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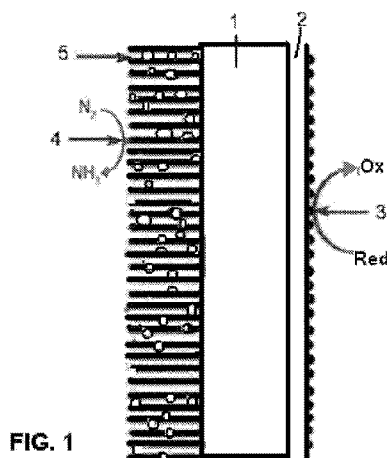


FIG. 1

(57) Abstract: The invention relates to a photo-electrocatalyst comprising a functionalised semiconductor, a method of preparing the photo-electrocatalyst and its use in a photo-electrochemical cell for purposes such as generating electricity. The functionalised semiconductor of the photo-electrocatalyst is typically chosen from the group comprising silicon, III-V type semi-conductors, II-VI semi-conductors, or oxide semi-conductors.

FUNCTIONALISED PHOTO-ELECTROCATALYST AND METHOD FOR CHEMICAL CONVERSION

FIELD OF INVENTION

[0001] The present invention relates to the field of photo-electrocatalysts.

[0002] In one form, the invention relates to a functionalised photo-electrocatalyst for use in chemical conversion.

[0003] In another form, the invention relates to photo-electrochemical processes.

[0004] In one particular aspect the present invention is suitable for use in sunlight driven ammonia synthesis.

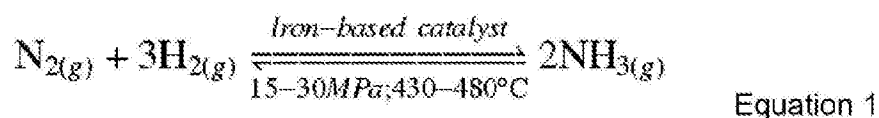
[0005] It will be convenient to hereinafter describe the invention in relation to production of ammonia, or the conversion of nitrogen to ammonia, however it should be appreciated that the present invention is not limited to that use only and can be used for a much wider range of reactions such as conversion reactions including the production of H₂ and the degradation of coloured dye solutions.

BACKGROUND ART

[0006] It is to be appreciated that any discussion of documents, devices, acts or knowledge in this specification is included to explain the context of the present invention. Further, the discussion throughout this specification comes about due to the realisation of the inventor and/or the identification of certain related art problems by the inventor. Moreover, any discussion of material such as documents, devices, acts or knowledge in this specification is included to explain the context of the invention in terms of the inventor's knowledge and experience and, accordingly, any such discussion should not be taken as an admission that any of the material forms part of the prior art base or the common general knowledge in the relevant art in Australia, or elsewhere, on or before the priority date of the disclosure and claims herein.

[0007] Ammonia (NH₃) is one of the most widely produced chemicals worldwide. More than 1% of global energy consumption is used for ammonia production. It has application in the production of many important chemicals, particularly in fertilisers, but also polymers, dyes, refrigerants and explosives. Ammonia is also, potentially, an important energy storage intermediate and clean energy carrier. Total ammonia production is predicted to reach 0.23 billion tonnes annually by 2019. (Tuna et al, Environ. Prog. & Sust. Energy, 2014, 33, 1290-1297)

[0008] For more than a hundred years, ammonia has been produced from nitrogen and hydrogen by the Haber–Bosch process, a discovery that has been of key importance in producing the inexpensive fertilisers that have supported the large global population growth over the past century. The Haber-Bosch process utilises an iron based catalyst, high pressures and high temperatures according to the following reaction:



[0009] Ammonia production, mostly for the aforementioned use in fertilisers, currently accounts for more than 1.6% of global CO₂ emissions. (Lan et al, Sci. Rep. 2013, 3.1145(1-7)) This process uses very high temperatures and pressures, and requires substantial amounts of natural gas, oil or coal for the production of the required hydrogen. Given the need to feed a growing world population, whilst simultaneously reducing global carbon emissions, it is highly desirable to break the link between industrial nitrogen-based fertiliser production and the use of fossil fuels. Therefore, researchers have been seeking alternative pathways to ammonia. (Anderson et al, Nature, 2013, 501, 84-88)

[0010] The ideal system for the conversion of nitrogen into ammonia would have few process stages, be easily scalable and would operate at ambient temperatures and pressures using renewable energy sources.

[0011] Attempts have been made in the past to harness solar energy for chemical reduction reactions using various processes including photo-electrochemical (PEC)

processes. The first PEC was demonstrated by Honda and co-workers in 1972, using a single crystal of TiO_2 to carry out photo-electrolysis of water under the influence of an anodic bias. (A. Fujishima and K. Honda, *Nature*, 1972, 238, 37) PEC methods involving p-type semiconductor electrodes have proved to be feasible for water and CO_2 reduction, and various p-type semiconductors have been investigated (Bachmeier et al, *J. Am. Chem. Soc.* 2014, 136, 13518-13521; Cao et al, *Chem. Comm.* 2013, 49, 3440-3442; Gu et al, *J. Am. Chem. Soc.*, 2014, 136, 830-833; Ji et al, *J. Am. Chem. Soc.*, 2013, 135, 11696-11699; Kou et al, *J. Catal.*, 2014, 310, 57-66)

[0012] In comparison with water splitting and CO_2 reduction, relatively few electro-catalysts, for example, palladium, and alloys, and polypyrrole and even fewer photo-catalysts, for example metal/ TiO_2 (Ranjit et al, *J. Phototchem. & Photobiol. A- Chemistry* 1996, 96, 181-185), diamond (Zhu et al, *Nature Materials*, 2013, 12, 836-841), and SrTiO_3 (Oshikiri et al, *Angew. Chem. –Int. Ed.*, 2014, 53, 9802-9806) have been reported for N_2 reduction. Van der Ham et al have recently reviewed the progress and challenges in achieving this goal. (Van der Ham et al, *Chem. Soc. Rev.* 2014, 43, 5183-5191). The main obstacle is the high stability and chemically inert nature of nitrogen. In addition, the low solubility of nitrogen in water (20 mg/L at 20°C and 1 bar) leads to low reactions rates.

[0013] Black silicon (BSi) is a relatively recently developed form of silicon in which its surface is covered by a layer of nanostructures (usually nanowires, nanorods or nanotips), which effectively suppresses reflection, by enhancing the scattering and absorption of light. (Lin et al, *Phys. Stat. Solidi C. Vol 7, No 11-12*, 2010, 7, 2778-2784). As a consequence, the silicon wafers appear black, instead of the silver-grey typical of planar silicon wafers. BSi possesses many attractive properties, including low reflectance, a large and chemically active surface area, super-hydrophobicity, and a high luminescence efficiency when surface-feature sizes are reduced to a few nanometers.

[0014] BSi has been considered as a promising candidate for efficient solar energy conversion. The morphology and orientation of silicon nanostructures can provide excellent photon trapping and absorption properties; an almost complete suppression of the reflectivity in a broad spectral range (250-1000nm) has been achieved by surface

texturing. Besides, the optical bandgap of nanostructured silicon can also be tuned by decreasing the size of the nano-features, due to the splitting of energy levels caused by quantum confinement.

