7 wt%, about 0.2 wt% to about 6 wt%, about 3 wt% to about 7 wt%, about 4 wt% to about 6 wt%, e.g., about 0.1 wt%, 0.2 wt%, 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, 10 wt%, 12 wt%, 15 wt% or 20 wt%.

[00108] Heteroatoms may be introduced into the carbon structure of CNTs by any suitable method. Methods for doping of CNTs with heteroatoms (e.g., nitrogen) are known in the art, for example, chemical vapour deposition (CVD), arc discharge, laser ablation, or solvothermal synthesis. The CNTs may be any suitable morphology, for example, they may be single-walled CNTs or they may be multi-walled CNTs, giving rise to single-walled heteroatom-doped CNTs or multi-walled N-CNTs respectively.

[00109] The heteroatom-doped CNTs described herein may be functionalised. Functional groups may be introduced at any suitable time during the process of preparing the heteroatom-doped CNTs, e.g., before, during or after heteroatom doping. In some embodiments, functional groups may be covalently bound to the heteroatom-doped CNTs by, for example, oxidation, esterification, amidation, halogenation, radical addition, cycloaddition, nucleophilic addition or electrophilic addition. Covalently bound functional groups may be attached onto the side wall or ends of the carbon nanotube. Additionally or alternatively, functional groups may be non-covalently bound to the heteroatom-doped CNTs, for example, by van der Waals forces,  $\pi$ - $\pi$  interactions, or adsorption of compounds on the surface of the heteroatom-doped CNTs, e.g.,

polynuclear aromatic compounds, surfactants, polymers or biomolecules. In some embodiments, precious and/or non-precious metals or metal salts may be incorporated into the CNT structure.

[00110] The heteroatom-doped CNTs may be in the form of nanoparticles having any suitable particle size. For example, each of the heteroatom-doped CNTs particles may have an equivalent spherical diameter in the range about 1 nm to less than about 100  $\mu\text{m}$ , about 1 nm to about 50  $\mu\text{m}$ , about 10 nm to about 50  $\mu\text{m}$ , about 100 nm to about 50  $\mu\text{m}$ , about 1  $\mu\text{m}$  to about 50  $\mu\text{m}$ , about 10 nm to about 500 nm, or about 500 nm to about 100  $\mu\text{m}$ . The heteroatom-doped CNT particles may have a mean equivalent spherical diameter in the range of about 1 nm to about 50  $\mu\text{m}$ , about 10 nm to about 50  $\mu\text{m}$ , about 100 nm to about 50  $\mu\text{m}$ , about 1  $\mu\text{m}$  to about 50  $\mu\text{m}$ , about 10 nm to about 500 nm, or about 500 nm to about 100  $\mu\text{m}$ . In some embodiments, the heteroatom-doped CNTs may be nanoporous.

[00111] The nanocomposites described herein may be formed by combining heteroatom-doped carbon nanostructures. For example, they may be formed by combining heteroatom-doped graphene and heteroatom-doped CNTs. The nanocomposites may be formed by any suitable method, for example, by adsorption of heteroatom-doped CNTs (e.g., N-CNTs) onto the surface of heteroatom-doped graphene (e.g., N-graphene). The heteroatom-doped graphene and heteroatom-doped CNTs may assemble in any arrangement to form the nanocomposites. In some embodiments, the heteroatom-doped graphene and heteroatom-doped CNTs self-assemble to form the nanocomposites. In some embodiments, the nanocomposites described herein may be formed by combining CNTs which have been pre-doped with one or more heteroatoms (e.g., nitrogen) with graphene which has been pre-doped with one heteroatoms (e.g., nitrogen). In other embodiments, a nanocomposite may be first formed by combining CNTs and graphene, and the nanocomposite subsequently doped with one or more heteroatoms. The present inventors have observed improved catalytic activity in embodiments in which the graphene and CNTs have been doped with one or more heteroatoms prior to formation of the nanocomposite. In some embodiments, the heteroatom-doped graphene (e.g., N-graphene) does not form agglomerates or stacks of more than about 10 layers. For example, the heteroatom-doped graphene may form agglomerates of less than about 10 layers, e.g., less than about 9, 8, 7, 6, 5, 4, 3 or 2 layers. Agglomeration may be ameliorated, for example, by spacing apart of the N-graphene particles with N-CNTs. In some embodiments, the heteroatom-doped graphene may be present substantially as single layer N-graphene. The nanocomposite may be formed on a solid support. In some embodiments, the nanocomposite is formed on a support which is not a hydroxide support. Alternatively, the nanocomposite may be formed without a solid support.

[00112] The nanocomposites described herein may be in any suitable form. For example, they may be in the form a dispersion or a solid, e.g., a powder. The nanocomposites may comprise heteroatom-doped graphene (e.g., N-graphene) and heteroatom-doped CNTs (e.g., N-CNTs) in a ratio of about 1:10 to about 10:1. For example, the ratio of N-graphene to N-CNTs may be about 1:10, 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1 or 10:1. The overall heteroatom (e.g., nitrogen) content of the nanocomposites described herein may be in the range of about 0.1 wt% to about 20 wt%. For example, the nitrogen content of the N-CNTs may be in the range of about 0.1 wt% to about 10 wt%, about 1 wt% to about 10 wt%, about 5 wt% to about 15 wt%, about 2 wt% to about 8 wt%, about 0.5 wt% to about 10 wt%, about 0.5 wt% to about 7 wt%, about 0.2 wt% to about 6 wt%, about 3 wt% to about 7 wt%, about 4 wt% to about 6 wt%, e.g., about 0.1 wt%, 0.2 wt%, 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, 10 wt%, 12 wt%, 15 wt% or 20 wt%.

[00113] The nanocomposites described herein may have any suitable particle size. For example, each of the nanocomposite particles may have an equivalent spherical diameter in the range of about 1 nm to less than about 1 mm, about 1 nm to about 500  $\mu$ m, about 10 nm to about 500  $\mu$ m, about 100 nm to about 50  $\mu$ m, about 1  $\mu$ m to about 500  $\mu$ m, about 10 nm to about 500 nm, or about 500 nm to about 500  $\mu$ m. The nanocomposite particles may have a mean equivalent spherical diameter in the range of about 1 nm to less than about 1 mm, about 1 nm to about 500  $\mu$ m, about 10 nm to about 500  $\mu$ m, about 100 nm to about 50  $\mu$ m, about 1  $\mu$ m to about 500  $\mu$ m, about 10 nm to about 500 nm, or about 500 nm to about 500  $\mu$ m. In some embodiments, the nanocomposites may be nanoporous. In some embodiments, the nanocomposites described herein may be formed by self-assembly of the heteroatom-doped graphene (e.g., N-graphene) and heteroatom-doped CNTs (e.g., N-CNTs) in solution. The heteroatom-doped graphene and heteroatom-doped CNTs may be combined in any suitable solvent (e.g., isopropanol) and optionally heated to facilitate formation of the nanocomposite and/or to facilitate evaporation of the solvent. The mixture may be optionally heated to a temperature between about 30 °C to about 150 °C. For example, the temperature may be between about 30 °C and about 100 °C, about 50 °C and about 150 °C, about 50 °C and about 100 °C, about 50 °C and about 80 °C, about 60 °C and about 90 °C, about 100 °C and about 150 °C, about 60 °C and about 80 °C, e.g., about 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C or 150 °C. The nanocomposite may be provided in the form of a dispersion, or it may be dried to form a solid, e.g., a powder.

[00114] Among other applications, the nanocomposites described herein may be used as catalysts for reduction and/or oxidation reactions. The nanocomposites may be used as a catalyst, for example, in hydrogen evolution reactions (HER), oxygen evolution reactions

(OER), oxygen reduction reaction (ORR), in reactions for converting carbon dioxide to carbon dioxide reduction products (e.g., fuels) by catalysing oxidation/proton generation reactions, and/or for the splitting of water.

[00115] In some embodiments, the nanocomposites described herein may be used in electrochemical cells, for example, fuel cells (e.g., hydrogen fuel cells), photoelectrochemical cells, or batteries (e.g., lithium ion batteries).

[00116] The electrochemical cells typically comprise an anode and a cathode. The anode and cathode may be in electrical communication with each other and comprise, respectively, an oxidation catalyst and a reduction catalyst. The oxidation catalyst may comprise a nanocomposite as described herein. Additionally or alternatively, the reduction catalyst may comprise a nanocomposite as described herein.

[00117] The nanocomposites described herein may be used as a catalyst, for example in a hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and/or the oxidation reduction reaction (ORR). The present inventors have found that the nanocomposites described herein outperform traditional Pt/C catalysts in various oxidation and/or reduction reactions.

[00118] By way of non-limiting example, the nanocomposites described herein may outperform traditional Pt/C catalysts in the HER, the most important reaction in the splitting of water.

[00119] In some embodiments, the nanocomposites may have less overpotential than a Pt/C catalyst in alkaline and/or acidic media (see Example 12). In some embodiments, the nanocomposites may have an overpotential measured by linear sweep voltammogram (LSV) curves of between about 10 mV and about 150 mV toward HER compared to Pt/C catalysts in alkaline or acidic media. For example, the nanocomposites may have an overpotential between about 10 mV and about 100 mV, about 50 mV and about 150 mV, about 50 mV and about 100 mV, about 30 mV and about 100 mV, about, e.g., about 10 mV, 20 mV, 30 mV, 40 mV, 50 mV, 60 mV, 70 mV, 80 mV, 90 mV, 100 mV, 110 mV, 120 mV, 130 mV, 140 mV, or 150 mV.

[00120] Additionally or alternatively, the nanocomposites may exhibit a higher current density in alkaline or acidic media than Pt/C, for example, between about 0.2 mA/cm<sup>2</sup> and about 30 mA/cm<sup>2</sup> higher than Pt/C e.g., about 0.2 mA/cm<sup>2</sup>, 0.3 mA/cm<sup>2</sup>, 0.5 mA/cm<sup>2</sup>, 1 mA/cm<sup>2</sup>, 2 mA/cm<sup>2</sup>, 5 mA/cm<sup>2</sup>, 10 mA/cm<sup>2</sup>, 15 mA/cm<sup>2</sup>, 20 mA/cm<sup>2</sup>, 25 mA/cm<sup>2</sup>, or 30 mA/cm<sup>2</sup>. The

present inventors have also found that less potential may be required for the HER reaction using the nanocomposites as a reduction catalyst compared to commercial Pt/C in alkaline or acidic environments (see Example 12). The nanocomposites may have a reduced potential compared to Pt/C in HER of between about 2 mV and about 80 mV. For example, the nanocomposites may have a reduced potential compared to Pt/C in HER of between about 10 mV and about 80 mV, about 2 mV and about 50 mV, about 5 mV and about 70 mV, about 10 mV and about 50 mV, or about 5 mV and about 60 mV, e.g., about 2 mV, 5 mV, 10 mV, 20 mV, 30 mV, 40 mV, 50 mV, 60 mV, 70 mV, or 80 mV. The nanocomposites may have a reduced potential compared to Pt/C in OER of between about 10 mV to about 200 mV. For example, the nanocomposites may have a reduced potential compared to Pt/C in OER of between about 10 mV and about 100 mV, about 5 mV and about 50 mV, about 10 mV and about 100 mV, about 50 mV and about 150 mV, or about 50 mV and about 200 mV, e.g., about 10 mV, 20 mV, 40 mV, 60 mV, 80 mV, 100 mV, 120 mV, 140 mV, 160 mV, 180 mV, or 200 mV.

[00121] Additionally or alternatively, the nanocomposites described herein may outperform Pt/C in the ORR. As known to persons skilled in the art, the ORR on a catalyst surface in alkaline solution can either produce peroxide ( $\text{H}_2\text{O}_2$ ), through a two-electron process, or water ( $\text{H}_2\text{O}$ ) through a four-electron process. The four-electron pathway is considered more efficient and favourable.

[00122] The present inventors have demonstrated using LSV on a rotating disk electrode (RDE) that the nanocomposites show a positively shifted onset potential in the ORR compared to CNT, N-CNT, RGO, and N-RGO (see Example 10). In some embodiments, the nanocomposites may show a positively shifted onset potential of between about -0.02 V and about -0.5 V compared to CNT, N-CNT, RGO, and N-RGO. For example, the nanocomposites may show a positively shifted onset potential of between about -0.02 V and about -0.5 V, -0.02 V and about -0.3 V, about -0.05 V and about -0.4 V, about -0.05 V and about -0.3 V, about -0.05 V and about -0.35 V, e.g., about -0.02 V, -0.04 V, -0.06 V, -0.08 V, -0.1 V, -0.15 V, -0.2 V, -0.25 V, -0.3 V, -0.35 V, -0.4 V, -0.45 V, or -0.5 V. The present inventors have found that the nanocomposites may demonstrate significantly higher steady state catalytic current than that of Pt/C. For example, the nanocomposites described herein exhibit a comparatively wide plateau corresponding to greater catalytic activity. A wide plateau indicates that, after a certain potential has been reached, the current does not change with increasing potential. This is referred to as a steady state current. A catalyst having a higher steady state current density in ORR is indicative of a higher rate of oxygen reduction.

[00123] An electrode comprising a nanocomposite as described herein may also have improved durability/stability toward the ORR than Pt/C. For example, the present inventors have shown that there is no obvious shape change in the cyclic voltammogram (CV) of the nanocomposite observed after 5000 consecutive potential cycling in O<sub>2</sub> saturated 0.1 M KOH, in contrast to the loss of the active surface area for a commercial Pt/C catalyst (see Example 10 and Figure 8). In some embodiments, the nanocomposite may show between about 75% and about 100% retention on its onset potential and steady state current density after 5000 continuous cycles. For example, it may show retention on its onset potential and steady state current density after 5000 continuous cycles between about 75% and about 95%, about 80% and about 100%, about 80% and about 95%, about 85% and about 95%, about 90% and about 95%, e.g., about 75%, 80%, 85%, 90%, 91%, 92%, 93%, 94%, 95%, 98%, or 100%. By comparison, commercial Pt/C may show more than 30% attenuation on onset potential and 40% loss of steady state current density (see Figure 8(b)). The present inventors have postulated that the excellent stability of the nanocomposites described herein may be the result of strong covalent bonds between the active sites and the graphitic lattice in the nanocomposite.

[00124] The nanocomposites described herein may be used as an oxidation catalyst, for example, in an oxygen evolution reaction (OER). The present inventors have shown that the nanocomposites described herein exhibit high catalytic activity towards OER (see Example 11). In some embodiments, the nanocomposites may show onset potential in the OER in alkaline or acidic solution between about 0.2 V and about 3 V. For example, the nanocomposites may show onset potential in the OER between about 0.2 V and about 2.5 V, about 0.2 V and about 2 V, about 0.5 V and about 3 V, about 0.5 V and about 2 V, about 0.5 V and about 1.5 V, e.g., about 0.2 V, 0.3 V, 0.4 V, 0.5 V, 0.6 V, 0.8 V, 0.9 V, 1 V, 1.2 V, 1.5 V, 2 V, 2.5 V, 3 V. The applied potential required to achieve a specific current density may be lower for the nanocomposites described herein than Pt/C in both acidic and alkaline media. In some embodiments, the difference in applied potential vs. Ag/AgCl to achieve a current density of 10 mA/cm<sup>2</sup> for the nanocomposites compared to Pt/C may be in the range of about 0.05 V to about 1 V. For example, it may be in the range of about 0.05 V to about 0.5 V, about 0.1 V to about 1 V, about 0.1 V to about 0.05 V, about 0.2 V to about 0.5 V, about 0.1 V to about 0.3 V, e.g., about 0.05 V, about 0.1 V, about 0.15 V, about 0.2 V, about 0.25 V, about 0.3 V, about 0.35 V, about 0.4 V, about 0.5 V, or about 1 V.

[00125] The present inventors have also demonstrated that lower potentials are needed to change the reaction from ORR to OER in both acidic and alkaline media for the nanocomposites described herein compared to commercial Pt/C (Example 11; Figure 10). The

potential needed to change the reaction from ORR to OER for the nanocomposites vs Ag/AgCl compared to Pt/C vs Ag/AgCl may be reduced by between about 0.02 V and about 2 V. For example, the potential may be reduced by between about 0.02 V and about 1 V, about 0.1 V and about 2 V, about 0.05 V and about 1 V, about 0.05 V and about 1.5 V, or about 0.5 V and about 1.5 V, e.g., about 0.02, 0.05 V, 0.1 V, 0.5 V, 1 V, 1.5 V, or 2 V.

[00126] Other aspects of the present invention relate to improved proton conductors for use in photoelectrochemical cells.

[00127] The proton conductors are typically porous, gas-permeable and at least partially transparent to electromagnetic (EM) radiation. The described proton conductors may be used in a variety of applications. For example, the described proton conductors may be used to provide a proton transfer pathway in a photoelectrochemical cell. In such applications, the porosity of the proton conductor may allow rapid diffusion of reactants (e.g., CO<sub>2</sub> and H<sub>2</sub>O) through the proton conductor to reach catalyst sites. Thus, there are also described herein photoelectrochemical cells comprising the described proton conductors.

[00128] Photoelectrochemical cells described herein may be solid-state. They do not require any liquid electrolyte as the proton transfer pathway is the porous proton conductor. Thus, the photoelectrochemical cells may operate entirely in the gas phase using, for example, a humid gaseous feed stream as a proton source. As no liquid media are required for any part of the cell construction or during the reactions within the cell, they do not suffer from ion migration or liquid leakage problems. In addition, they are relatively simple to assemble, operate and maintain. Furthermore, any liquid reaction products (e.g., alcohols) produced by the photoelectrochemical cell may be readily collected without the need to separate the products from a liquid electrolyte phase. The photoelectrochemical cells may also be used with liquid feed streams if required.

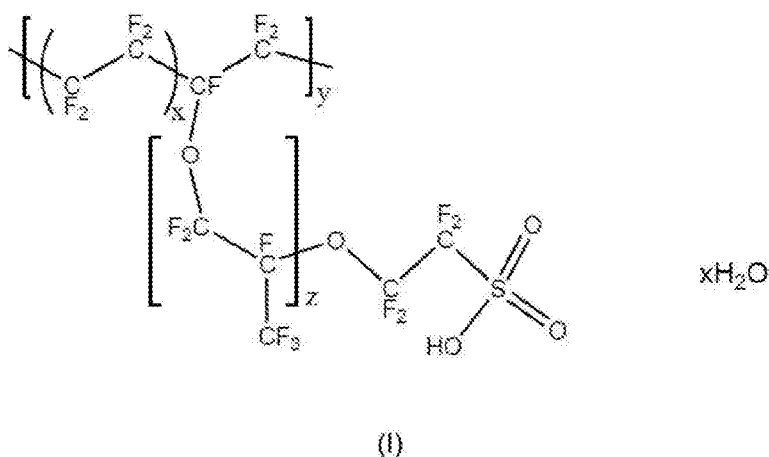
[00129] By virtue of the porosity and the at least partial transparency of the proton conductor, which allow transmission of reactants and EM radiation, the proton conductor may be used as an external coating on components of the photoelectrochemical cells. This allows for configurations of photoelectrochemical cells wherein the electrical conductivity is provided without the need for conductive wires, as discussed in greater detail herein. Wireless photoelectrochemical cells are simpler to assemble and maintain than cells that require conductive wires. The use of the proton conductor as an at least partially transparent film around the other components of the device also provides improved efficiency as it allows simultaneous photocatalytic oxidation and reduction reactions. In addition, some embodiments

of the photoelectrochemical cells described herein include a photovoltaic cell, which provides energy to drive photoelectrochemical reactions in the cell. Such photoelectrochemical cells thus work in the presence of EM radiation (e.g., sunlight), no other power source being required for their operation.

[00130] The photoelectrochemical cells may be used at room temperature and at atmospheric pressure. However, for some applications it may be appropriate to use a higher temperature, a higher pressure or both in order to tune product selectivity (e.g., where higher molecular weight reduction products are to be formed). In some embodiments, the photoelectrochemical cells described herein have a modular design, enabling easy scale-up and easy disassembly if required. The photoelectrochemical cells described herein may be produced so as to be extremely light weight. They may also be flexible, allowing a variety of shapes (e.g., curved or flat). In addition, the photoelectrochemical cells may be regenerated by washing and/or application of the proton conductor.

[00131] The porous proton conductor described herein is at least partially transparent to electromagnetic (EM) radiation and comprises a gas-permeable polymeric material. In some embodiments, the porosity of the proton conductor is provided by a nano-fibrous structure or a three-dimensional network of bonded nano-fibres.

[00132] The proton conductor may comprise any suitable proton-conducting polymeric material(s). In some embodiments, the proton conductor may comprise one or more perfluorinated sulfonic acids, radiation-grafted polyelectrolytes, sulfonated thermostable polymers, polymers obtained by acid complexation, hydrocarbon-based block copolymers or a combination thereof. In some embodiments, the proton-conducting polymeric material(s) may comprise a perfluorinated polymer electrolyte having the formula (I):



wherein x, y and z depend on the degree of polymerisation of the monomers used to prepare the polymer. Suitable perfluorinated polymer electrolytes include Nafion<sup>®</sup>, Aciplex<sup>®</sup>, Flemion<sup>®</sup>, GORE-SELECT<sup>®</sup> membrane and 3M660 PFSA, which is a product of 3M company.

[00133] The proton conductor may be at least partially transparent to EM radiation having any suitable wavelength. The proton conductor may be at least partially transparent to EM radiation having a wavelength suitable for the intended application of the proton conductor. For example, the proton conductor may be at least partially transparent to EM radiation having a wavelength suitable for driving photoreactions in a photoelectrochemical cell. In some embodiments, the proton conductor may be at least partially transparent to EM radiation having a wavelength in the range 350 to 850 nm. In some embodiments, the amount of incident EM radiation of a specific wavelength within that range that is transmitted by the proton conductor may be greater than 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% or 95%.

[00134] The proton conductor may have any suitable thickness. In general, a thinner proton conductor allows greater transmission of EM radiation, whereas a thicker proton conductor provides more material for proton conduction. The optimal proton conductor thickness may therefore depend on the specific application for which the proton conductor is employed. A proton conductor may have a thickness of between about 500 nm and about 100  $\mu$ m, between about 750 nm and about 80  $\mu$ m, between about 1  $\mu$ m and about 60  $\mu$ m, or between about 10  $\mu$ m and about 40  $\mu$ m. In some embodiments, the proton conductor has a thickness of about 20  $\mu$ m. However, it will be understood that a thinner or thicker proton conductor may be suitable for certain applications and is within the scope of this disclosure. The individual fibres within a proton conductor may have any suitable diameter. The individual fibres of a proton conductor may have a mean diameter of less than about 1  $\mu$ m, less than about 900 nm, less than about 800 nm, less than about 700 nm, less than about 600 nm, less than about 500 nm, less than about 400 nm, less than about 300 nm, less than about 200 nm or less than about 100 nm. In some embodiments, the individual fibres of a proton conductor may have a mean thickness of between about 100 nm and about 800 nm or between about 200 nm and about 600 nm. The individual fibres within a proton conductor may have any suitable morphology. The individual fibres may have a cross-sectional aspect ratio ranging from high (e.g., a ribbon-like morphology) to low (e.g., a cylindrical morphology).

[00135] The proton conductor described herein may be produced by any suitable means. In some embodiments, the proton conductor is prepared by electrospinning a polymeric material. The process of electrospinning uses an electrical charge to draw a fine fibre from a liquid (e.g.,

having nano- or micro-scale thickness). Thus, there is described herein a process for preparing a proton conductor comprising the steps of: (i) providing a gas-permeable polymeric material; and (ii) electrospinning the polymeric material, thereby producing a porous gas-permeable proton conductor.

[00136] Many proton-conductive polymers, such as Nafion<sup>®</sup>, have low polymer chain entanglement. Attempting to electrospin such polymers in pure form results in the formation of droplets of Nafion<sup>®</sup> on the target surface. In effect, this process is electrospraying and it results in the formation of a non-porous film on the target surface. It has now been found that if a carrier polymer is added to such materials to form a polymer composition, the resulting polymer composition may be electrospun to provide a proton-conductor that is porous, gas-permeable and at least partially transparent to EM radiation. Any suitable carrier polymer or combination of carrier polymers may be used to prepare the polymer composition. Suitable carrier polymers are generally soluble in the same solvent system as the proton-conductive polymer. They may be able to store electric charge. They may have high polymer chain entanglement. An example of a suitable carrier polymer for use with Nafion<sup>®</sup> is polyethylene oxide (PEO). In some embodiments, the PEO has a molecular weight in the range of 100 to 8000 kDa, in the range of 100 to 600 kDa, or in the range of 600 to 8000 kDa. Where the composition includes a carrier polymer, the proton conducting polymer and carrier polymer(s) may be combined at any suitable mass ratio. In some embodiments, the proton conducting polymer may be present at a concentration of at least about 50 wt.%, at least about 80 wt.%, at least about 90 wt.%, at least about 95 wt.%, at least about 98 wt.% or at least about 99 wt.% relative to the combined mass of the proton conducting polymer and carrier polymer(s). In preparing the composition for electrospinning, the proton-conducting polymer and carrier polymer may be dissolved in a solvent system comprising one or more solvents. In some embodiments, the solvent system may include one or more lower aliphatic alcohols (e.g., methanol), isopropanol, 1-propanol, dimethylformamide, deionised water or a combination thereof. Where the composition comprises a solvent system, the total polymer concentration in the composition may be any suitable concentration. In some embodiments, the total polymer concentration in the composition is at least about 20 wt.%.

[00137] In some embodiments, the process of preparing the proton conductor may also include a step of thermally treating the proton conductor to anneal the individual fibres. In some embodiments, after the proton conductor is prepared it may be heated for sufficient time to anneal individual fibres within the proton conductor to form a bonded three-dimensional fibrous network. For example, in embodiments where the gas-permeable polymeric material is Nafion<sup>®</sup>, the proton conductor may be thermally treated at a temperature of about 150 °C

under vacuum for a period of about 2 hours. However, it will be understood that any suitable combination of temperature and time may be used to achieve a desired degree of annealing.

[00138] In some embodiments, the process of preparing the proton conductor may also include a step of boiling the proton conductor in a strong acid (e.g.,  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) in order to further protonate the proton conductor and thereby increase its conductivity.

[00139] The porosity of the proton conductor may be defined in terms of its void fraction, which is the volume of empty space in the proton conductor relative to the total volume of the proton conductor. The void fraction of the proton conductor may be dependent on the molecular weight and structure of the proton-conducting polymer and any carrier polymer, if any. The void fraction of the proton conductor may be controlled by adjusting various parameters of the electrospinning process. For example, the void fraction may be increased or decreased by adjusting the relative humidity, temperature, spinneret to target distance, voltage, and needle gauge. Additionally, or alternatively, the void fraction of a proton conductor may be lowered by thermal annealing or hot pressing the proton conductor, or it may be lowered by filling the voids with another polymer. The proton conductor may have any suitable void fraction. In general, a higher void fraction corresponds to greater transparency to EM radiation and more rapid permeation of reactants through the proton conductor. However, a higher void fraction also generally corresponds to a lower number of fibres per unit volume and higher resistance to proton conduction. A suitable void fraction may therefore balance these effects. In some embodiments, the void fraction may be between about 0.3 and about 0.4, between about 0.4 and about 0.5, between about 0.5 and about 0.6, between about 0.6 and about 0.7, or between about 0.7 and about 0.8.

[00140] Among other applications, the proton conductor described herein may be used to provide a proton transfer pathway in a photoelectrochemical cell. Photoelectrochemical cells may be used, for example, for converting carbon dioxide to carbon dioxide reduction products (e.g., fuels) or for converting water to hydrogen gas.

[00141] Photoelectrochemical cells described herein comprise an anode and a cathode. The anode and cathode are in electrical communication with each other and comprise, respectively, an oxidation catalyst and a reduction catalyst. Connecting the anode and cathode is the porous proton conductor described herein, which comprises a gas-permeable polymeric material and is at least partially transparent to electromagnetic (EM) radiation. The photoelectrochemical cell may further comprise an electrically conductive substrate. The

electrically conductive substrate may be included to provide mechanical support to any components of the photoelectrochemical cell disposed thereon.

[00142] When used in a photoelectrochemical cell described herein, the proton conductor allows transfer of protons between the anode and cathode. The porosity of the proton conductor allows for rapid diffusion of reactants (e.g.,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) through the proton conductor. Furthermore, as the proton conductor is at least partially transparent to electromagnetic (EM) radiation, it allows transmission of EM radiation through the proton conductor. Thus, the proton conductor described herein may be used as a membrane on or around the catalyst components of a photoelectrochemical cell while allowing reactants and EM radiation to reach the oxidation and reduction catalyst sites. In some embodiments, the proton conductor may partially or completely envelop the anode, the cathode or both while still allowing reactants and EM radiation to reach the oxidation and reduction catalyst sites.

[00143] In some embodiments, a photoelectrochemical cell comprises an anode including an oxidation catalyst disposed on a surface of a photovoltaic cell and a cathode including a reduction catalyst. The photoelectrochemical cell further comprises an electrically conductive substrate. The anode and cathode are each disposed on a surface of the electrically conductive substrate, thereby providing electrical communication between the anode and cathode. Also connecting the anode and cathode is the porous proton conductor described herein, which comprises a gas-permeable polymeric material and is at least partially transparent to electromagnetic (EM) radiation. The proton conductor at least partially envelops the anode, cathode and electrically conductive substrate. In some embodiments, the proton conductor is in contact with the anode and cathode, but not in contact with the electrically conductive substrate.

[00144] The anode of the photoelectrochemical cells described includes an oxidation catalyst. In some embodiments, the oxidation catalyst may be deposited on a substrate to provide mechanical support for the catalyst. The substrate may form part of the anode, or it may be the electrically conductive substrate described herein.

[00145] The oxidation catalyst may comprise any suitable material(s) capable of catalysing an oxidation reaction. For example, the oxidation catalyst may be a water-oxidising catalyst. That is, the oxidation catalyst may be a material that catalyses the conversion of water to oxygen gas, protons and electrons. In some embodiments, the oxidation catalyst may be a photocatalyst, such that the anode is a photoanode. In some embodiments, the oxidation catalyst may comprise one or more metal oxides. For example, the oxidation catalyst may be

selected from the group consisting of cobalt oxides, cobalt phosphate, manganese oxides, nickel oxides, and iron oxides and combinations thereof. In some embodiments, the oxidation catalyst comprises or consists essentially of cobalt (II,III) oxide ( $\text{Co}_3\text{O}_4$ ).

[00146] The oxidation catalyst may have any suitable morphology. The oxidation catalyst may be in the form of a sheet or nanoparticles. As used herein, the term "nanoparticles" includes any particle of sub-micron dimensions, including nano-platelets, nano-rods and nanotubes. Where the oxidation catalyst is in the form of nanoparticles, the nanoparticles may have any suitable size. For example, each of the oxidation catalyst nanoparticles may have an equivalent spherical diameter in the range about 1 nm to less than about 1  $\mu\text{m}$ , about 1 nm to about 500 nm, about 2 nm to about 100 nm, about 5 nm to about 70 nm or about 10 nm to about 50 nm. The oxidation catalyst nanoparticles may have a mean equivalent spherical diameter in the range of about 5 nm to 750 nm, about 5 nm to about 500 nm, about 10 nm to about 100 nm, about 15 nm to about 50 nm or about 20 nm to about 35 nm. In some embodiments, the nanoparticles may be nanoporous. In some embodiments, the oxidation catalyst comprises or consists essentially of  $\text{Co}_3\text{O}_4$  nanoparticles. In some embodiments, the reduction catalyst may be a nanocomposite as described herein.