[0015] Functionalisation of the BSi by combination of its surface with nano-metals can be used to further improve the efficiency of charge separation, charge transfer and catalytic processes. The resultant shift in the Fermi level has been observed to result in an increase of photocatalytic reduction efficiency and photocurrent generation in water splitting. The metal nano-particle can also in many cases act as a catalytic site for the reduction reaction. In addition, the surface plasmon resonance (SPR) exhibited by noble metals such as silver and gold can enhance absorption and hence this kind of functionalisation has significant promise in photo-catalysis. This effect has been successfully used in solar cells and solar-driven water splitting. More recently, plasmon induced ammonia synthesis has been demonstrated on gold nanoparticles on a Nb doped SrTiO₃ photoelectrode, although the yield is very low (less than 6 nano mol per day). (Oshikiri et al, Angew. Chemie-Int. Ed. 2014, 53, 9802-9806)

[0016] A prior attempt to synthesise ammonia using nano-size metal or metal alloy catalyst particles has been described in US patent application 2012/0308467 (US serial no. 13/585,640). Hydrogen and nitrogen gases are passed through a system comprising, nano-sized metal catalyst particles disposed on a ferrous support and in the presence of a nano-sized promoter. This would include, for example, using a bed of magnetite supporting nano-size iron or iron alloy catalyst particles having an oxide layer that forms the catalyst.

[0017] Another prior attempt to synthesise ammonia has been described in US patent 8,801,915 (US serial no. 13/809,677). In this synthesis method, an anode and a cathode are arranged in an electrolyte phase at a predetermined interval; a photocatalyst is provided to the anode; water is supplied to an anode zone and light is radiated so that water is decomposed by a photocatalytic reaction to generate protons, electrons, and oxygen gas. Nitrogen gas is supplied to a cathode zone, and the electrons generated in the anode zone are allowed to transfer to the cathode zone through a lead, thereby generating N³⁻ in the cathode zone. Ammonia is synthesized through the reaction between the protons that have moved toward the cathode zone from the anode zone in

the electrolyte phase and N_3^- , characterized in that an anode substrate is made of indium tin oxide or fluorine tin oxide. The cathode is a Ni porous body, a nickel-, iron-, or ruthenium-loaded Ni porous body, carbon paper, or nickel-, iron-, or ruthenium-loaded carbon paper; and the photocatalyst is a visible light-responsive photocatalyst comprising an oxynitride compound, an oxysulfide compound, or an oxide containing metal ions of d^{10} electron state.

[0018] Ammonia has also been produced using a mixture of N_2 and steam in a molten hydroxide suspension of nano- Fe_2O_3 at a cell voltage of 1.2 V and columbic efficiency of 35%. (Licht et al. *Science* **345**, 637-640 (2014)). Although this advance shows great promise for competition with current ammonia industry processes, the high temperature used ($\sim 200^\circ C$) still requires significant input of heat and energy. So far, electrochemical conversion has not been sufficiently successful to be considered as a viable replacement for the Haber-Bosch process. Furthermore, electrochemical conversion of the prior art has not reached sufficiently high efficiency levels such as those exhibited by dinitrogen-fixating bacteria. (Rosca et al, *Chemical Reviews*, **2009**, 109, 2209-2244)

[0019] US patent application 2006/0049063 and US patent 6,712,950 teach the synthesis of ammonia gas by anodic reaction from nitrogen-containing species or dinitrogen gas, and hydrogen-containing species or hydrogen gas in a non-aqueous liquid electrolyte such as a molten salt or a liquid salt. The method involves the production of the N_3^- ion in the electrolyte and then the reaction of the N_3^- ion at the anode to produce ammonia. This method is limited by the need for the medium to be selected such that it can dissolve useful amounts of the N_3^- to support practical rates of ammonia production.

[0020] In contrast to hydrogen generation or CO_2 reduction, very few prior art electro-catalysts or photo-catalysts have been reported to exhibit useful activity for N_2 reduction. Little is known about the requirements or possible mechanisms for such reactions. However it is known that to become commercially viable, electrochemical conversion of dinitrogen has to overcome the obstacles presented by the high stability and chemically inert nature of dinitrogen.

[0021] Ammonia has the potential to become an important energy storage intermediate and clean energy carrier if an energy efficient technology can be developed for its generation. The use of ammonia as a fuel, ideally in a fuel cell, generates only N_2 and water and hence could be part of a sustainable fuel cycle. This is a strong driver for provision of new and efficient ways to generate ammonia. Although various processes for converting nitrogen (in its various forms or as dinitrogen) to ammonia have been proposed in the prior art, it is important that the conversion process can be realized by using renewable energy sources

SUMMARY OF INVENTION

[0022] An object of the present invention is to provide a novel family of nanostructured photo-electrocatalysts.

[0023] Another object of the present invention is to provide a system for the conversion of nitrogen in any convenient form, such as dinitrogen, into ammonia.

[0024] Another object of the present invention is to provide a system for conversion of nitrogen, such as sunlight driven synthesis of ammonia.

[0025] Another object of the present invention is to provide a catalyst material that can replace fossil fuel based chemical processes with solar energy based processes.

[0026] A further object of the present invention is to alleviate at least one disadvantage associated with the related art.

[0027] It is an object of the embodiments described herein to overcome or alleviate at least one of the above noted drawbacks of related art systems or to at least provide a useful alternative to related art systems.

[0028] In a first aspect of embodiments described herein there is provided a photo-electrocatalyst comprising a functionalised semiconductor.

[0029] Preferably the semiconductor is chosen from the group comprising Si such as black silicon (BSi), III-V type semi-conductors such as GaAs or InP, II-VI semiconductors such as ZnS, CdS, CdSe, TeSe, or oxide semiconductors such as BiVO₄ or iron oxide.

[0030] In a particularly preferred embodiment the semiconductor is a silicon nanostructure, or more preferably a BSi nanostructure.

[0031] Where used herein the term 'photo-electrocatalyst' is intended to refer to a catalyst structure comprising one or more materials which have the effect of absorbing light energy and creating separated electrons and holes. The electrons are capable of driving a reduction reaction and the holes are capable of participating in an oxidation reaction. The aforementioned oxidation and reduction reactions may take place on a single isolated particle of the catalyst or may take place on one or more separate electrodes connected to the catalyst.

[0032] In a second aspect of embodiments described herein there is provided a photo-electrocatalyst comprising a functionalised black silicon (BSi) nanostructure in which the BSi is functionalised by one or more types of nanoparticle. Without wishing to be bound by theory it is believed that the functionalisation of the BSi nanostructure allows highly efficient charge carrier generation and separation and provides a large number of reactive sites for the adsorption and conversion of nitrogen.

[0033] In a third aspect of embodiments described herein there is provided a photo-electrocatalyst comprising a functionalised black silicon (BSi) nanostructure in which the BSi is functionalised by one or more thin layer coating(s). Optionally the photo-electrocatalyst may be functionalised by both one or more types of nanoparticles and one or more thin layer coating(s).

[0034] In a preferred embodiment the nanoparticle or layer for functionalisation is chosen from chemical species that optimise the reactions at the photo-electrocatalyst, for example, through plasmonic enhancement effect or by providing electrocatalytic sites for the electrochemical reactions.

[0035] With reference to FIG. 1 and without wishing to be bound by theory it is noted that photoexcitation in the semiconductor (1), produces holes and electrons. The holes migrate across the junction with the hole collector (2) (such as Cr, PEDOT, ITO), which is chosen such that it has a lower work function than Si. This aids in increasing the lifetime of the photogenerated holes and electrons. The hole then migrates to the oxidation electrocatalyst (3) (such as Cr, MnO_x , CoO_x), where an oxidation reaction takes place. The electrons migrate to the reduction electrocatalyst (4) (such as Fe, Noble metals, carbon, polypyrrole), where the desired reduction reaction takes place. Plasmonic nanoparticles (5) (such as Au, Pt, Cu) may serve to enhance the photoabsorption efficiency of the Si through a plasmonic resonance effect. It is possible that a single material may carry out several of these functions.