[00147] In some embodiments of the photoelectrochemical cell described herein, the anode further comprises a photovoltaic cell. The inclusion of a photovoltaic cell provides a voltage source which drives the reduction reaction at the reduction catalyst sites, the oxidation reaction at the oxidation catalyst sites or both. Thus, some embodiments of the photoelectrochemical cells described herein function in the presence of EM radiation (e.g., sunlight) without the need for an external power source. The anode may comprise any suitable photovoltaic cell. The photovoltaic cell may be a multi-junction photovoltaic cell. For example, the photovoltaic cell may be a triple junction amorphous silicon (a-Si) based photovoltaic cell or an inverted metamorphic multi-junction cell. The photovoltaic cell may include an electrically conductive layer at a *p*-side surface and/or *n*-side surface. An electrically conductive layer may provide mechanical support to the photovoltaic cell and therefore the photoelectrochemical cell. It may also act as an electron collector. In some embodiments, the photovoltaic cell may comprise one or more electrically conductive layers selected from stainless steel, indium tin oxide (ITO) and fluorine doped tin oxide (FTO).

[00148] Where the anode comprises a photovoltaic cell, the oxidation catalyst may be disposed on a surface of the photovoltaic cell. In general, the oxidation catalyst is disposed on a *p*-side of the photovoltaic cell. Such a configuration maximises the driving force for electrons produced at the oxidation catalyst site through the photovoltaic cell. In some embodiments, a

surface of the photovoltaic cell, such as an ITO coated silicon surface, may act as an oxidation catalyst.

[00149] The cathode of the photoelectrochemical cell described herein includes a reduction catalyst. In some embodiments, the reduction catalyst may be deposited on a substrate (e.g., copper or alumina) to provide mechanical support for the catalyst. The substrate may form part of the cathode, or it may be the electrically conductive substrate described herein.

[00150] The reduction catalyst may comprise any suitable material(s) capable of catalysing a reduction reaction. For example, in some embodiments the reduction catalyst may be a proton-reducing catalyst or a carbon dioxide-reducing catalyst. In some embodiments, the reduction catalyst may be a photocatalyst, such that the cathode is a photocathode. The reduction catalyst may comprise one or more metals or metal oxides. For example, in some embodiments the reduction catalyst comprises one or more materials selected from the group consisting of copper (I) oxide ( $\text{Cu}_2\text{O}$ ), copper (II) oxide ( $\text{CuO}$ ), copper, iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ), iron, cobalt, nickel, zinc, graphene, graphene oxide, carbon nanotubes and combinations thereof. In some embodiments, the reduction catalyst may be combined with potassium chloride ( $\text{KCl}$ ) or potassium carbonate ( $\text{K}_2\text{CO}_3$ ).

[00151] The reduction catalyst may have any suitable morphology. For example, in some embodiments the reduction catalyst may be in the form of a sheet, a mesh, nanoparticles or any combination thereof. Where the reduction catalyst is in the form of nanoparticles, the nanoparticles may have any suitable size. For example, in some embodiments each of the reduction catalyst nanoparticles may have an equivalent spherical diameter in the range of about 1 nm to less than about 1  $\mu\text{m}$ , about 1 nm to about 500 nm, about 2 nm to about 100 nm, about 5 nm to about 70 nm or about 10 nm to about 50 nm. In some embodiments, the reduction catalyst nanoparticles may have a mean equivalent spherical diameter in the range of about 5 nm to about 750 nm, about 5 nm to about 500 nm, about 10 nm to about 100 nm, about 15 nm to about 50 nm or about 20 nm to about 35 nm. In some embodiments, the nanoparticles may be nanoporous.

[00152] In some embodiments, the reduction catalyst comprises one or more of the group consisting of iron nanorods; nickel nanorods; graphene oxide/carbon nanotube composites, optionally loaded with copper, iron, cobalt or platinum nanoparticles; nitrogen, boron or sulfur doped graphene; carbon nanotubes, reduced graphite oxide in pure state loaded with copper, iron, cobalt or platinum nanoparticles; and cerium (III) oxide ( $\text{Ce}_2\text{O}_3$ ) hollow spheres. In some embodiments, the reduction catalyst comprises or consists essentially of copper (I) oxide

(Cu<sub>2</sub>O) nanoparticles. In some embodiments, the reduction catalyst comprises or consists of Cu<sub>2</sub>O/CuO hybrid nanorods. In other embodiments, the reduction catalyst may be a nanocomposite as described herein.

[00153] The photoelectrochemical cell described herein may further comprise an electrically conductive substrate. The electrically conductive substrate may be included to provide mechanical support to any components of the photoelectrochemical cell disposed thereon. Additionally or alternatively, it may be included to facilitate electron collection. One or both of the anode and cathode may be disposed on a surface of the electrically conductive substrate. Where the anode is disposed on a surface of the electrically conductive substrate, the oxidation catalyst may be disposed directly on a surface of the electrically conductive substrate or, where present, the photovoltaic cell may be disposed on a surface of the electrically conductive substrate.

[00154] In embodiments where both the anode and cathode are disposed on a surface of the electrically conductive substrate, the electrically conductive substrate provides the electrical communication between the anode and cathode. Thus, the inclusion of the electrically conductive substrate may allow for electrical communication between the anode and cathode without the need for conductive wires.

[00155] Where both the anode and cathode are disposed on a surface of the electrically conductive substrate, the anode and cathode may be disposed on different surfaces of the electrically conductive substrate. For example, the electrically conductive substrate may form a layer between the anode and cathode. An example of such a configuration is shown schematically in Fig. 13(a), wherein an electrically conductive substrate 10 has disposed on a single surface alternating regions of anode 11 and cathode 12. In other embodiments, the anode and cathode may be disposed on the same surface of the electrically conductive substrate, such that the electrically conductive substrate forms a first layer and the anode and cathode form a second layer. An example of such a configuration is shown schematically in Fig. 13(b), wherein an electrically conductive substrate 13 has disposed on a first surface an anode 14 and on a second surface a cathode 15.

[00156] The electrically conductive substrate may comprise any suitable electrically conductive material(s) and, optionally, one or more semi-conductive materials. In some embodiments, the electrically conductive substrate may comprise one or more materials selected from the groups consisting of electrically conductive polymers and metals. For example, in some embodiments the electrically conductive substrate may comprise one or more materials selected from the

group consisting of stainless steel, copper, nickel, iron, gold and combinations thereof. In some embodiments, the electrically conductive substrate consists of a stainless steel sheet.

[00157] The electrically conductive substrate may comprise a single layer of conductive material or two or more layers of conductive material. Each layer may comprise any suitable conductive material(s) and may have any suitable form, as described herein. In some embodiments, the electrically conductive substrate consists of a single layer, which is a stainless steel sheet. In some embodiments, the electrically conductive substrate consists of a first layer, which is a stainless steel sheet, and a second layer, which is a nickel mesh.

[00158] The electrically conductive substrate may have any suitable shape and dimensions. For example, the electrically conductive substrate may be in the form of a sheet, a block, a mesh or any combination thereof. In such case, the thickness of the electrically conductive substrate will typically be less than the dimensions of any face of the substrate on which the anode, cathode or both are disposed. For example, the electrically conductive substrate may be in the form of a sheet, where the thickness of the sheet is less than the minimum dimension of the face of the sheet. Where the anode and cathode are disposed on opposing sides of an electrically conductive substrate, the thickness of the electrically conductive substrate may be minimised in order to minimise the electron path from the anode to the cathode. In some embodiments, the electrically conductive substrate may have a thickness of between about 1 mm and about 0.05 mm, between about 0.1 mm and about 0.8 mm, between about 0.15 mm and about 0.6 mm, or between about 0.2 mm and about 0.4 mm. The electrically conductive substrate may have a facial area of between about 1 cm<sup>2</sup> and about 100 cm<sup>2</sup>, between about 1.5 cm<sup>2</sup> and about 75 cm<sup>2</sup>, between about 2 cm<sup>2</sup> and about 50 cm<sup>2</sup>, between about 4 cm<sup>2</sup> and about 25 cm<sup>2</sup>, or between about 9 cm<sup>2</sup> and about 16 cm<sup>2</sup>. However, it will be understood that an electrically conductive substrate having smaller or larger dimensions may be suitable for certain applications and is within the scope of this disclosure.

[00159] In some embodiments, the photoelectrochemical cell described herein may not comprise an electrically conductive substrate. In such embodiments, mechanical support for the photoelectrochemical cell may be provided by forming the oxidation catalyst, reduction catalyst or both into a sheet or mesh. Electrical communication between the anode and cathode may, for example, be provided by direct contact between the anode and cathode.

[00160] The photoelectrochemical cell may further comprise a thermal sink in thermal contact with one or more components of the photoelectrochemical cell. For example, in embodiments where the anode and cathode are disposed on the same surface of the electrically conductive

substrate, the thermal sink may be mounted on the opposing surface of the electrically conductive substrate. Inclusion of a thermal sink in the photoelectrochemical cell may stabilise the current produce by the photoelectrochemical cell.

[00161] The photoelectrochemical cell may further comprise a means of providing one or more gaseous feed streams to the photoelectrochemical cell. The means of providing one or more gaseous feed streams to the photoelectrochemical cell may be configured such that a gaseous feed stream contacts the oxidation catalyst, the reduction catalyst or both. In some embodiments, the photoelectrochemical cell is provided with a means of providing a single gaseous feed stream to the photoelectrochemical cell, such that the feed stream contacts both the oxidation catalyst and the reduction catalyst.

[00162] A non-limiting embodiment of a wireless photoelectrochemical cell for reducing CO<sub>2</sub> to CO<sub>2</sub> reduction products is shown in Fig. 14. The photoelectrochemical cell 20 comprises an oxidation catalyst 21 in the form of cobalt (II,III) oxide (Co<sub>3</sub>O<sub>4</sub>) nanoparticles deposited on the *p*-side surface of an a-Si triple junction photovoltaic cell 22. The cobalt (II,III) oxide (Co<sub>3</sub>O<sub>4</sub>) nanoparticles have a mean diameter of between about 5 and about 50 nm. The cobalt (II,III) oxide (Co<sub>3</sub>O<sub>4</sub>) nanoparticles are deposited on the surface of the photovoltaic cell 22 by spin coating, sputter coating, drop casting or evaporative coating. The a-Si triple junction photovoltaic cell 22 is a commercial photovoltaic cell with earth abundant elements manufactured by Xunlight USA, which includes an electrically conductive substrate in the form of a stainless steel sheet 23 adhered to the *n*-side surface of the photovoltaic cell 22. The stainless steel sheet 23 has a thickness of about 0.2 mm and provides the photovoltaic cell with mechanical strength, while also acting as electron collector. Adhered to the surface of the stainless steel sheet 23 distal the photovoltaic cell 22 is a cathode substrate 24. The cathode substrate 24 is a copper sheet having a thickness of about 0.5 mm. The cathode may be adhered to the stainless steel substrate by any suitable means, such as by a conductive tape (e.g., copper tape) or a conductive paste. The cathode substrate 24 and stainless steel sheet 23 combine to form a 2-layer electrically conductive substrate, which allows transport of electrons within the photoelectrochemical cell 20. Deposited on the surface of the cathode substrate 24 distal the stainless steel sheet 23 is a reduction catalyst 25 in the form of copper (I) oxide (Cu<sub>2</sub>O) nanoparticles. The reduction catalyst 25 nanoparticles are deposited on the surface of the copper sheet by spin coating, sputter coating, drop casting or evaporative coating, or they are grown on the copper sheet by oxidation of the surface of the copper sheet at 400 °C for about 2 to about 6 hours under air. In contact with and connecting the surfaces of the oxidation catalyst 21 and reduction catalyst 25 is a proton conductor 26 in the form of Nafion<sup>®</sup> nano-fibres. The Nafion<sup>®</sup> nano-fibres are transparent, porous and gas permeable and

form an outer coating on the cell. The mean thickness of the proton conductor is approximately 20  $\mu\text{m}$  and the individual fibres within the proton conductor have a diameter of from about 200 nm to about 600 nm. The nano-fibrous proton conductor is applied to the outer surfaces of the photoelectrochemical cell 20 by electrospinning a Nafion<sup>®</sup> solution. The photoelectrochemical cell 20 has facial dimensions of approximately 2 cm x 3 cm.

[00163] Photoelectrochemical cells described herein may be used for reducing any suitable feed stream to reduction products. In some embodiments, photoelectrochemical cells described herein may be used for reducing a humid carbon dioxide ( $\text{CO}_2$ ) gas stream to  $\text{CO}_2$  reduction products. Such reduction products may include fuels or other useful chemicals, which may be compatible with existing transportation and consumption infrastructure.

[00164] In using the photoelectrochemical cell described herein for reducing  $\text{CO}_2$  to  $\text{CO}_2$  reduction products, a single humid  $\text{CO}_2$  gas stream may be fed to the photoelectrochemical cell, whereby the gaseous feed stream contacts both the anode and the cathode. In other embodiments, water vapour and  $\text{CO}_2$  gas may be provided to the photoelectrochemical cell by separate feed streams, such that the water vapour stream contacts the anode and the  $\text{CO}_2$  gas stream contacts the cathode. Upon illumination of the anode by an EM radiation source, the oxidation catalyst oxidises the water present to form  $\text{O}_2$  gas, electrons, and protons. Where the anode includes a photovoltaic cell, illumination of the photovoltaic cell by the EM radiation source provides a voltage that drives the oxidation reaction. In the absence of a photovoltaic cell, an external voltage source may be used to drive the oxidation reaction. As the anode and cathode are in electrical communication, the electrons generated at the anode move through the photoelectrochemical cell to the cathode. The protons generated at the anode are transported to the cathode via the proton conductor. The  $\text{O}_2$  gas produced at the anode may be collected or it may be allowed to escape. At the reduction catalysts sites on the cathode,  $\text{CO}_2$  from the feed stream is adsorbed at the surface. The protons and electrons transported from the anode are utilised in reduction reactions of the  $\text{CO}_2$  adsorbed at the surface of the reduction catalyst, thereby producing  $\text{CO}_2$  reduction products.

[00165] Thus, there is also described herein a method for reducing carbon dioxide ( $\text{CO}_2$ ) to  $\text{CO}_2$  reduction products. The method for reducing  $\text{CO}_2$  to  $\text{CO}_2$  reduction products described herein comprises the steps of: (i) providing water vapour and a  $\text{CO}_2$  gas stream to a photoelectrochemical cell described herein, whereby the water vapour contacts the oxidation catalyst and the  $\text{CO}_2$  gas contacts the reduction catalyst; (ii) exposing the anode to an electromagnetic (EM) radiation source, thereby oxidising the water vapour to oxygen gas, protons and electrons; (iii) transporting the protons and electrons to the cathode; and (iv)

exposing the cathode to the electromagnetic (EM) radiation source, thereby reducing the CO<sub>2</sub> gas to CO<sub>2</sub> reduction products. The method may further comprise the step of: (iv) collecting the CO<sub>2</sub> reduction products.

[00166] The water vapour and gas may be provided as a single gaseous feed stream or as multiple gaseous feed streams. In some embodiments of the method for reducing CO<sub>2</sub> to CO<sub>2</sub> reduction products, the water vapour and CO<sub>2</sub> gas are provided in a single gaseous feed stream of humid CO<sub>2</sub>. Where the water vapour and CO<sub>2</sub> gas are provided in a single gaseous feed stream, the gaseous feed stream may have any suitable water content. In some embodiments, the relative humidity of the humid CO<sub>2</sub> feed stream is between about 50% and about 100%. For example, the relative humidity of the humid CO<sub>2</sub> feed stream may be between about 90% and about 100%, between about 80% and about 90%, between about 70% and about 80%, between about 60% and about 70% or between about 50% and 60%.

[00167] The EM radiation may be provided by any suitable EM radiation source. The EM radiation source generally provides EM radiation having a wavelength or range of wavelengths which are transmitted by the proton conductor and which provide sufficient energy to drive the oxidation reaction at the anode. In some embodiments, the EM radiation source provides EM radiation of having one or more wavelengths within the range 350 to 850 nm. For example, the EM radiation source may be the sun or a sunlight simulator. The CO<sub>2</sub> reduction products may be determined by the reduction catalyst, the oxidation catalyst or both. In some embodiments, the CO<sub>2</sub> reduction products may include one or more of the group consisting of water, carbon, carbon monoxide, alcohols, ketones, carboxylic acids, aldehydes, heterocycles, C<sub>1-10</sub> hydrocarbons. As used herein the term "hydrocarbons" includes alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, cycloalkynes and aromatic hydrocarbons.

## Examples

[00168] The invention will now be described with reference to specific examples, which should not be construed as in any way limiting.

### [00169] Example 1

[00170] In this Example, a method is described for preparing graphene oxide (GO) by chemical oxidation and exfoliation of natural graphite under acidic conditions according to the Hummer's method. In order to prepare the graphene oxide dispersion, first natural graphite flakes (from Asbury Graphite Mills, US) were thermally exfoliated in a furnace at 1050 °C for 15 seconds.

The resultant expanded graphite was further oxidised using a modified Hummers method. Sulfuric acid and  $\text{KMnO}_4$  were added to a glass vessel with the exfoliated graphite for 24 hours. Then, distilled water and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were added to the same vessel to obtain graphite oxide. The graphite oxide was stirred for 30 minutes and the resulting suspension was washed and centrifuged with diluted HCl followed by several washings using distilled water until the pH of the solution became 5-6, meaning that all impurities were washed and removed. This stirring and washing process formed a graphene oxide colloidal solution that was dried using oven at 80 °C for 12 hours in order to obtain graphene powder.

[00171] Example 2

[00172] In this Example, a method is described for preparing nitrogen doped graphene (N-RGO). The graphene sheets (approx. 20 mg) were dispersed in water by ultrasonication for 30 min at a frequency of 50 Hz, then mixed with uric acid in a ratio of 1:10 by mass. The mixtures were then stirred continuously and heated at 80 °C for 10-12 h to remove the water. The resulting solids were transferred to a tubular furnace and heated in an argon atmosphere at 5 °C min<sup>-1</sup> to 800 °C, then annealed for 2 hr.

[00173] Example 3

[00174] Nitrogen doped carbon nanotubes (N-CNTs) were synthesised by chemical vapour deposition in a dual zone furnace (MTI OTF-1200 X 2-II) using a 1 m long, 44 mm inner diameter quartz tube. 1.2 g of 5 wt% Fe on  $\text{Al}_2\text{O}_3$  catalyst (125–150 µm size fraction, calcined in air at 700 °C for 8 hr) was placed in an 89 mm × 13 mm alumina boat, which was placed in the second furnace zone. The first and second furnace zones were pre-heated to 300 °C and 800 °C at 10 °C/min respectively. During pre-heating, 475 sccm Ar and 25 sccm  $\text{H}_2$  were passed through the furnace for purging and in-situ reduction of the iron catalyst. Flowrates of Ar and  $\text{H}_2$  were controlled with mass flow controllers (Alicat Scientific). When temperatures were reached, ethylenediamine precursor was injected to the first zone at 0.5 mL/min and carried to the second zone under 400 sccm Ar and 140 sccm  $\text{H}_2$  gas. The synthesis was carried out for 45 min, after which the furnace was cooled to ambient temperature under 500 sccm Ar.

[00175] Following synthesis, N-CNTs were purified by microwave-assisted 2.5M  $\text{H}_2\text{SO}_4$  digestion for 45 min at 230 °C. Subsequently, N-CNTs were air oxidised at 375 °C to remove carbon impurities.

[00176] Example 4

[00177] In this Example, a method is described for preparing nanocomposites of N-RGO and N-CNTs (N-CNT-N-RGO). 10.0 mg N-RGO and 7.0 mg N-CNT sonicated with 34 mL isopropanol (Sigma-Aldrich) for 2hr. The mixture solution was stirred magnetically at 70 °C overnight to allow the solvent evaporate, and the nanocomposites were collected.

[00178] Example 5

[00179] The microstructures and morphology of nanocomposites synthesised by the method of Example 4 were investigated by Field Emission Scanning Electron Microscopy (FESEM, Zeiss ULTRA plus) and High-Resolution Transmission Electron Microscopy (HRTEM, JEOL 2200FS) with an acceleration voltage of 200 kV. Raman spectra were collected with Renishaw inVia Raman Spectrometer with a laser wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) analyses were performed by ESCALAB250Xi (Thermo Scientific, UK) with a monochromated Al K $\alpha$  (energy 1486.68 eV) operating at 150 W (13 kV  $\times$  12 mA) under a vacuum of  $2 \times 10^{-9}$  mbar. The analysis spot was 500  $\mu$ m in diameter.

[00180] Example 6

[00181] For electrochemical characterization and measurement of the nanocomposites synthesised by the method of Example 4, 1 mg of the nitrogen-doped composites were dispersed in the 1 mL solution (0.04 wt% Nafion in Isopropanol: Water, 5:1), prepared by sonicating for 30 min. 20.0  $\mu$ L of this suspension was dropped and adhered on a glassy-carbon electrode. The glassy-carbon working electrode (5 mm outside diameter) had been polished mechanically with a slurry of 0.05- $\mu$ m alumina particles, washed with Milli-Q water and acetone, and allowed to dry beforehand. It was then tested in a three-electrode cell, using platinum wire as the counter electrode and an Ag/AgCl, KCl (3 M) electrode as the reference electrode. Measurements were taken using Bio-logic SP300 potentiostat and CHI 760 work station. The O<sub>2</sub> and Ar-saturated 0.1 M KOH, and 0.5M H<sub>2</sub>SO<sub>4</sub> solutions were used at room temperature as alkaline and acidic electrolytes.

[00182] Example 7

[00183] The morphology of the resulting nanocomposite synthesised by the method of Example 4 was characterised by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figures 2(a) and (b) show the SEM and High-Resolution SEM

images of the N-CNT-N-RGO composite. It can be observed that tangled N-CNTs with lengths of several hundred nanometres are sparsely distributed on thin graphene sheets. The TEM and High-Resolution TEM images of the N-CNT-N-RGO composite are presented in Figures 2 (c) and (d). A ringlike diffraction pattern (Figure 2(e)) with dispersed bright spots of the graphene sheet and bamboo shape structure of Carbon Nano Tubes (CNTs) in N-CNT-N-RGO composite (Figure 2(f)) imply on intercalation of nitrogen atoms into the graphitic plans of this type of composite. Electron energy loss spectroscopy (EELS) (Figure 3(a)) spectrum and high-resolution transmission electron microscopy energy dispersive X-ray (HRTEM-EDX) (Figure 3(b)) mapping images, reveal the uniform distribution for the C, and N atoms and confirm that large-scale N-doped composite was prepared.

#### [00184] Example 8

[00185] X-ray photoelectron spectroscopy (XPS) was carried out to probe the elemental compositions and nitrogen state of the nanocomposites synthesised by the method of Example 4. As shown in Figure 4a, the presence of C, O, and N with a nitrogen content of 5.09% in N-CNT-N-RGO was found from the survey spectrum.

[00186] From the high resolution of N1s spectrum of the composite (Figure 4(b)), predominantly four kinds of nitrogen were doped: nitrogen in 6-member ring (Pyridinic N: N-6), nitrogen in 5-member ring (Pyrrolic N: N-5), nitrogen in graphene basal plane (Graphitic N: N-G) and oxygenated nitrogen (N-O) with binding energies of 398.3, 399.6, 401, and 403 eV, respectively (Figure 5 shows a schematic structure of bonding configurations of the N atoms). Pyridinic N is more prevalent than other types with a content of 42.85%. Interestingly, the ratio of Graphitic N to Pyridinic N in N-CNT-N-RGO is very high with the value of 0.87. Among these functionalities, nitrogen bonding contributions into the graphitic basal plane plays a crucial role in the electrocatalytic performances, whereas other types of nitrogen species mainly existed on the edges (see Figure 5), do not significantly contribute to the electrocatalytic performance and are unstable under electrochemical operating conditions.

#### [00187] Example 9

[00188] Raman spectroscopy provided further information of the N-doping effect in the composite and aligned with the XPS analysis (Figure 6). The downshift of the G peak from CNT-RGO ( $1594.93\text{ cm}^{-1}$ ) to NCNT-N-RGO ( $1585.77\text{ cm}^{-1}$ ) could be related to the electron donating capability of N heteroatoms which caused the charge transfer from the doped nitrogen to the carbon atoms in basal plane.

[00189] In addition, increase in the intensity ratio of the D to G band ( $I_D/I_G$ ) in company with slight upshift of the D band from CNT-RGO to N-CNT-N-RGO can be indicated to higher degree of defects and increase of defect density in the graphite structure and the deformation induced by N-doping in the edge plane, respectively.

#### [00190] Example 10

[00191] The ORR performance of the metal-free electrocatalyst (N-CNT-N-RGO) was evaluated by conducting a series of linear sweep voltammograms (LSV) on a rotating disk electrode (RDE). The onset potential and steady state current for the ORR are important criteria to estimate qualitatively the activity of an electrocatalyst. For comparison, CNT, N-CNT, RGO, N-RGO and the commercial Platinum on Carbon Black (Pt/C) were prepared. As shown in Figure 7, the N-CNT-N-RGO shows a positively shifted onset potential at  $\sim -0.070$  V, compared with  $\sim -0.126$  V,  $-0.076$  V,  $-0.309$  V and  $-0.145$  V measured on CNT, N-CNT, RGO and N-RGO, respectively, with only  $\sim 0.06$  V more overpotential than that of commercial Pt/C.

[00192] The N-CNT-N-RGO composite demonstrated significantly higher steady state catalytic current than that of Pt/C with a wide plateau considered as the strong limiting diffusion current, indicating a diffusion-controlled process related to an efficient  $4e^-$  dominated ORR pathway.

[00193] The durability of the N-CNT-N-RGO electrode toward ORR was investigated by performing continuous potential cycling. As can be seen in Figure 8(a), no obvious shape change in the CV of N-CNT-N-RGO was observed after 5000 consecutive potential cycling in  $O_2$  saturated 0.1 M KOH, which is in contrast to the loss of the active surface area for a commercial Pt/C catalyst. The ORR data also reveal the reliable stability of N-CNT-N-RGO with 92 and 90 percent retention on its onset potential and steady state current density after 5000 continuous cycles, compared to commercial Pt/C with more than 30% attenuation on onset potential and 40% loss of steady state current density (Figure 8(b)).

#### [00194] Example 11

[00195] The performance of N-CNT-N-RGO catalyst towards water oxidation or Oxygen Evolution Reaction (OER) was characterised by using rotating disc electrode (RDE) voltammetry in Ar-saturated 0.1 M KOH and 0.5  $H_2SO_4$  electrolytes. The N-CNT-N-RGO electrode exhibits high catalytic activity towards OER with an onset potential as low as 0.51 V and 1.44 V vs. Ag/AgCl in alkaline and acidic environments (Figure 9a, b), respectively. The applied potential of 0.91 and 1.81 V vs. Ag/AgCl are required to achieve a current density of 10

mA/cm<sub>2</sub> and 20 mA/cm<sub>2</sub> for N-CNT-N-RGO compared to 1.1 and 1.85 V vs. Ag/AgCl for the commercial Pt/C in alkaline and acidic electrolytes, corresponding to superior OER activity of this composite. Moreover, the OER performance of the N-CNT-N-RGO was evaluated by Tafel plot (Figure 10), revealing that low potentials are needed to change the reaction from ORR to OER in both acidic and alkaline media for N-CNT-N-RGO than commercial Pt/C which is in agreement with OER performance test.

#### [00196] Example 12

[00197] The electrocatalytic activity of the composite for Hydrogen Evolution Reaction (HER) was examined by LSV in Ar-saturated 0.1M KOH and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions (Figures 11 (a) and (b)). The onset potential for HER was observed at -1.32 V vs. Ag/AgCl for N-CNT-N-RGO in alkaline solution, which is 40 mV more positive than commercial catalysts. Whereas, it only shows 90 mV overpotential toward HER compared to Pt/C catalyst in acidic media. The N-CNT-N-RGO composite exhibits a high current density of 3.12 mA/cm<sup>2</sup> at the potential of -1.5 V vs. Ag/AgCl compared to commercial Pt/C catalyst of 2.64 mA/cm<sup>2</sup> in 0.1 M KOH (Figure 11 (a)). However, almost the same current density of 42 mA/cm<sup>2</sup> is obtained for both catalysts in an acidic electrolyte (Figure 11 (b)). To further assess HER performance, Tafel plots were constructed (Figures 12 (a) and (b)), showing that less potential is required for the HER reaction for N-CNT-N-RGO than commercial Pt/C in an alkaline environment, while the opposite occurs in an acidic environment. An important parameter to evaluate the activity of HER is the Tafel slope (b) which is determined by fitting polarization data to the Tafel equation ( $\eta = a + b \log |J|$ , where  $\eta$  is the overpotential, b is the Tafel slope, and, J is the current density). The N-CNT-N-RGO composite exhibits exceptional HER catalytic activity with low Tafel slope of 46.8 mV/dec in acidic solution and 64.7 mV/dec in alkaline electrolyte, which is lower than the commercial Pt/C catalyst which has values of 48.6 and 96.5 mV/dec, respectively. The Tafel slopes are consistent with the HER performance analysis.

#### [00198] Example 13

[00199] In this Example, a method is described for producing a porous Nafion<sup>®</sup> proton conductor that is at least partially transparent to EM radiation. Polyethylene oxide (PEO) having an average molecular weight of approximately 8000 kDa is dissolved in a first 2:1 co-solvent system of 2-propanol and water to make a 5 wt% solution. Nafion<sup>®</sup> pellets are produced by drying an aqueous solution of Nafion<sup>®</sup>. The pellets are then dissolved in a second 2:1 co-solvent system of 2-propanol and water to make a 35 wt% solution. The two solvent solutions are combined in an appropriate ratio to give a 20 wt% solution of Nafion<sup>®</sup> and PEO

and mixed for 2 hours using a magnetic stirrer. After mixing, the product solution is allowed to rest for about 2 days. It was found that the resting step made electrospinning easier leading to a more uniform proton conductor. However, this step may be omitted if a quicker process is desired. The solution is then poured into a syringe for electrospinning in an electrospinner that has a controllable internal atmosphere. The solution is electrospun at 8V with a spinneret to target distance of about 15 cm, a relative humidity of about 32% and a temperature of about 24 °C. The resulting material is a uniform porous network of Nafion® fibres having a ribbon-like morphology.

[00200] Scanning electron microscope images of the proton conductor produced in this Example are shown Figs. 15(a) and (b). The nano-fibrous structure produced by the electrospinning process can be seen in these images. The proton conductor allows at least partial transmission of EM radiation having wavelengths in the visible and ultra-violet regions.

[00201] Example 14

[00202] A photoelectrochemical cell was prepared having a configuration as shown in Fig. 16. The photoelectrochemical cell 40 comprises an anode 41 including an oxidation catalyst, namely  $\text{Co}_3\text{O}_4$  nanoparticles. The oxidation catalyst is deposited on a *p*-side surface of a triple-junction a-Si photovoltaic cell 42 (Xunlight USA). The edges of the a-Si photovoltaic cell 42 are etched with 1.0 M HCl to remove the conductive layer. Mounted on the *n*-side surface of the photovoltaic cell 42 is a cathode 43. The cathode 43 is a reduction catalyst, which consists of  $\text{Cu}_2\text{O}$  nanoparticles deposited on a copper sheet. A porous Nafion® proton conductor 44 is deposited on the photoelectrochemical cell 40 by the method described in Example 13 such that it is in contact with and coating the anode 41 and cathode 43.