[0036] By manipulating the composition, shape and size of the functionalising nanoparticles or layers, it is possible to design nanostructures that interact with the entire solar spectrum and beyond. Catalysts such as carbon quantum dots, poly(3,4-ethylenedioxythiophene) (PEDOT) also exhibit excellent activities for CO_2 or O_2 reduction and can be used to functionalize semiconductors such as BSi. These functionalisation effects can be synergistically combined to develop high-efficiency photo-electrocatalytic devices for chemical conversion, such as the conversion of nitrogen to ammonia. Typically the photo-electrocatalytic device is driven by solar power.

[0037] In another embodiment described herein there is provided a photo-electrocatalyst for the reduction of nitrogen to ammonia and/or ammonium salts or other ammonia based products, the photo-electrocatalyst comprising a metal nanoparticle or layer modified BSi nanostructure. In a preferred embodiment the metal shows a good plasmonic absorption effect. Preferably the metal nanoparticles or layer are chosen from the group comprising gold, silver, copper, platinum, palladium and alloys thereof. In a particularly preferred embodiment the metal nanoparticles are gold nanoparticles.

[0038] In a further preferred embodiment the photo-electrocatalyst of the present invention may have a further functionalising nanoparticle or layer for the purpose of providing the site or sites for the accompanying oxidation reaction. Preferably this

additional functionalization is Cr, Pt, Ni, or indium tin oxide or fluorine doped tin oxide or carbon, or manganese oxide, or cobalt oxide, or nickel oxide.

[0039] In a particularly preferred embodiment the oxidation reaction is the oxidation of sulphite to sulphate. In an alternative preferred embodiment, the oxidation is the oxidation of water to oxygen.

[0040] In a further preferred embodiment the photo-electrocatalyst of the present invention may have a further functionalising nanoparticle or layer for the purpose of providing the site or sites for the desired reduction reaction. Preferably this additional functionalization species is chosen from the group comprising Au, Ag, Pt, Pd, Cu, Fe and their alloys, carbon quantum dots and polypyrrole or poly(3,4-ethylenedioxythiophene) (PEDOT). Preferably the functionalising species are deposited on the surface of the BSi by E-beam sputtering, or wet chemical methods, or electrochemical methods.

[0041] Optionally the photo-electrocatalyst of the present invention can catalyse reactions using solar energy at ambient temperature and pressures.

[0042] In another aspect of embodiments described herein there is provided a method of preparing a photo-electrocatalyst comprising the step of nano-scale deposition of a functionalising species on the surface of a semiconductor.

[0043] The method may optionally include an initial step of passivation of the surface of the semiconductor.

[0044] In yet a further aspect of embodiments described herein there is provided a method of functionalising a semiconductor to provide a photo-electrocatalyst, the method including the steps of:

- (i) optional passivation of the surface of the semiconductor, and
- (ii) nano-scale deposition of a functionalising species on the surface of the semiconductor.

[0045] As described above, the photo-electrocatalyst comprising a functionalised semiconductor according to the present invention can be used for the reduction of nitrogen to ammonia and/or ammonium salts or other ammonia based products.

[0046] In a further aspect of the present invention there is provided a photo-electrochemical cell suitable the cell comprising:

- (i) a functionalised semiconductor photo-electrocatalyst according to the present invention, and
- (ii) an aqueous, non-aqueous or liquid salt electrolyte.

[0047] In a preferred embodiment, nitrogen is introduced to the electrolyte and the products of the photo-electrochemical cell are ammonia based products including ammonia *per se* and ammonia salts.

Liquid Salt Electrolyte

[0048] Where used herein the term liquid salt is intended to refer to an electrolyte medium that is liquid at the temperature of use and that contains one or more salts. The salts may be chosen from any suitable metal salts, organic salts, complex ion salts or the like.

[0049] The liquid salt medium can also be formed by mixing two or more salts, which individually may be liquid or solid at room temperature, to create a liquid salt of the desired characteristics.

[0050] While the liquid salt medium is principally comprised of ions it may contain additional components including water or other molecular liquids.

[0051] The liquid salt electrolyte (LSE) provides an ion conductive, non-volatile medium in which the process reactions occur.

[0052] In a preferred embodiment the LSE comprises one or more eFAP salts (where eFAP is tris(pentafluoroethyl)trifluorophosphate)

[0053] In a preferred embodiment the LSE comprises one or more hydrophobic liquids based on the $P_{6,6,6,14}$ cation. In a particularly preferred embodiment the LSE is substantially comprised of $P_{6,6,6,14}$ eFAP.

[0054] In a particularly preferred embodiment the LSE is preconditioned prior to use, such as, by contacting it with an aqueous hydroxide solution. Without wishing to be bound by theory, the preconditioning may introduce a trace amount of OH^- into the liquid salt that provides a defined proton activity in the LSE.

[0055] In a particularly preferred embodiment the photo-electrocatalyst comprising a functionalised semiconductor according to the present invention can be used for cathodic dinitrogen reduction.

[0056] In a further aspect of embodiments described herein there is provided a photo-electrochemical cell comprising:

- a cathodic working electrode comprising a functionalised semiconductor photo-electrocatalyst according to the present invention for reduction of dinitrogen,
- a counter electrode connected electrically to the cathodic working electrode, and
- an electrolyte comprising an aqueous solution, or a liquid salt electrolyte comprising one or more liquid salts in contact with the working electrode.

[0057] In a further aspect of embodiments described herein there is provided a method for the electrochemical reduction of dinitrogen to ammonia, the method comprising the steps of:

- contacting a cathodic working electrode comprising a nanostructured photo-electrocatalyst comprising a functionalised semiconductor with an electrolyte comprising one or more liquid salts,

- introducing dinitrogen and a source of hydrogen to the electrolyte,

wherein the dinitrogen is reduced to ammonia at the cathodic working electrode.

[0058] Typically the dinitrogen is reduced at the cathodic working electrode to ammonia in the presence of a source of hydrogen, preferably water. In a particularly preferred embodiment of the method, the dinitrogen gas is humidified with water vapour to a controlled degree and then the humidified gas is passed in a stream over the cathode where the dinitrogen is electrochemically reduced to form ammonia.

[0059] Typically, when the source of hydrogen is water, the anodic counter electrode converts the hydroxyl ions formed at the cathode into water and oxygen.

[0060] The counter electrode may be placed in the same electrolyte or may be separated by a membrane or separator material. The counter electrode compartment may contain a different electrolyte medium, such as an aqueous solution.

[0061] The counter electrode reaction may be water oxidation or another advantageous oxidation reaction such as sulphite oxidation.

[0062] Preferably the photo-electrochemical reaction is solely driven by photoelectric energy from sunlight.

[0063] The present invention may further provide a method of generating electricity comprising the steps of:

1. photoelectric generation of ammonia using the photo-electrochemical cell of the present invention; and
2. providing at least part of the ammonia generated in step 1 to an ammonia fuel cell for generation of electricity and nitrogen.

[0064] In a preferred embodiment, at least part of the ammonia generated in step 1 is stored in a reservoir for supply to the ammonia fuel cell as needed.

[0065] In another preferred embodiment, at least part of the nitrogen generated in step 2 is recycled into to step 1.

[0066] In a further aspect of the present invention there is provided a device for electricity generation according to the aforementioned method, the device comprising a photo-electrochemical cell according to the present invention and an ammonia fuel cell, wherein in use;

1. the photo-electric cell is driven by photoelectric energy from sunlight to generate ammonia; and
2. at least part of the ammonia generated in step 1 is provided to an ammonia fuel cell for generation of electricity and nitrogen.

[0067] In a preferred embodiment, the device includes a reservoir for storage of ammonia generated in step 1.

[0068] In another preferred embodiment, at least part of the nitrogen generated in step 2 is recycled into to step 1.