[00203] The current produced by the photoelectrochemical cell shown in Fig. 16 was measured using a potentiostat. The experimental setup for measuring the charge produced by the photoelectrochemical cell is shown in Fig. 17. A  $\text{CO}_2$  or Ar gas stream is provided to a reactor in which the photoelectrochemical cell (PEC) is installed. Water is provided to the gas stream, as required, by passing the gas stream through a bubbler. The PEC is under continuous purge of the wet or dry gas. The reactor is fitted with a quartz glass window to allow EM radiation into the reactor and onto the PEC. The PEC is held in suspension in the reactor with the aid of two copper wires such there is no contact between the PEC and the reactor wall or glass window. The copper wires are connected to a working electrode, a reference electrode and a counter electrode of the potentiostat. The EM radiation source is a sun simulator with 1 sun output intensity. The intensity of incoming light is periodically measured by

a pyrometer to ensure the 1 sun output intensity is preserved. The reaction products produced by the PEC exit the reactor through the outlet on right hand side of the reactor. These reaction products may be analysed using, for example, a mass spectrometer or gas chromatographer.

[00204] The current produced by the photoelectrochemical cell, as measured by potentiostat, is shown in Figs. 18(a)-(d) for various feed streams. The feed streams are: (a) a first humid CO<sub>2</sub> gas stream; (b) a humid Ar gas stream; (c) a CO<sub>2</sub> gas stream; and (d) a second humid CO<sub>2</sub> gas stream. The relative humidity of the feed streams in the case of Figs. 18(a), (b) and (d) was 98%. Troughs in each case correspond to periods during which the photoelectrochemical cell is illuminated by the EM radiation source and current is thereby produced. The measured current in Figs. 18(a) and (d) is related to the reduction of carbon dioxide at the cathode surface. The measured current in Fig. 18(b) is related to water splitting and H<sub>2</sub> formation at the cathode surface. As there is no water present in the feed stream of Fig. 18(c), no protons are generated to be used by the cathode for the CO<sub>2</sub> reduction reaction and therefore no current is produced.

[00205] As shown in Figs. 18(a) and (d), the humid CO<sub>2</sub> feed stream produces a strong current, whereas the humid Ar stream produces a weaker current (Fig. 18(b)). The lower current in the case of the humid Ar stream compared to the humid CO<sub>2</sub> stream (by over one order of magnitude) indicates that the selectivity of the photoelectrochemical cell toward CO<sub>2</sub> reduction is much higher than the selectivity toward H<sub>2</sub> formation (selectivity > 90%).

#### [00206] Example 15

[00207] A photoelectrochemical cell was prepared having a configuration as shown in Fig. 19. The photoelectrochemical cell 70 comprises an anode 71 including an oxidation catalyst, namely Co<sub>3</sub>O<sub>4</sub> nanoparticles. The oxidation catalyst is deposited on a *p*-side surface of a triple-junction a-Si photovoltaic cell 72 (Xunlight USA). Also mounted on the *p*-side surface of the photovoltaic cell 72 are four cathodes 73. The cathodes 73 are reduction catalysts, which consist of copper sheets. A porous Nafion<sup>®</sup> proton conductor 74 is deposited on the photoelectrochemical cell 70 by the method described in Example 13 such that it is in contact with and coating the anode 71 and cathode 73.

#### [00208] Example 16

[00209] The current produced by the photoelectrochemical cell shown in Fig. 19 was measured using the same method as described in Example 15. The current produced by the

photoelectrochemical cell is shown in Fig. 20 for a humid Ar gas stream and a humid CO<sub>2</sub> gas stream. The relative humidity of the feed streams in each case was 98%.

[00210] Example 17

[00211] A photoelectrochemical cell was prepared having a thermal sink mounted to the electrically conductive substrate a photoelectrochemical cell described herein. The current produced by the photoelectrochemical cell was measure as described in Example 15 both prior to installing the thermal sink and after installation of the thermal sink. The current produced by the photoelectrochemical cell prior to installation of the thermal sink is shown in Fig. 21(a) for a humid Ar gas stream and a humid CO<sub>2</sub> gas stream. The current produced by the photoelectrochemical cell after installation of the thermal sink is shown in Fig. 21(b) for a humid Ar gas stream and a humid CO<sub>2</sub> gas stream. The relative humidity of the feed streams in all cases was 98%. Fig. 21 shows that current drop is much less for the photoelectrochemical cell that includes a thermal sink.

**CLAIMS:**

1. A nanocomposite comprising heteroatom-doped graphene and heteroatom-doped carbon nanotubes (CNTs), wherein the nanocomposite has a heteroatom content of at least about 1 wt%.
2. The nanocomposite of claim 1, wherein the heteroatom-doped CNTs are multi-walled carbon nanotubes.
3. The nanocomposite of claim 1 or claim 2, wherein the heteroatom content in the heteroatom-doped graphene is in the range of about 1 wt% to about 10 wt%.
4. The nanocomposite of any one of claims 1 to 3, wherein the heteroatom content in the heteroatom-doped CNTs is in the range of about 1 wt% to about 10 wt%.
5. The nanocomposite of any one of claims 1 to 4, wherein the heteroatom-doped graphene and heteroatom-doped CNTs are present in a ratio of between about 10:1 and about 1:10.
6. The nanocomposite of any one of claims 1 to 5, wherein the heteroatom-doped CNTs are adsorbed onto the surface and/or between layers of the heteroatom-doped graphene.
7. The nanocomposite of any one of claims 1 to 6, wherein the heteroatom-doped graphene does not form agglomerates of more than about ten layers.
8. The nanocomposite of any one of claims 1 to 7, wherein the heteroatom is selected from the group consisting of nitrogen, sulfur, phosphorus, boron, silicon, aluminium and combinations thereof.
9. A process for producing a nanocomposite of any one of claims 1 to 8, said process comprising:
  - (a) providing heteroatom-doped graphene;
  - (b) providing heteroatom-doped CNTs; and
  - (c) combining the heteroatom-doped graphene and heteroatom-doped CNTs in a solution to form the nanocomposite.
10. The process of claim 9, wherein step (c) further comprises heating the solution to facilitate formation of the nanocomposite.

11. The process of claim 9 or claim 10, further comprising:
  - (d) drying the nanocomposite produced in step (c) to form a solid.
12. The process of any one of claims 9 to 11, further comprising producing the heteroatom-doped graphene provided in step (a).
13. The process of any one of claims 9 to 12, further comprising a step of producing the graphene oxide.
14. The process of any one of claims 9 to 13, further comprising a step of producing the heteroatom-doped CNTs.
15. An electrode comprising a nanocomposite of any one of claims 1 to 14.
16. An electrochemical cell comprising a nanocomposite of any one of claims 1 to 14.
17. The electrochemical cell of claim 16, wherein the battery is a lithium battery.
18. Use of the nanocomposite of any one of claims 1 to 14 as a catalyst for a reduction reaction.
19. The use of claim 18, wherein the reduction reaction is a hydrogen evolution reaction (HER), or the reduction reaction is an oxygen reduction reaction (ORR), or the reduction reaction is reduction of carbon dioxide (CO<sub>2</sub>).
20. Use of the nanocomposite of any one of claims 1 to 14 as a catalyst for an oxidation reaction, or as a catalyst for splitting water.
21. Use of an electrochemical cell according to claim 16 or claim 17 for splitting water.
22. A photoelectrochemical cell comprising:
  - (a) an anode comprising at least one oxidation catalyst;
  - (b) a cathode comprising at least one reduction catalyst, wherein the cathode is in electrical communication with the anode; and
  - (c) a proton conductor having a porous structure,wherein the proton conductor connects the anode and the cathode, thereby allowing transfer of protons between the anode and the cathode.

23. The photoelectrochemical cell of claim 22, wherein the porous structure of the proton conductor is provided by bonded or non-bonded nano-fibres.
24. The photoelectrochemical cell of claim 22 or claim 23, wherein the proton conductor comprises a polymeric material.
25. The photoelectrochemical cell of claim 24, wherein the polymeric material is gas-permeable.
26. The photoelectrochemical cell of any one of claims 22 to 25, wherein the proton conductor is at least partially transparent to EM radiation having a wavelength in the range of about 350 to about 850 nm.
27. The photoelectrochemical cell of any one of claims 22 to 26, further comprising an electrically conductive substrate.
28. The photoelectrochemical cell of claim 27, wherein the electrically conductive substrate comprises two or more layers.
29. The photoelectrochemical cell of any one of claims 22 to 28, wherein the anode comprises a photovoltaic cell.
30. The photoelectrochemical cell of any one of claims 22 to 29, wherein the at least one oxidation catalyst is a water-oxidising catalyst.
31. The photoelectrochemical cell of any one of claims 22 to 30, wherein the at least one oxidation catalyst is selected from the group consisting of cobalt oxides, manganese oxides, nickel oxides, iron oxides and combinations thereof.
32. The photoelectrochemical cell of any one of claims 22 to 31, wherein the at least one oxidation catalyst is in the form of nanoparticles.
33. The photoelectrochemical cell of any one of claims 22 to 32, wherein the at least one reduction catalyst is a carbon dioxide-reducing catalyst, or a proton-reducing catalyst, or copper (I) oxide.

34. The photoelectrochemical cell of any one of claims 22 to 33, wherein the at least one reduction catalyst is in the form of nanoparticles.
35. A photoelectrochemical cell comprising:
- (a) an anode comprising an oxidation catalyst disposed on a surface of a photovoltaic cell;
  - (b) a cathode comprising a reduction catalyst;
  - (c) a proton conductor having a porous structure, wherein the proton conductor connects the anode and the cathode; and
  - (d) an electrically conductive substrate,
- wherein the anode and cathode are each disposed on a surface of the electrically conductive substrate, thereby providing electrical communication between the anode and the cathode; and
- wherein the proton conductor comprises a gas-permeable polymeric material, which is at least partially transparent to electromagnetic (EM) radiation, the proton conductor at least partially enveloping the anode, cathode and electrically conductive substrate.
36. A proton conductor having a porous structure, wherein said porous structure allows permeation of a gas through said proton conductor.
37. The proton conductor of claim 36, wherein the porous structure is provided by bonded or non-bonded nano-fibres.
38. The proton conductor of claim 36 or claim 37, wherein the porous structure of the proton conductor is formed by electrospinning the polymeric material.
39. The proton conductor of any one of claims 36 to 38, wherein the proton conductor is at least partially transparent to electromagnetic (EM) radiation.
40. A process for preparing a porous proton conductor comprising the steps of:
- (i) providing a proton-conducting polymeric material; and
  - (ii) electrospinning the polymeric material, thereby producing a porous proton conductor.
41. A method of reducing carbon dioxide (CO<sub>2</sub>) to CO<sub>2</sub>-reduction products, the method comprising the steps of:

(i) providing water vapour and CO<sub>2</sub> gas stream to the photoelectrochemical cell of any one of claims 22 to 35, whereby the water vapour contacts the oxidation catalyst and the CO<sub>2</sub> gas contacts the reduction catalyst;

(ii) exposing the anode to an electromagnetic (EM) radiation source, thereby converting the water vapour to oxygen gas, protons and/or electrons;

(iii) transporting the protons and electrons to the cathode via the proton conductor; and

(iv) exposing the cathode to the electromagnetic (EM) radiation source, thereby reducing the CO<sub>2</sub> gas in the presence of the protons and electrons to CO<sub>2</sub> reduction products.

42. The method of claim 41, wherein the water vapour and CO<sub>2</sub> gas are provided in a single gaseous feed stream.

43. The method of claim 42, wherein the gaseous feed stream has a relative humidity of between 50% and 100%.

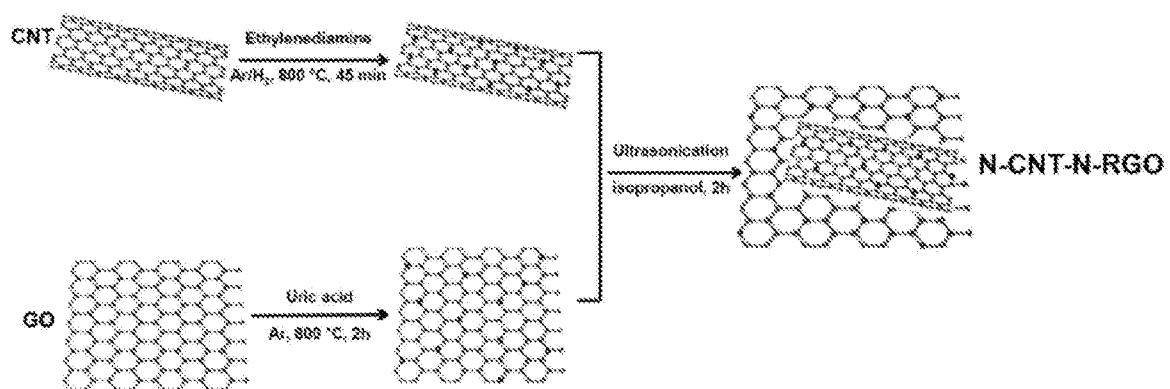


Fig. 1

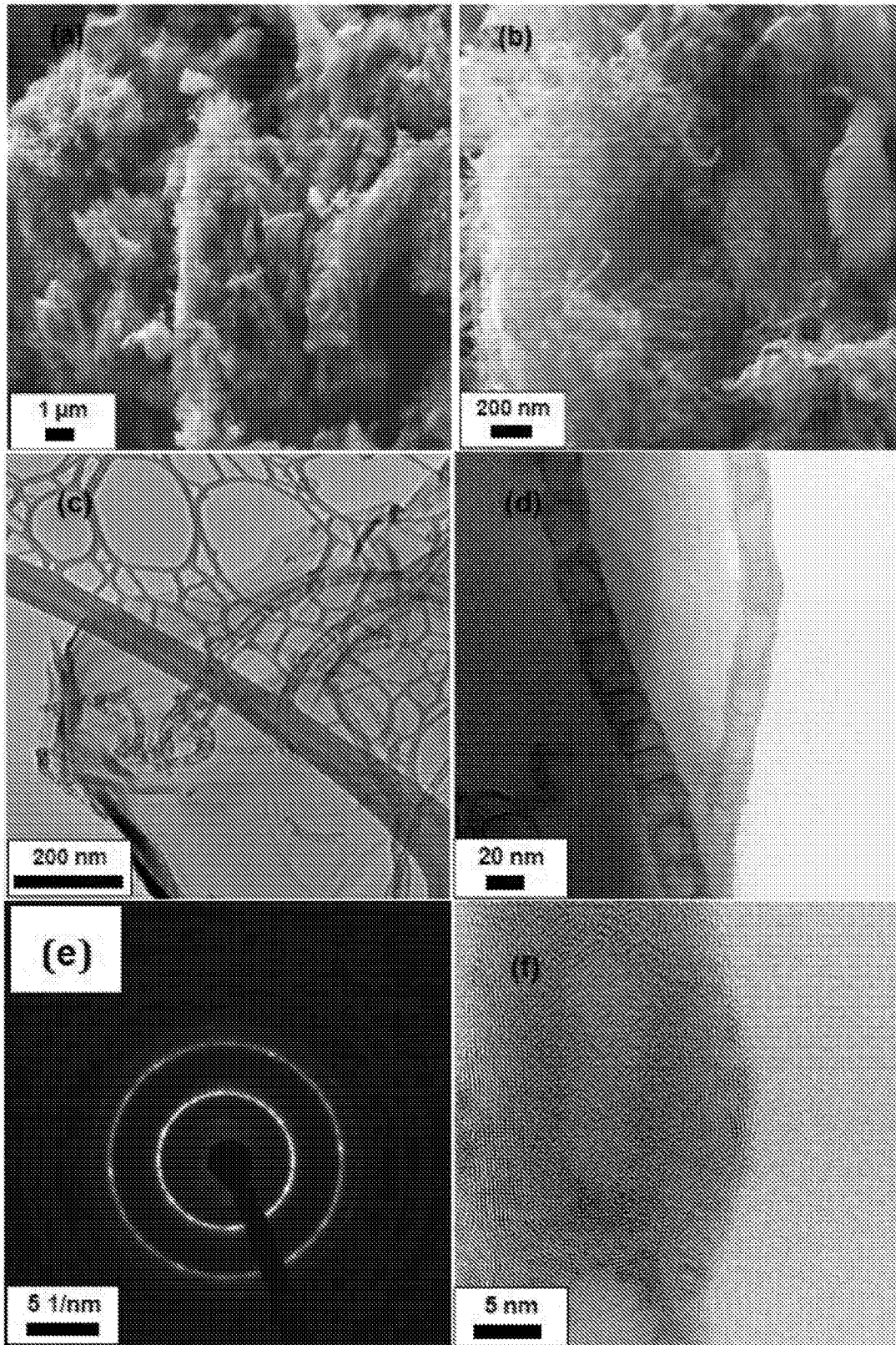


Fig. 2

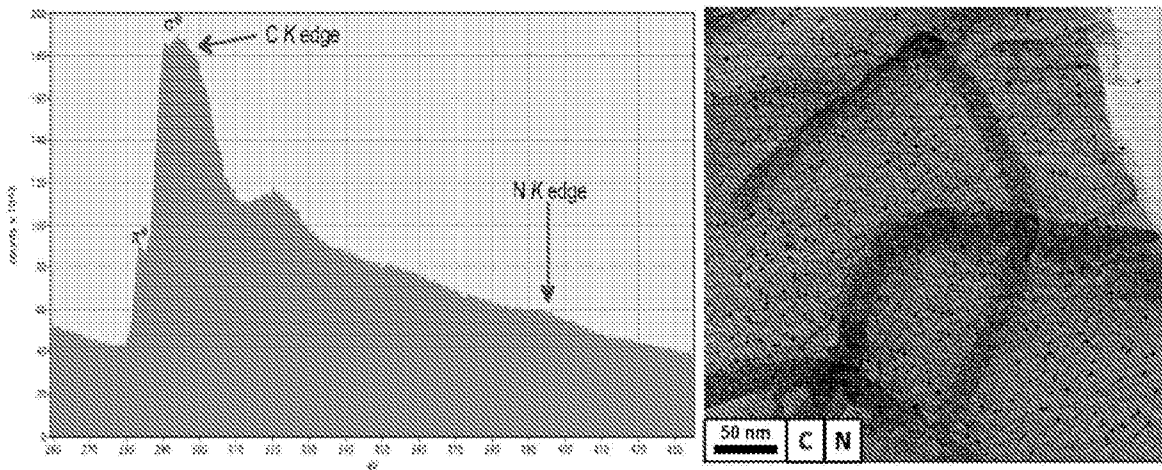


Fig. 3

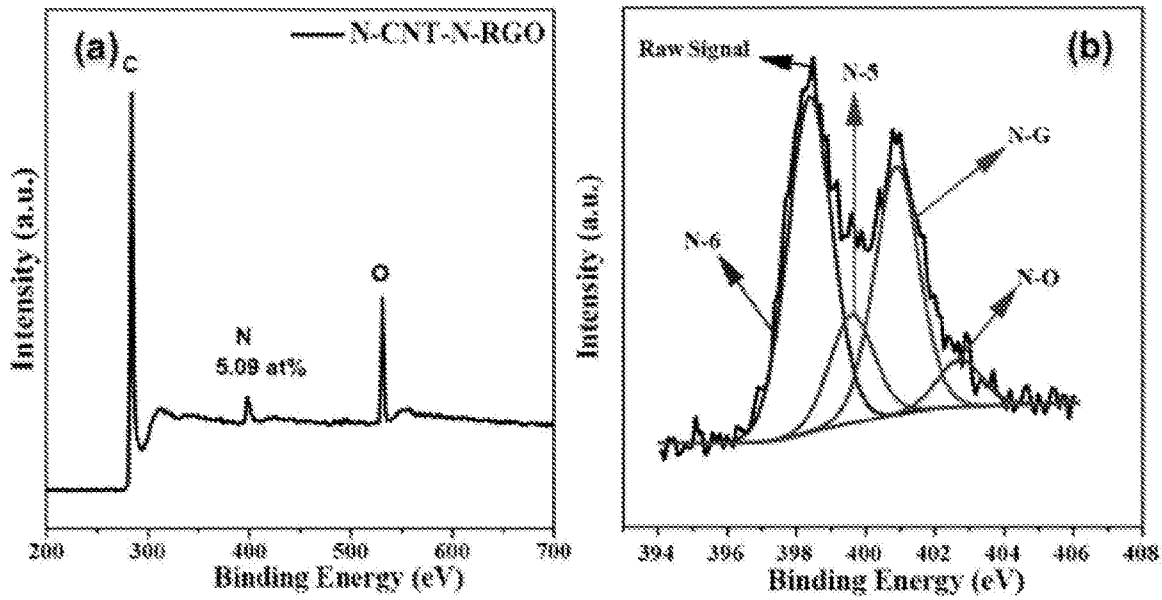


Fig. 4

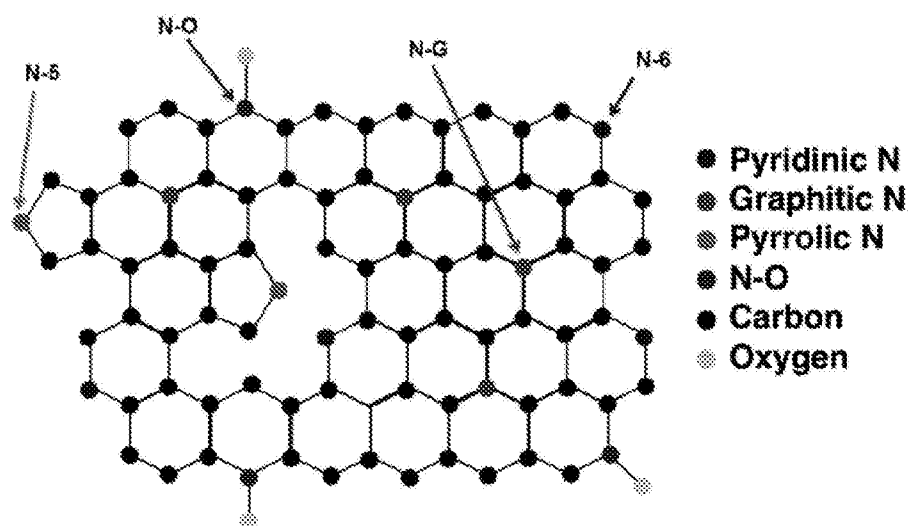


Fig. 5

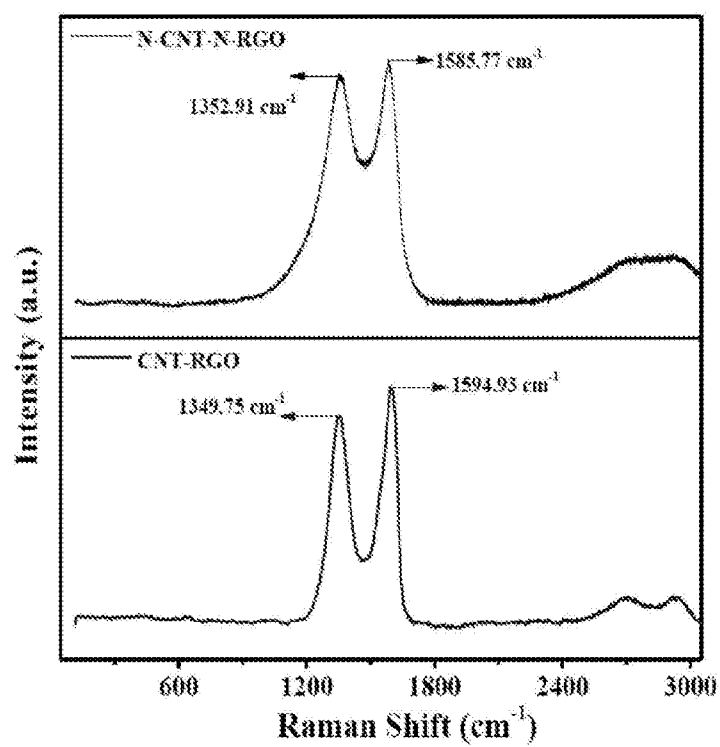


Fig. 6

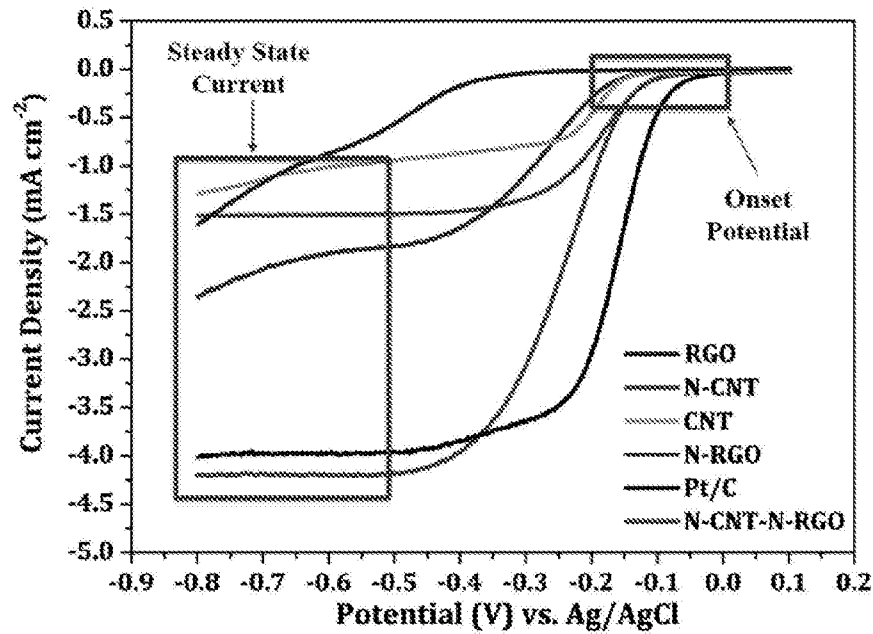


Fig. 7

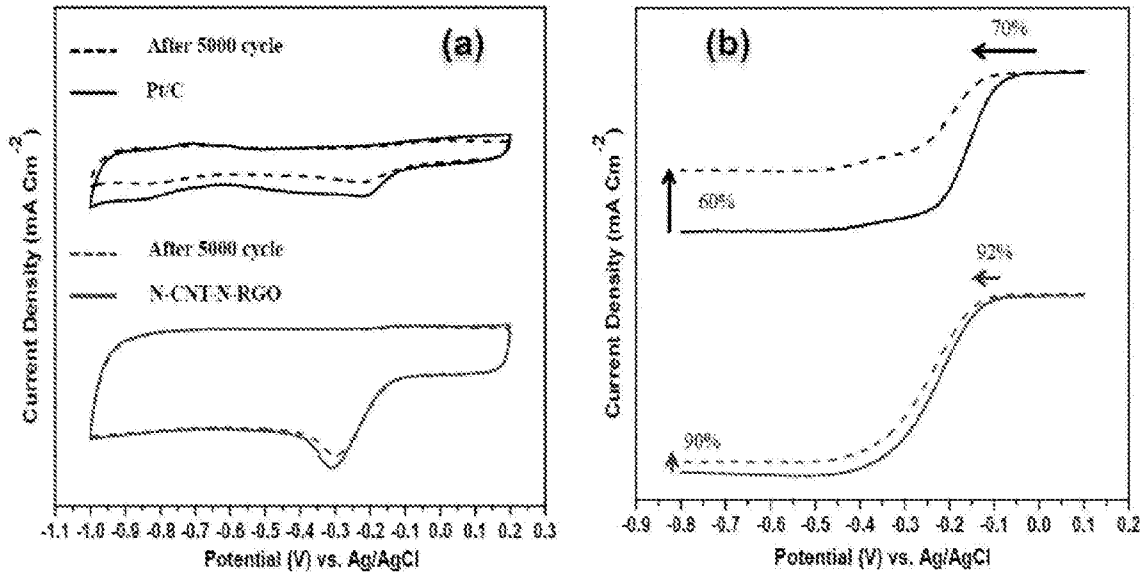


Fig. 8

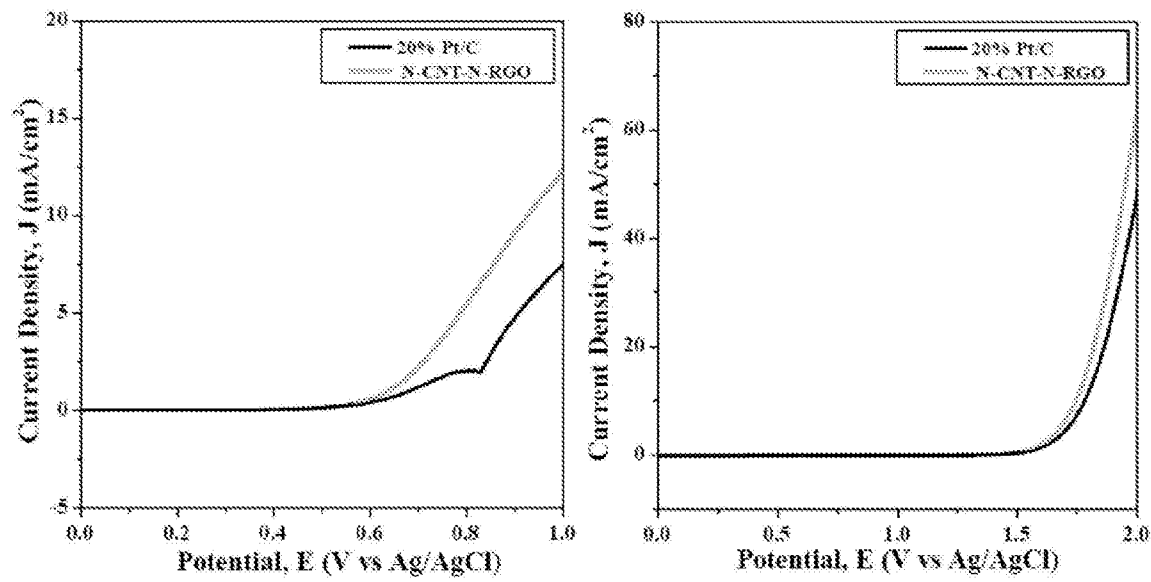


Fig. 9

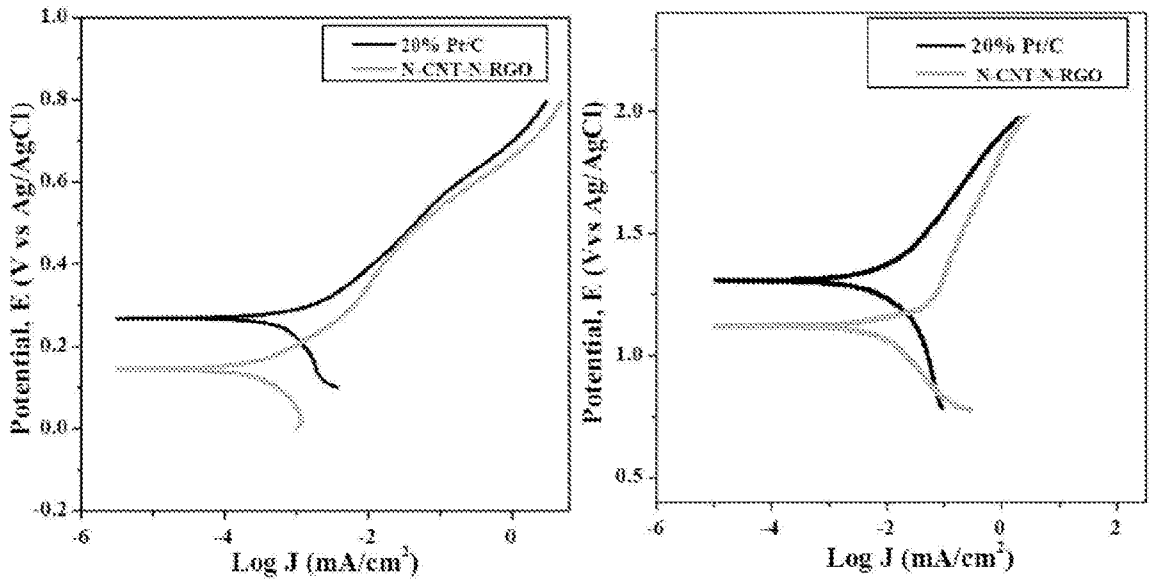


Fig. 10

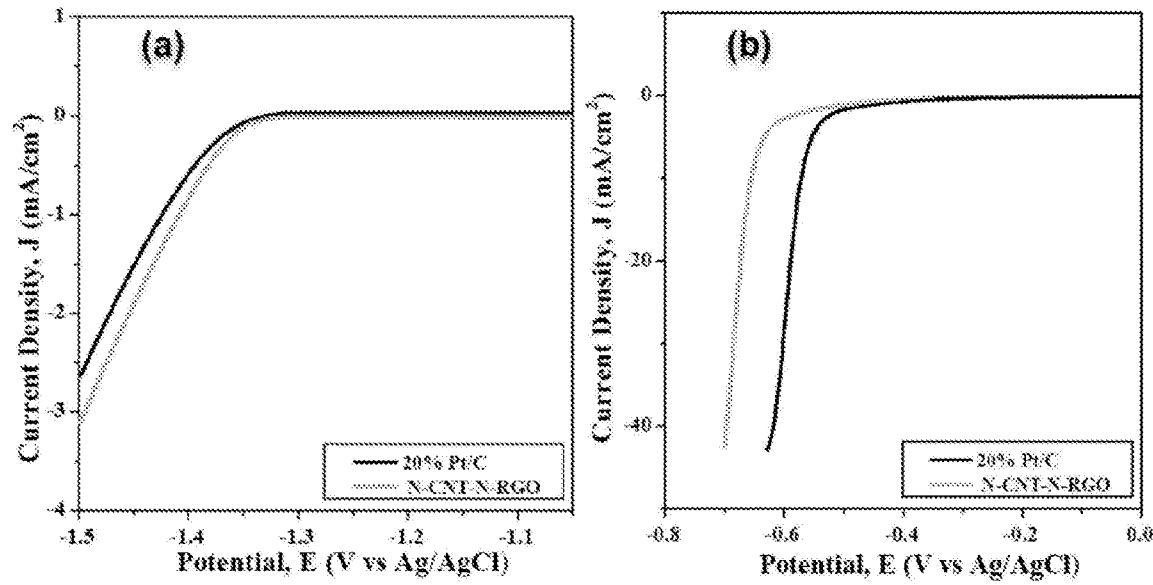


Fig. 11

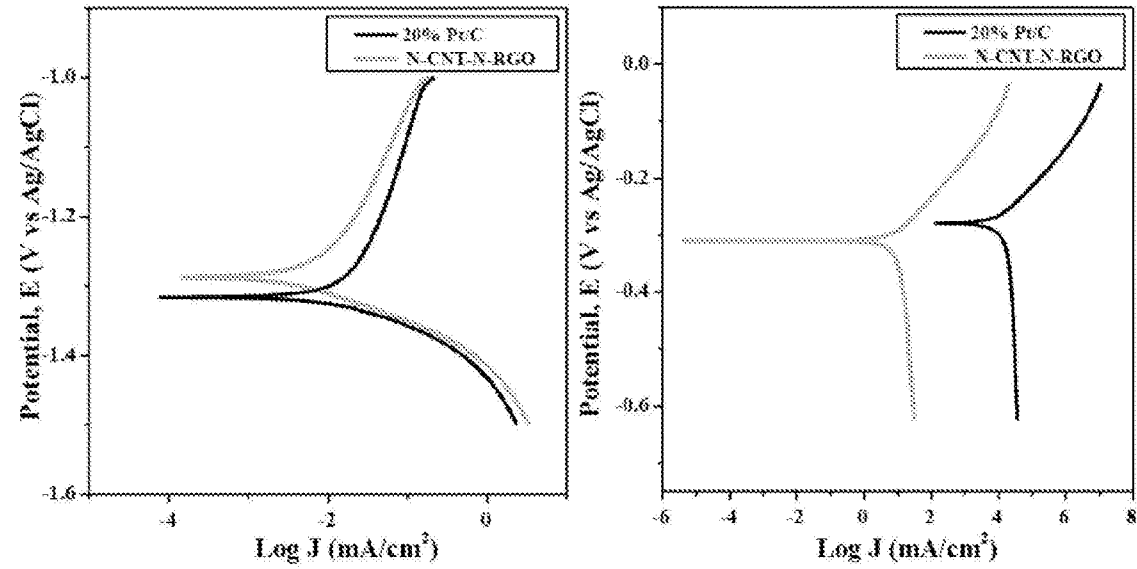


Fig. 12

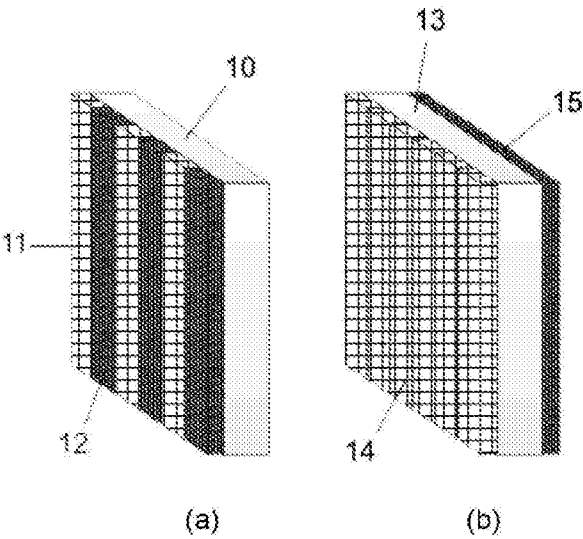


Fig. 13

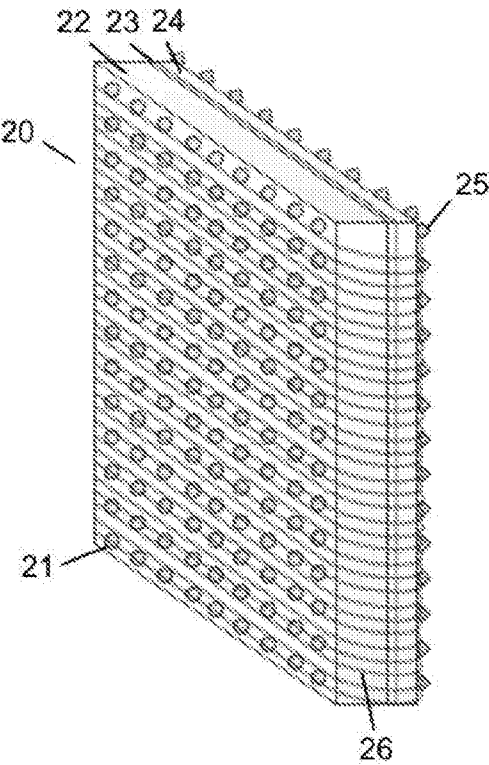


Fig. 14

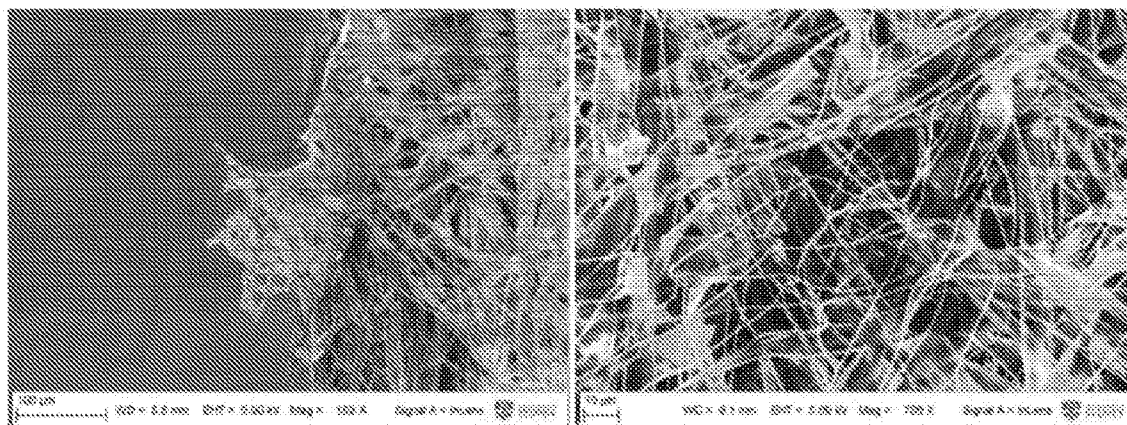


Fig. 15

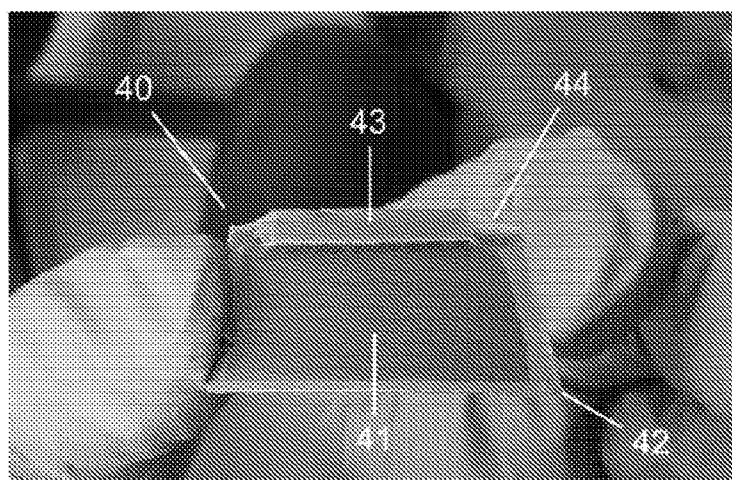


Fig. 16

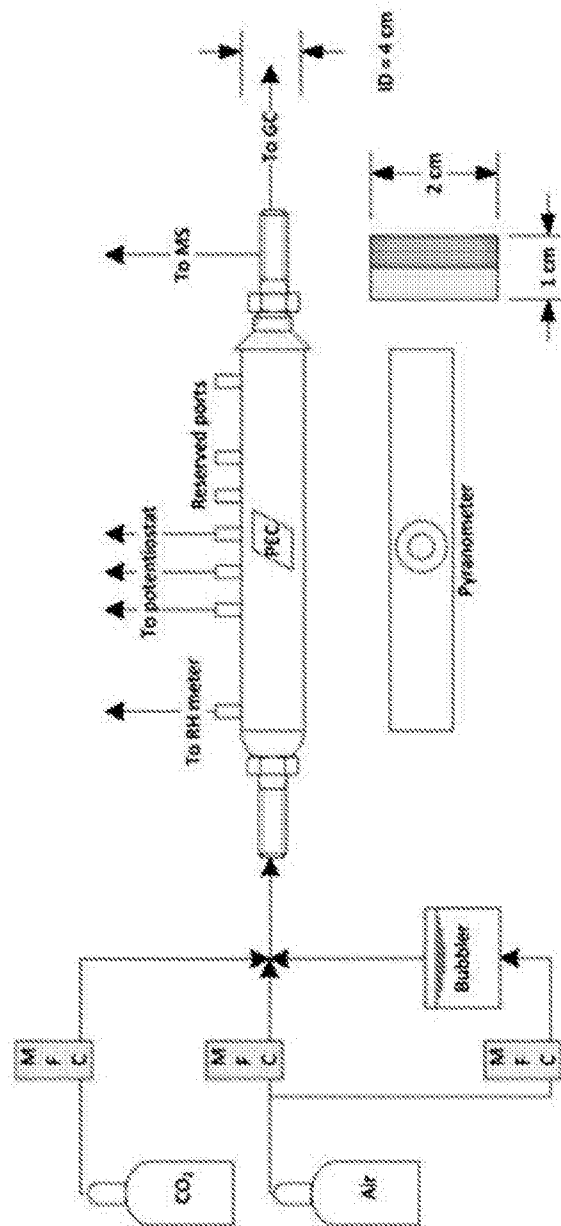


Fig. 17

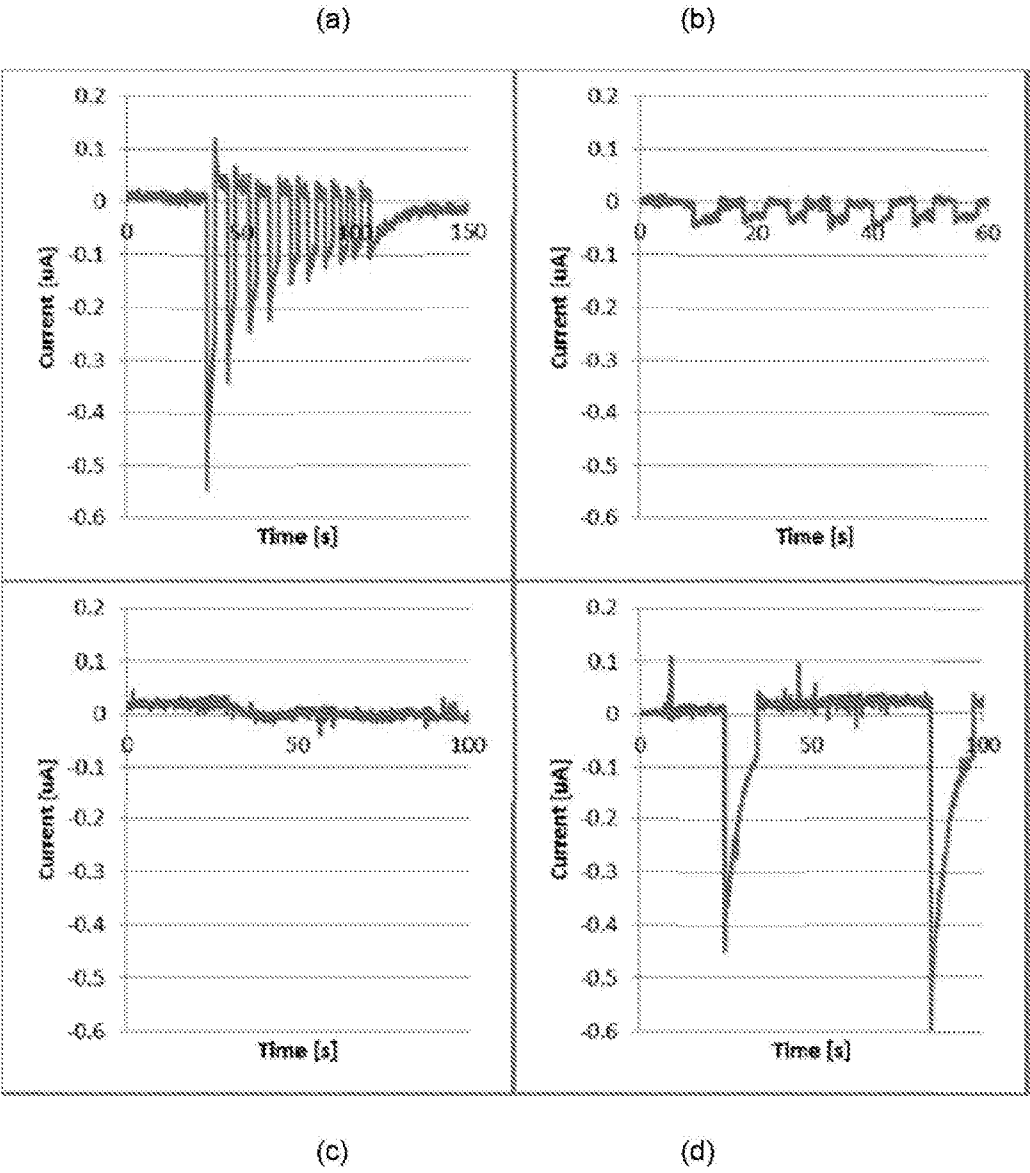


Fig. 18

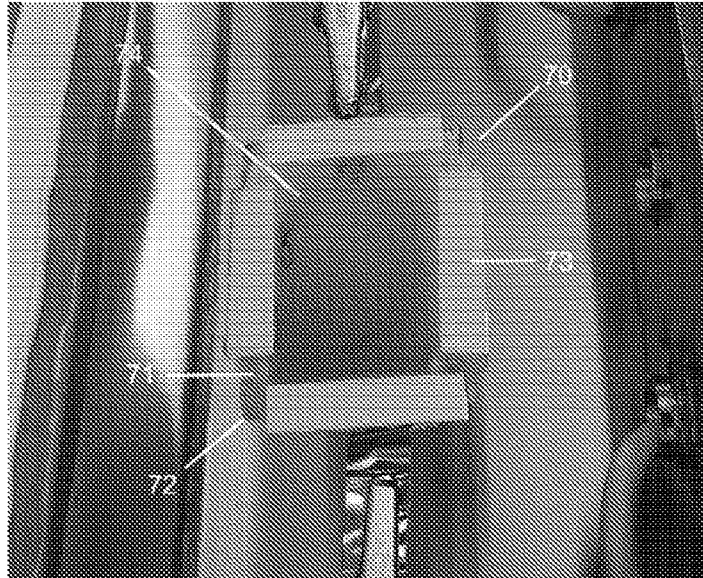


Fig. 19

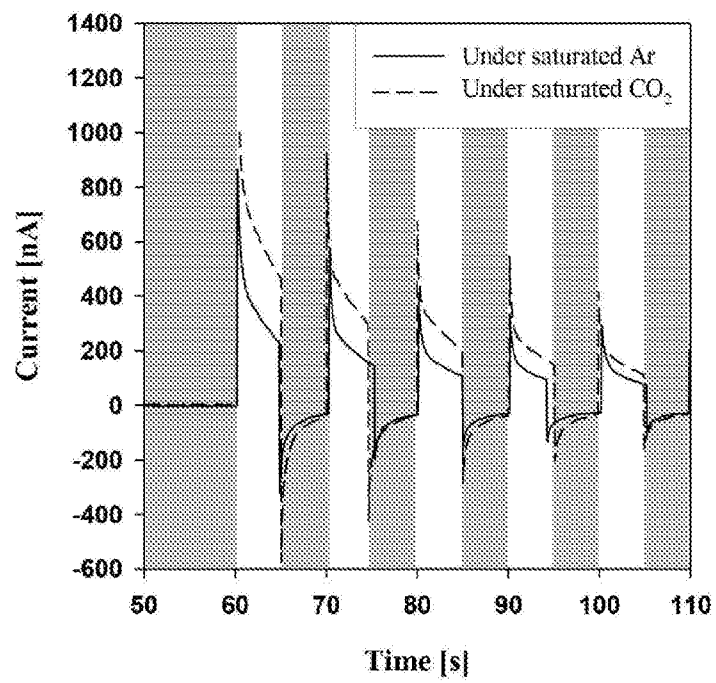


Fig. 20

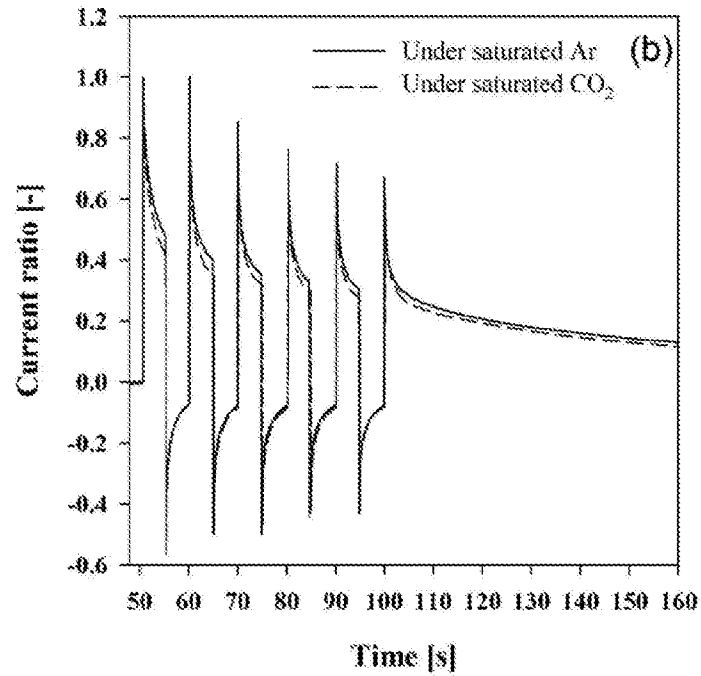
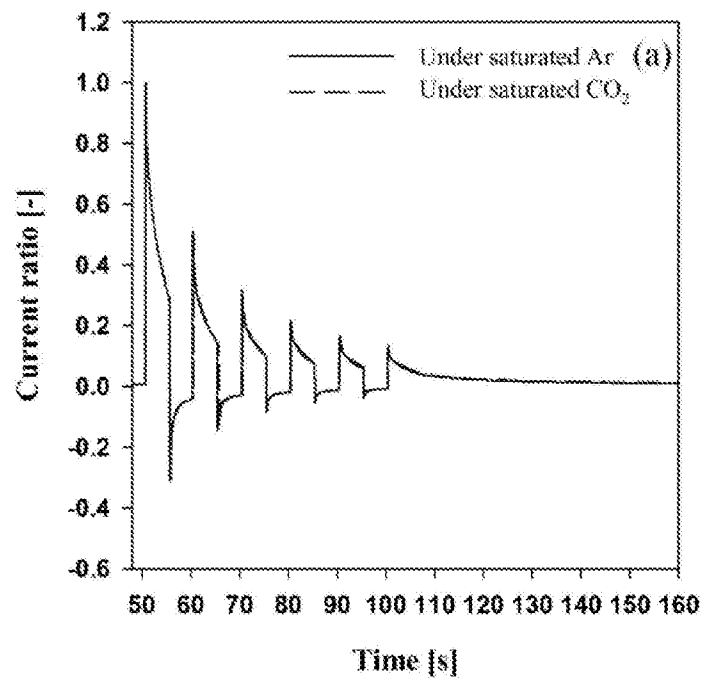


Fig. 21

## INTERNATIONAL SEARCH REPORT

 International application No.  
**PCT/AU2016/000081**

## A. CLASSIFICATION OF SUBJECT MATTER

**C01B 31/02 (2006.01) B82Y 30/00 (2011.01) H01M 4/96 (2006.01) H01M 4/00 (2006.01) H01M 8/00 (2016.01)**  
**H01M 14/00 (2006.01) B01J 35/02 (2006.01) B01J 37/00 (2006.01) B01J 21/18 (2006.01)**

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)

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)

Database: EPODOC, WPIAP, CAPLUS, Google Scholar, Google Patents. Keywords: carbon nanotube, graphene, doping, electrochemical, hydrogen evolution reaction, oxygen evolution reaction, oxygen reduction reaction, water split, HER, OER, ORR, hetero atom, nitrogen, sulphur, phosphorus, boron, silicon, aluminium, photo\_ electrochemical, electrocatalyst and similar. IPC Marks: C01B31/02/LOW, B82Y30/0, H01M4/96/LOW, H01M4/133/LOW, H01M4/1393/LOW, H01M14/00/LOW, H01M8/00/LOW, B01J35/02/LOW, B01J37/12/LOW, B01J37/16/LOW, B01J21/18/LOW. CPC Marks: C01B31/022/LOW, C01B31/0438, H01M4/0438/LOW, H01M4/133, H01M4/583/LOW, H01M4/86/LOW, H01M4/96/LOW, H01M8/00/LOW, H01M4/625/LOW, H01M4/583/LOW, H01M4/663/LOW, B01J32/00/LOW, B01J37/00/LOW, B01J21/18/LOW, B01J35/00/LOW, B82Y30/00. Applicant/Inventor search in CAPLUS.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
|           | Documents are listed in the continuation of Box C                                  |                       |



Further documents are listed in the continuation of Box C



See patent family annex

|          |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |
|----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| *<br>"A" | Special categories of cited documents:<br>document defining the general state of the art which is not considered to be of particular relevance                      | "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                                              |
| "E"      | earlier application or patent but published on or after the international filing date                                                                               | "X" | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |
| "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) | "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 |
| "O"      | document referring to an oral disclosure, use, exhibition or other means                                                                                            | "&" | document member of the same patent family                                                                                                                                                                                                    |
| "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<br>24 May 2016                                                                                         | Date of mailing of the international search report<br>24 May 2016                                                                                   |
| <b>Name and mailing address of the ISA/AU</b><br><br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>Email address: pct@ipaaustralia.gov.au | <b>Authorised officer</b><br><br>Sunilkumar Edamula<br>AUSTRALIAN PATENT OFFICE<br>(ISO 9001 Quality Certified Service)<br>Telephone No. 0262832927 |

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:  
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

**See Supplemental Box for Details**

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
**1-21**

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

| INTERNATIONAL SEARCH REPORT                           |                                                                                                                                                                                                                                                                                                                                                                                               | International application No. |
|-------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|
| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                                                               | PCT/AU2016/000081             |
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                            | Relevant to claim No.         |