[0069] Using this method and device, at times of low solar input the ammonia solution can be used to power an ammonia fuel cell to generate electricity. Nitrogen generated in this step can be recycled for a further solar energy capture, when needed.

[0070] An alternative embodiment of the photo-electrochemical cell of the present invention has a functionalised semiconductor (preferably BSi) photo-electrocatalyst connected electrically to a second electrode. The oxidation reaction occurs on the second electrode. In this embodiment it is possible to include a voltage source in the electrical circuit to provide energy input additional to the light energy.

[0071] Other aspects and preferred forms are disclosed in the specification and/or defined in the appended claims, forming a part of the description of the invention.

[0072] In essence, embodiments of the present invention stem from the realization that by manipulating the composition, shape and size of the functionalising nanoparticles, it is possible to design nanostructures that work in a synergistic combination to develop high-efficiency PEC devices for conversion of nitrogen to ammonia, more particularly, solar-driven conversion.

[0073] Advantages provided by the present invention comprise the following:

- the catalyst can replace fossil fuel based process with solar energy based processes with obvious positive impact on greenhouse gas induced climate change;
- can be used for solar powered reactors (eg for ammonia generation) capable of wider geographical distribution, increasing access and lowering transportation costs;
- provision of high catalytic efficiency, specificity and selectivity under mild conditions;
- a new paradigm in the production of ammonia and ammonia based compounds;
- a system for conversion of nitrogen into ammonia having few process stages, easily scalable and operating at ambient temperatures and pressures.

[0074] Further scope of applicability of embodiments of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure herein will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0075] Further disclosure, objects, advantages and aspects of preferred and other embodiments of the present application may be better understood by those skilled in the relevant art by reference to the following description of embodiments taken in conjunction with the accompanying drawings, which are given by way of illustration only, and thus are not limitative of the disclosure herein, and in which:

FIG. 1 illustrates the structure of the catalyst and the roles of the different functionalised sites.

FIG. 2 illustrates the band positions of silicon (7, BSi CB; 9, BSi VB) in contact with aqueous solution at pH = 0.

FIG. 3 illustrates graphically the ammonia yields from photo-electrochemical reduction of N₂ at nanofunctionalised BSi under 2 Sun illumination (11) and in the dark (13).

FIG. 4 comprises schematic illustrations of the photo-electrochemical cell designs: FIG. 4a represents the internal connected "wireless" cell; FIG. 4b represents a wired two electrode PEC; and FIG. 4c represents a driven PEC. In each illustration is shown the P-Si (15), nanocatalyst/BSi layer (17), carbon (19), oxidation catalyst (21) and ITO or FTO (23).

FIG. 5 is a schematic diagram of the cell used showing the light source (25), N₂ inlet pipe (27), N₂ outlet pipe (29), electrolyte (31), and electrode (33)

FIG. 6 illustrates the yield of ammonia obtained on different substrates after illumination with 2 Sun for 24 hours (catalyst geometric area = 1 cm² (=0.12 g catalyst), nitrogen flow rate 10ml/min in 10 ml deionized water, where: (A) P-type silicon, (B) bSi, (C) (gold nano-particles) GNP/bSi, (D) GNP/bSi/Cr, and (E) Au/Si/Cr after illumination with 2 suns and (F) GNP/bSi/Cr in dark;

FIG. 7 is a schematic representation of the mechanism N_2 reduction at the catalyst surface comprising chrome (41) and black silicon (43), with light (45) impinging on the black silicon.

FIG. 8 illustrates aspects of the example described herein, more specifically, it illustrates the cell design for photoelectrochemical experiments. In this view can clearly be seen the light source (50), N_2 inlet pipe (51), N_2 outlet pipe (53), electrolyte (55), reference electrode (57), anode (59), cathode (61) and potentiostat (63). electron flow is in the direction of the arrow. The inset (65) illustrates the catalyst surface as shown in FIG. 7.

FIG 9 graphically illustrates the light intensity dependence of ammonia yield obtained after illumination for 3 hours (error bars are an estimate of the combined errors of measurements)

FIG. 10 graphically illustrates UV-Vis spectra of gold nanoparticle coated bSi (60) compared with the pristine Si (62). The difference in absorption is a result of the nano-structure modification created by the dry etching. Also, the plasmonic effect of the attached GNP appears at 513nm.

FIG. 11 illustrates the quantum efficiency ($\eta\% \times 10^3$) of ammonia synthesis on a GNP/bSi/Cr photoelectrochemical cell as a function of wavelength (error bars are estimates of the combined errors of measurements);

FIG. 12 illustrates the yield of ammonia in three hours as a function of nitrogen gas pressure at 2 suns illumination in a fixed volume glass reactor (error bars are the standard deviation of at least three replicates of independent measurement).

FIG.13 is a flow chart illustrating the use of a solar powered (81) ammonia generating photo-electrochemical cell (80) according to the present invention in conjunction with an ammonia fuel cell (81) for generation of electricity and nitrogen, the nitrogen being made available for recycling for further solar driven energy capture. Specifically, atmospheric nitrogen (83) is fed into the cell (80) which generates ammonia solution (85) that is transferred to an ammonia storage

tank (87) until it is needed for consumption in the fuel cell (81). Nitrogen and media from the fuel cell (81) can be recycled (89) to the cell (80)

DETAILED DESCRIPTION

[0076] The present invention will now be described with reference to the following non-limiting examples and descriptions of experiments.

[0077] Photoexcitation in a semiconductor is fundamental to operation of the present invention and FIG. 1 illustrates how it produces holes and electrons. The holes migrate across the junction with the hole collector, which has is chosen such that it has a lower work function than Si. This aids in increasing the lifetime of the photogenerated holes and electrons. The hole then migrates to the oxidation electrocatalyst where an oxidation reaction takes place. The electrons migrate to the reduction electrocatalyst where the desired reduction reaction takes place. The plasmonic metal particles serve to enhance the photoabsorption efficiency of the Si through a plasmonic resonance effect. It is possible that a single material carries out several of these functions.

[0078] Photo-electrodes based on gold nanoparticle decorated BSi have been fabricated and their optical properties and photo-electrochemical activity have been measured. Black silicon is a surface modification of silicon with very low reflectivity and correspondingly high absorption of visible and infrared light. Recent investigations have shown that BSi exhibits enhanced photo-electrochemical and photocatalytic performance. BSi is known to have relatively small band gap (about 1.1 eV), and its conduction band level appear to be high enough to reduce nitrogen.

[0079] The gold nanoparticle modified BSi nanostructure of the present invention allows highly efficient charge carrier generation and separation and provides a large number of reactive sites for the adsorption and conversion of nitrogen.

[0080] For a photo-electrochemical reaction to be possible, the band-gap of the photo-active component, usually a semiconductor, should exceed the free energy of the reaction, as well as have band energies suitable for the individual half reactions that need to be driven. Based on the disclosures and teaching of the prior art it is not

apparent whether silicon can be used to reduce nitrogen to ammonia. Specifically, the potential for nitrogen reduction under standard conditions is:



which is slightly more positive than the potential of hydrogen generation. In other words, thermodynamically N_2 reduction requires less reducing conditions than proton reduction. In fact, the onset of conversion of nitrogen into ammonia has been observed at potentials higher than the H^+/H_2 potential. (Koleli and Kayan, J.Electroanal. Chem. 2010, 638, 119-122). As shown in FIG. 2, the nitrogen reduction potential is also suitably lower than the conduction band energy level of Si.

[0081] Accordingly investigations were carried out to show that nitrogen reduction can be driven by conduction band electrons in Si. More specifically, the investigations were directed at confirming that p-type silicon can be successfully used for nitrogen reduction, benefiting from its suitable band edge energies, and whether the band edge position can be tuned and the band-bending can be enhanced by changing the doping conditions.

[0082] The N_2 reduction capability of the photo-electrocatalyst of the present invention may be optimised by the choice of solvent.

Nitrogen Conversion

[0083] Photo-electrodes have been fabricated based on gold nanoparticle decorated BSi and the optical properties and photo-electrochemical activity of these electrodes have been measured.

[0084] In particular, nitrogen has been successfully converted to ammonia in high yield (FIG. 3). The yield is $33 \mu\text{g}/\text{cm}^2$ after 24 hours under 2 Suns (AM 1.5 G) solar equivalent irradiation, which is about 18 times and 350 times higher than previously reported results using diamond (Zhu et al, Nature Materials, 2013, 12, 836-841) and gold nanoparticle/ SrTiO_3 photoelectrode, (Oshikiri et al, Angew.Chem. - International Edition, 2014, 53, 9802-9806) respectively. It can be inferred that the gold nanoparticle modified BSi nanostructure allows highly efficient charge carrier generation and separation and

provides a large number of reactive sites for the adsorption and conversion of nitrogen.

Fabrication of Functionalised Nanostructured BSi

Fabrication of BSi by Reactive Etching

[0085] Most of the work on the fabrication of BSi to date can be classified into two types of method: wet etching and dry etching. The wet etching method uses etchants, typically HF based solutions, to remove materials from the wafer or surface. (Algasinger et al, J, Advanced Energy Materials, 2013, 3, 1068-1074)

[0086] The present invention provides a novel process which avoids the use of HF. This method is significantly more benign to operate and can be scaled up easily.

[0087] The dry etching method refers to the removal of material, typically in a masked pattern, by ion bombardment that dislodges portions of the material from the exposed surface. The desired surface morphology is achieved by controlling the plasma chemistry, radio frequency (RF) power, and pressure and using a mask. The resulting morphology can be isotropic, positively and negatively tapered, or even fully vertical, walls.

[0088] Etching methods, using p-type silicon of different doping concentrations, can also be used to achieve the highest electrochemically active and accessible surface area, consistent with high photo-absorption and charge transport in the Si.

Functionalisation of BSi

[0089] Nanometals Au, Ag, Pt, Cu and their alloys, and some existing catalysts such as carbon quantum dots and PEDOT, with controlled size, morphology and amount may be used to functionalize the nanostructured BSi. Nanoparticles and nanolayers can be deposited on BSi by using E-beam sputtering and wet chemical or electrochemical methods. One of the roles of these nanomaterials is to act as reduction electro-catalysts. For photocathodes prepared for use in aqueous electrolytes, the surface of

the BSi may be protected through surface passivation beforehand, based on the existing techniques.

Material Characterisation

[0090] The phase formation and growth mechanism of nanostructures can be characterised using a wide range of techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Their optical properties can be characterised using known methods including UV-vis absorption, as well as surface enhanced Raman spectroscopy and in-situ Fourier transform IR spectroscopy.

Photocathodes for Solar-Driven Conversion of Nitrogen to Ammonia

[0091] The photo-electrocatalysts of the present invention may be used as photo-electrochemical cathodes for solar-driven conversion of nitrogen to ammonia. For example, a standard two- or three-electrode photo-electrochemical cell configuration may be suitable.

[0092] In a preferred embodiment the photo-electrocatalysts of the present invention are used as photo-electrochemical cathodes for solar-driven conversion in the presence of sacrificial reductants such as SO_3^{2-} . By providing a low potential oxidation reaction, these reagents ensure efficient capture of the photo-generated holes. Sulfite in the form of sulfurous acid is particularly attractive in this role ($\text{SO}_3^{2-} + \text{H}_2\text{O} = \text{SO}_4^{2-} + 2\text{e}^- + 2\text{H}^+$, $E_0 = +0.16$ vs NHE at pH=0) since the overall product of the reaction is ammonium sulfate, which is directly useful as a fertiliser. In the absence of a sacrificial reductant, the desired counter-electrode oxidation reaction is water oxidation.

[0093] This may require additional applied potential over and above that available at the valence band edge of Si however, the band adjustment that can be achieved by the presence of the metal nano-particle may reduce this need for applied potential.

[0094] Both aqueous and liquid salt electrolytes may be utilized and investigated as follows:

[0095] Aqueous electrolytes: The effect of the ion components, pH, concentration, nitrogen flow rate and temperature of the electrolytes on the nitrogen conversion reaction can affect the reaction, and thus the performance of the photocathode including quantum efficiency, turn-over number, and ammonia yield. The pH is preferably controlled by the use of an appropriate buffer medium.

[0096] The production of ammonia based products, such as ammonium sulfate may be achieved through the addition of the corresponding anions (either as the sulphite or the sulphate anions or their monoprotonated forms) into the aqueous electrolytes where such compounds can be easily separated.

[0097] Liquid salt electrolytes: Various liquid salt can be used, and for this purpose the highly fluorinated anions such as bis(trifluoromethanesulfonyl) amide and tris(perfluoroethyl) trifluorophosphate anion based families of liquid salts are of interest. Recent discoveries have shown that certain liquid salts can lower the energy of a solvated (CO_2)–intermediate, and thereby lower the initial reduction barrier in CO_2 conversion.

Product Identification and Quantification

[0098] The products of nitrogen conversion can be characterised by known techniques such as nuclear magnetic resonance spectroscopy (NMR), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and other standard analysis techniques. For example, two concordant methods of quantifying the NH_3 yield are (i) the ion selective electrode method, and (ii) the indophenol method. The photo-activity can be quantified at different light intensities and the action spectrum determined by use of bandpass filters.

Solar-powered photo-electrochemical cell for the synthesis of ammonia and ammonia based products

[0099] Cell designs: There are a number of approaches to designing and operating a photo-driven cell suitable for use with the photoelectrochemical catalyst of the present invention. FIG. 4 shows a schematic of possible PEC designs. FIG. 4a shows the

“wireless” setup in which the counter-electrode, such as a carbon layer, is deposited onto the back of the BSi layer to support the oxidation process. Sodium sulfite is used as a sacrificial hole-absorber. Thus, the whole electrochemical device is integrated into a single component. This has the advantage that the distance the photo-generated hole has to travel before engaging in the oxidation reaction is minimised.

[0100] FIG. 4b shows a “wired” design which separates the oxidation and reduction electrodes. This has several practical advantages - (i) it allows direct external measurement of the current in the cell and therefore rapid characterisation of its response to parameters such as light intensity, wavelength, electrolyte, etc (ii) it allows separation of the products from one another such that reverse reactions are minimised, improving the Faradic efficiency of the process.

[0101] FIG. 4c shows the wired PEC cell with an applied bias, allowing additional potential to be applied if this is needed to drive the desired counter electrode reaction.

Example 1

[0102] The present invention will be further described with reference to the following non-limiting example which illustrates solar light driven conversion of nitrogen to ammonia using a photoelectrochemical structure, based on plasmon enhanced bSi, as the photo absorber, decorated with gold nano-particles as the reduction catalysis sites and a hole-sink layer of Cr. This multi-layer structure creates an autonomous electrochemical device capable of carrying out oxidation and reduction reactions on different areas of the device, powered by photo-excitation

[0103] To prepare the nanostructured photo-catalyst in this work, a p-type boron-doped commercial silicon wafer was used as a substrate material and etched using a dry etching method. A gold nanoparticle (GNP) layer was sputtered onto the etched surface as the photocathode. A chromium metal (Cr) layer with a thickness about 50 nm was sputtered onto the back surface of the silicon wafer as an anode. Without wishing to be bound by theory, it is believed that the GNP's enhance the scattering of light within the silicon structure and generate a plasmonic resonance contribution to the absorption in the 500-560nm region of the spectrum. Also, more importantly it could act as a sink for

electrons, enhancing separation from the holes. Also, research has confirmed the ability of metals to facilitate the reduction process by weakening the nitrogen triple bond through the interaction with the metal surface, suggesting that the coordination by $d\pi \rightarrow p\pi$ interaction may be essential for efficient reduction of dinitrogen.