| X                                                     | CN 105225844 A (UNIV NANJING AERONAUTICS & ASTRONAUTICS) 06 January 2016, Derwent Abstract Accession No. 2016-05645E<br>Abstract                                                                                                                                                                                                                                                              | 1-15, 18-21                   |
| X                                                     | CN 103407985 A (UNIV TSINGHUA ) 27 November 2013<br>Abstract; Claims 1-2                                                                                                                                                                                                                                                                                                                      | 1-8, 15-21                    |
| X                                                     | RATSO, S. et al., 'Highly active nitrogen-doped few-layer graphene/ carbon nanotube composite electrocatalyst for oxygen reduction reaction in alkaline media', ELSEVIER, Carbon, 73, 2014, Pages 361-370, <a href="http://dx.doi.org/10.1016/j.carbon.2014.02.076">http://dx.doi.org/10.1016/j.carbon.2014.02.076</a> .<br>Abstract; Section 2.2 on pages 362-363; first paragraph, page 364 | 1-21                          |
| X                                                     | HIGGINS, D.C. et al., 'Oxygen Reduction on Graphene–Carbon Nanotube Composites Doped Sequentially with Nitrogen and Sulfur', ACS Catal. 2014, 4, Pages 2734–2740, <a href="http://dx.doi.org/10.1021/cs5003806">dx.doi.org/10.1021/cs5003806</a> .<br>Abstract; Sections: Synthesis of the GC nano-composite & Sequential Doping of GC-NLS, pages 2735-2736; Page 2736, last paragraph        | 1-21                          |
| X                                                     | CHEN, P. et al., 'A Nitrogen-Doped Graphene/Carbon Nanotube Nanocomposite with Synergistically Enhanced Electrochemical Activity', Adv. Mater. 2013, 25, 3192–3196, DOI: 10. 1002/adma.201300515.<br>Last two paragraphs on page 3192                                                                                                                                                         | 1-21                          |
| A                                                     | US 2013/0252499 A1 (ZHOU et al. ) 26 September 2013<br>Abstract                                                                                                                                                                                                                                                                                                                               | 9-14                          |
| A                                                     | CN 103896240 A (OCEANS KING LIGHTING SCIENCE et al. ) 02 July 2014<br>Abstract                                                                                                                                                                                                                                                                                                                | 9-14                          |
|                                                       |                                                                                                                                                                                                                                                                                                                                                                                               |                               |

**Supplemental Box****Continuation of: Box III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

**Group 1. Claims 1-21**

This group of claims are directed to a nano-composite, a process of producing a nano-composite, an electrode comprising a nano-composite, an electrochemical cell comprising a nano-composite wherein the nano-composite comprises of heteroatom doped graphene and carbon nanotubes having heteroatom content of at least about 1.0 wt%.

**Group 2. Claims 22-39, 41-43**

This group of claims are directed to a photo-electrochemical cell and a corresponding method wherein a photo-electrochemical cell comprising (a) an anode comprising at least one oxidation catalyst (b) a cathode comprising at least one reduction catalyst wherein the cathode is in electrical communication with the anode and a (c) a proton conductor having a porous structure wherein the proton conductor connects the anode and the cathode thereby allowing transfer of protons between the anode and the cathode.

**Group 3. Claim 40**

This group of claim is directed to a process for preparing a porous proton conductor comprising the steps of : (i) providing a proton-conducting polymeric materials; and (ii) electrospinning the polymeric materials, thereby producing a porous proton conductor.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

It is considered that search and examination for the other inventions will require more than negligible additional search and examination effort over that for the first invention, and therefore the search and opinion is restricted to claims 1-21.

| INTERNATIONAL SEARCH REPORT                                                                                                                                                                                                                                           |                   | International application No. |                  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|-------------------------------|------------------|