[0104] The attachments of a metal to semiconductor surface may enhance the overall efficiency of semiconductor in their reduction or oxidation processes. The chromium metal layer is expected to play the role of the counter-electrode; in other words, Cr facilitates hole collection and transfer to the solution. Because, the chromium work function is about (4.5 eV) which is smaller than that of p-Si (5.0–5.2) eV, holes will readily transfer into the Cr from the p-Si.

[0105] A nitrogen photo-reduction cell was constructed (FIG. 5), with nitrogen gas from an inlet (27) bubbling over the surface of the BSi catalyst (33) and using artificial solar light (300W Xe lamp) as an illumination source (25). The medium used is distilled water (pH 5.8). The yield of ammonia was measured as a function of time with a regularly calibrated ammonia-ammonium ion selective electrode. The final yield was confirmed using the indo-phenol method. The yield of ammonia over 24 hours obtained on different substrates is shown in FIG. 6 for (A) P-type silicon, (B) bSi, (C) GNP/bSi, (D) GNP/bSi/Cr, and (E) Au/Si/Cr after illumination with 2 suns and (F) GNP/bSi/Cr in dark. The GNP/bSi/Cr photoelectrochemical cell exhibits yield of 320 mg/m² over 24 hours.

[0106] Control experiments were conducted (i) without light, (ii) using un-etched silicon (reflective) and (iii) using pure gold alone and in all of these cases there was no ammonia produced.

[0107] The p-BSi(GNP) material shows superior yield over the catalyst containing p-BSi only. This comparatively high yield is expected given the plasmonic and other effects of gold. With p-BSi(GNP) plated (from the back) with Cr even better reduction efficiency is observed. Ammonia production can be observed at a low level on bSi; however, after coating with gold nanoparticles, the yield of ammonia is increased by nearly 4 times.

Example 2

[0108] To avoid silicon oxidation and enhance charge separation, a Cr layer was coated on the silicon in Example 1 to act as the hole sink and anode; in other words, Cr facilitates hole collection from the Si and acts in this case as a sacrificial anode. However, the oxidation of Cr was also observed, indicating that the hole energy exceeds the $\text{Cr}_2\text{O}_3/\text{HCrO}_4^-$ potential (0.7 V vs NHE at pH = 6) thus Cr is playing the role of a sacrificial agent in this process. To protect the Cr from dissolution, sulphite (SO_3^{2-} , redox potential = - 0.18 vs NHE at pH= 6), was added to the solution as a sacrificial agent. No oxidation of Cr was then detectable. While a number of possible reagents could be used in this role, this sacrificial reagent was chosen on the basis that this reagent when used in its aqueous acid form (routinely produced from SO_2) product of the overall reaction in this case is ammonium sulfate.



[0109] This is a commonly used form of ammonia as a fertiliser; the sulphate beneficially adds sulphur to the soil in addition to the nitrogen from the ammonia; the residual acid in this process can be neutralised with KOH to form K_2SO_4 which is also used in fertiliser formulations.

[0110] In this example a Na_2SO_3 at 150ppm in distilled water is used as the medium. To ensure that the added Na_2SO_3 did not interfere with the ammonia analysis methods, the ISE was recalibrated using standard solutions containing the same amount of sacrificial agent. The final product under these conditions over a 24 hour period was 320 mg per m^2 or 13 $\text{mg}/\text{m}^2/\text{h}$. A durability test consisting of repeated 3 hours runs using this sodium sulphite electrolyte also showed very reproducible and stable behaviour for up to 18 hours.

Example 3

[0111] Since the reduction reaction of N_2 involves protons a variety of media with different pH values were studied. pH was adjusted between 2 and 9 by adding appropriate amounts of HCl or KOH to water. The yield (with 2 Sun illumination for 3

hours) was optimised in the region pH 4 – 5. The highest yield was 71 mg/m^2 , or $23.6 \text{ mg/m}^2/\text{h}$.

Example 4

[0112] Since the process is fundamentally consists of two coupled redox reactions taking place on different areas of the material, it is also possible to construct a “wired” version of the catalyst in which the two reactions are separated onto different electrodes (FIG. 8). This allows direct measurement of the photogenerated electron flow in the cell. In this wired cell, the (photo) cathode consists of p-Si (GNP) while the other electrode, the anode, is Cr metal in a Na_2SO_3 electrolyte solution. Two experiments were conducted to separate the current generated from the reduction of nitrogen from other reduction processes that may generate current. Different potentials (-0.1 to -0.5V) were applied using Ag/AgCl reference electrode. The data obtained shows that, the photocurrent generated below -0.3V (about $10 \mu\text{A/cm}^2$) may be attributed to nitrogen reduction.

Example 5

[0113] To understand the effect of light intensity, the intensity was varied as shown in Fig 90. The conversion reaches a maximum at about 2 Suns in this Example. This limit is likely to be related to other factors such as the concentration of N_2 in the medium.

Example 6

[0114] Quantum yield experiments (FIG. 11) were carried out with 50 nm wide bandpass filters, confirming that the nitrogen reduction can occur in whole visible range, dropping away as the band gap energy of Si is approached. A small absorption maximum that is observed in the region of the surface plasmon resonance region for gold nanoparticles also appears at 513 nm (FIG. 10). This suggests that excitation of surface plasmons in the GNP particles provides an additional photoexcitation mechanism that contributes to the overall yield in this region of the spectrum, as has been observed in other SPR enhanced processes.

Example 7

[0115] To understand the relationship between the dissolved amounts of nitrogen in the solution and the generated ammonia-ammonium yield, the effect of N_2 pressure on the reaction was investigated in a closed glass pressure vessel. An approximately linear dependence of yield on pressure was observed (FIG. 12) over the range studied, and the yield was $60 \text{ mg/m}^2/\text{h}$ at 7 atmospheres. As would be expected from a Henry's law dependence of nitrogen solubility on pressure in the aqueous medium. This suggests that the concentration of nitrogen at the reactive sites on the surface is a rate limiting factor in these experiments. On the other hand, in our ambient condition experiments, bubbling nitrogen gas generates strong agitation of the medium created near the surface as well as a dynamic gas-liquid-solid interface, which enhances reaction rates by facilitating transport to and from the reaction sites in the structure (this also explains the relatively lower yields at lower pressures in (FIG. 12). This suggests that strategies to further enhance yield in either case could seek to enhance the kinetics of these processes via further manipulation of the nanostructure of the bSi.

Example 8

[0116] FIG. 13 is a flow diagram illustrating a further example of the use of a solar driven photo-electrochemical cell (80) according to the present invention in conjunction with a fuel cell (81) for generation of electricity. In this example the photo-electrochemical cell generates ammonia (85) which is passed to a storage tank (87) for later use. When needed the ammonia solution flows into the ammonia fuel cell (81) to generate electric power. The spent solution and the nitrogen produced in the fuel cell is passed back (89) to the generating cell (80) for reuse.

[0117] While this invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification(s). This application is intended to cover any variations, uses or adaptations of the invention following in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth.

[0118] As the present invention may be embodied in several forms without departing from the spirit of the essential characteristics of the invention, it should be understood that the above described embodiments are not to limit the present invention unless otherwise specified, but rather should be construed broadly within the spirit and scope of the invention as defined in the appended claims. The described embodiments are to be considered in all respects as illustrative only and not restrictive.

[0119] Various modifications and equivalent arrangements are intended to be included within the spirit and scope of the invention and appended claims. Therefore, the specific embodiments are to be understood to be illustrative of the many ways in which the principles of the present invention may be practiced. In the following claims, means-plus-function clauses are intended to cover structures as performing the defined function and not only structural equivalents, but also equivalent structures.

[0120] "Comprises/comprising" and "includes/including" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', 'includes', 'including' and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

CLAIMS

1. A photo-electrocatalyst comprising a functionalised semiconductor.
2. A photo-electrocatalyst according to claim 1 wherein the semiconductor that is functionalised is chosen from the group comprising silicon, III-V type semi-conductors, II-VI semiconductors, or oxide semiconductors.
3. A photo-electrocatalyst according to claim 1 wherein the semiconductor that is functionalised is a black silicon nanostructure.
4. A photo-electrocatalyst according to claim 1 wherein the semiconductor is functionalised by one or more types of nanoparticles.
5. A photo-electrocatalyst according to claim 1 wherein the semiconductor is functionalised by one or more thin layer coating(s).
6. The photo-electrocatalyst of claim 1 when used to convert nitrogen to an ammonia product.
7. A method of preparing a photo-electrocatalyst comprising the step of nano-scale deposition of a functionalising species on the surface of the semiconductor.
8. A method of functionalising a semiconductor to provide a photo-electrocatalyst according to claim 1, the method comprising the step of nano-scale deposition of a functionalising species on the surface of the semiconductor.
9. A photo-electrochemical cell the cell comprising
 - (i) a first electrode comprising a functionalised semiconductor photo-electrocatalyst according to claim 1, and
 - (ii) an aqueous or liquid salt electrolyte.

10. A photo-electrochemical cell according to claim 9 wherein the functionalised semiconductor is connected electrically to a second electrode and an oxidation reaction occurs at the second electrode.
11. A photo-electrochemical cell according to claim 9 wherein:
- the first electrode is a cathodic working electrode comprising the functionalised semiconductor photo-electrocatalyst according to claim 1,
 - the first electrode is connected electrically to a counter electrode, and
 - an electrolyte comprising an aqueous solution, or one or more liquid salts in contact with the working electrode.
12. A photo-electrochemical cell according to claim 11 when used for the reduction of dinitrogen to ammonia, the reduction of the dinitrogen occurring at the cathodic working electrode.
13. A method of generating electricity comprising the steps of:
1. photoelectric generation of ammonia using the photo-electrochemical cell of claim 9; and
 2. providing at least part of the ammonia generated in step 1 to an ammonia fuel cell for generation of electricity and nitrogen.
14. A method according to claim 13 wherein at least part least part of the ammonia generated in step 1 is stored in a reservoir for supply to the ammonia fuel cell as needed.
15. A method according to claim 13 wherein at least part of the nitrogen generated in step 2 is recycled into to step 1.

16. A device for electricity generation according to the method of claim 13, the device comprising a photo-electrochemical cell according to claim 9 and an ammonia fuel cell, wherein in use:

1. the photo-electric cell is driven by photoelectric energy from sunlight to generate ammonia; and
2. at least part of the ammonia generated in step 1 is provided to an ammonia fuel cell for generation of electricity and nitrogen.

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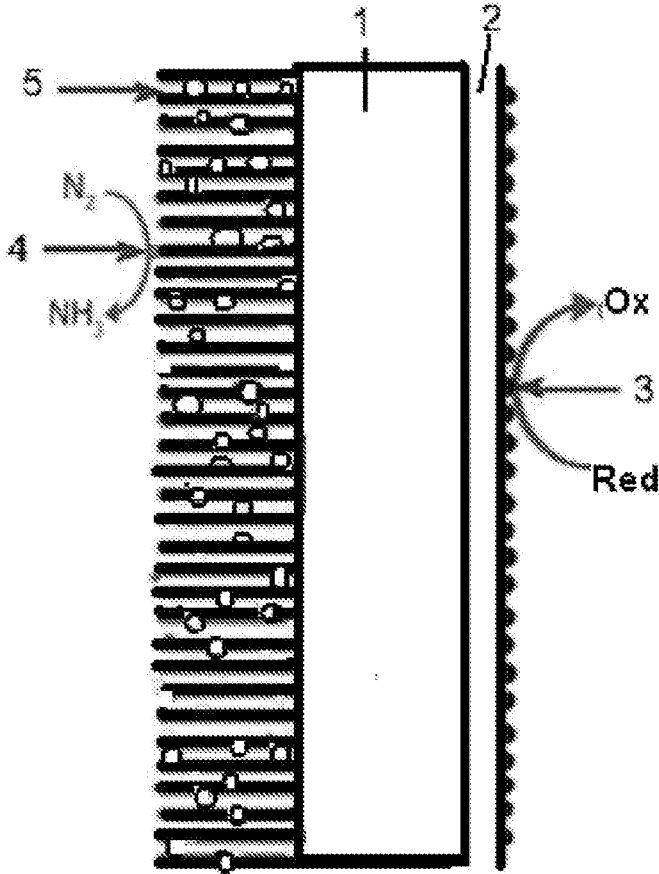