| Information on patent family members                                                                                                                                                                                                                                  |                   | PCT/AU2016/000081             |                  |
| This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information. |                   |                               |                  |
| Patent Document/s Cited in Search Report                                                                                                                                                                                                                              |                   | Patent Family Member/s        |                  |
| Publication Number                                                                                                                                                                                                                                                    | Publication Date  | Publication Number            | Publication Date |
| CN 105225844 A                                                                                                                                                                                                                                                        | 06 January 2016   | CN 105225844 A                | 06 Jan 2016      |
| CN 103407985 A                                                                                                                                                                                                                                                        | 27 November 2013  | CN 103407985 A                | 27 Nov 2013      |
|                                                                                                                                                                                                                                                                       |                   | CN 103407985 B                | 11 May 2016      |
| US 2013/0252499 A1                                                                                                                                                                                                                                                    | 26 September 2013 | US 2013252499 A1              | 26 Sep 2013      |
|                                                                                                                                                                                                                                                                       |                   | CN 103153843 A                | 12 Jun 2013      |
|                                                                                                                                                                                                                                                                       |                   | CN 103153843 B                | 02 Apr 2014      |
|                                                                                                                                                                                                                                                                       |                   | EP 2660192 A1                 | 06 Nov 2013      |
|                                                                                                                                                                                                                                                                       |                   | JP 2014505650 A               | 06 Mar 2014      |
|                                                                                                                                                                                                                                                                       |                   | JP 5775603 B2                 | 09 Sep 2015      |
|                                                                                                                                                                                                                                                                       |                   | WO 2012088697 A1              | 05 Jul 2012      |
| CN 103896240 A                                                                                                                                                                                                                                                        | 02 July 2014      | CN 103896240 A                | 02 Jul 2014      |
|                                                                                                                                                                                                                                                                       |                   | CN 103896240 B                | 20 Jan 2016      |
| End of Annex                                                                                                                                                                                                                                                          |                   |                               |                  |
| Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.                                                                                                                                             |                   |                               |                  |