FIG. 1

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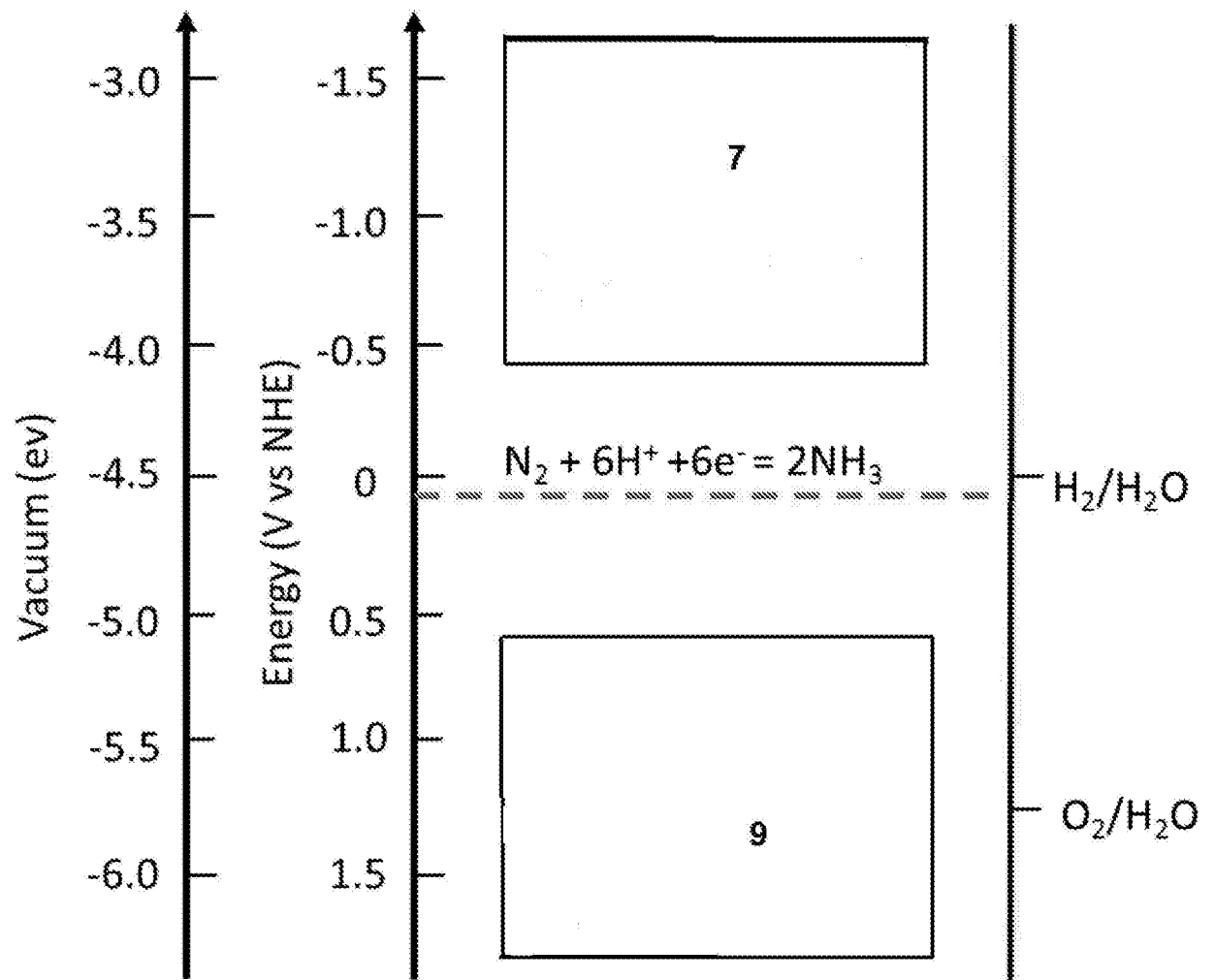
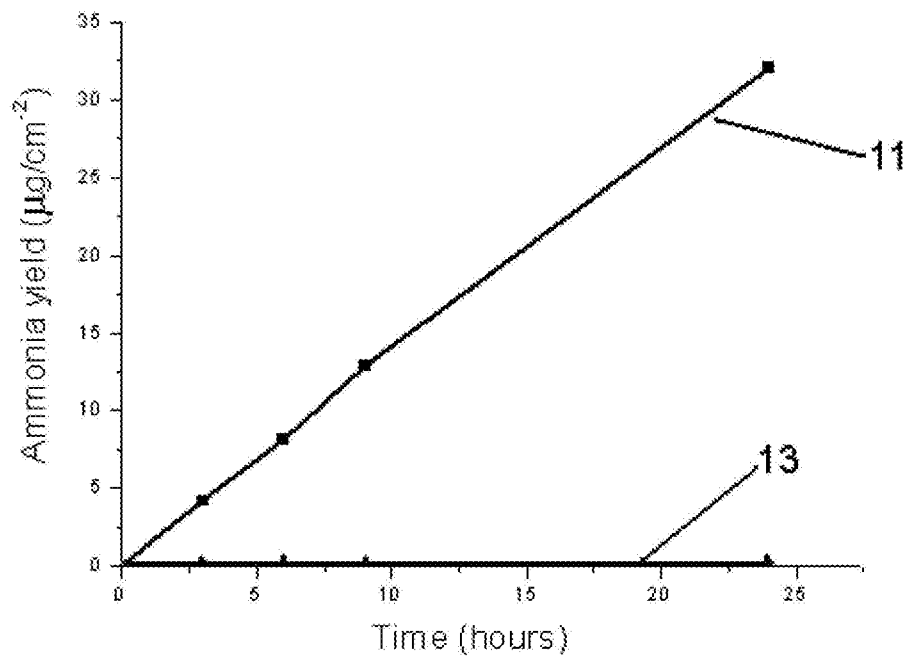


FIG. 2

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**FIG. 3**

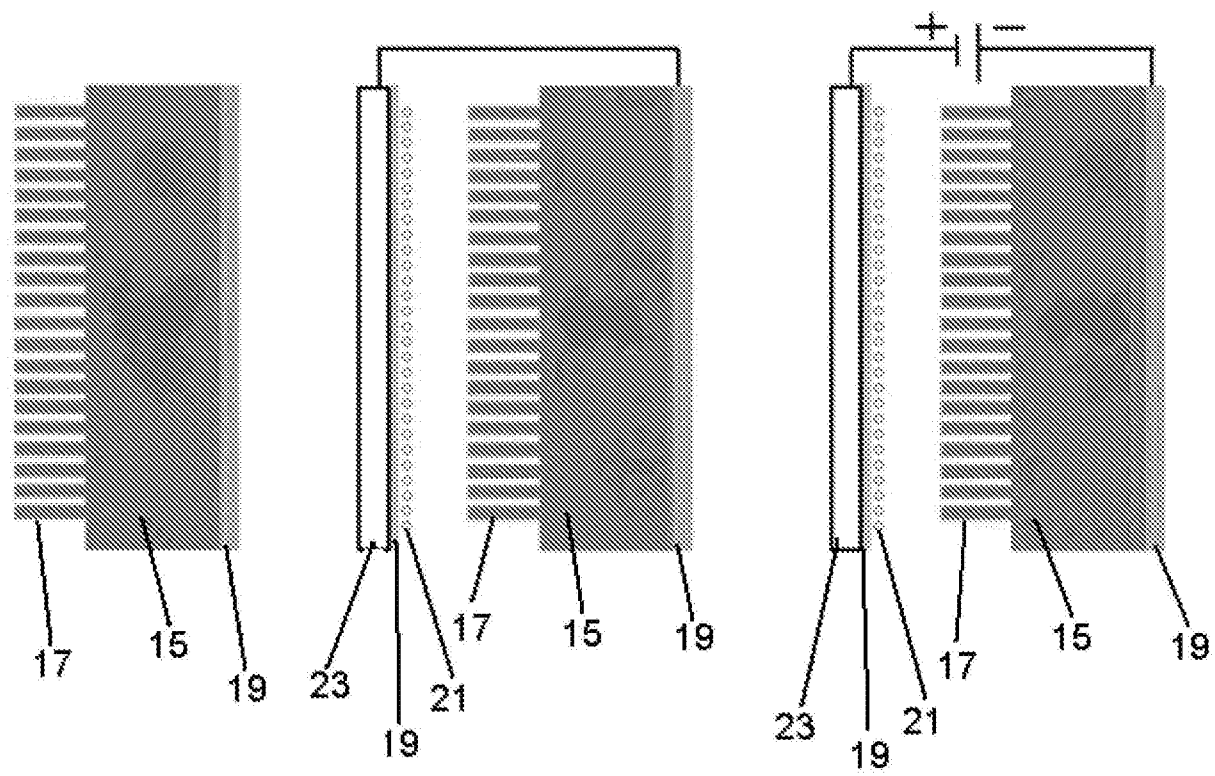


FIG. 4a

FIG. 4b

FIG. 4c

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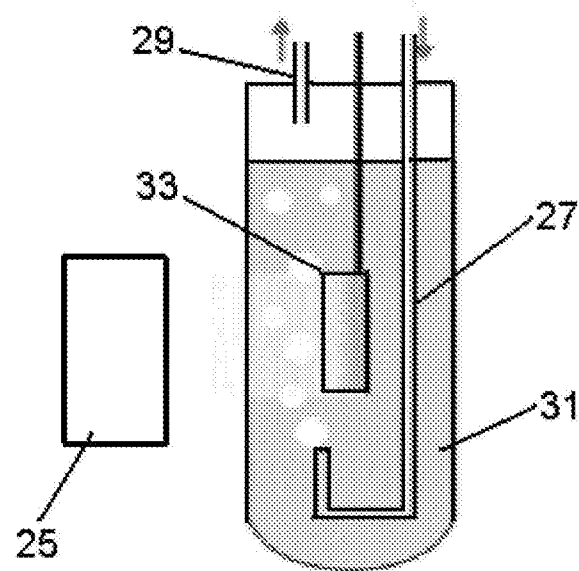


FIG. 5

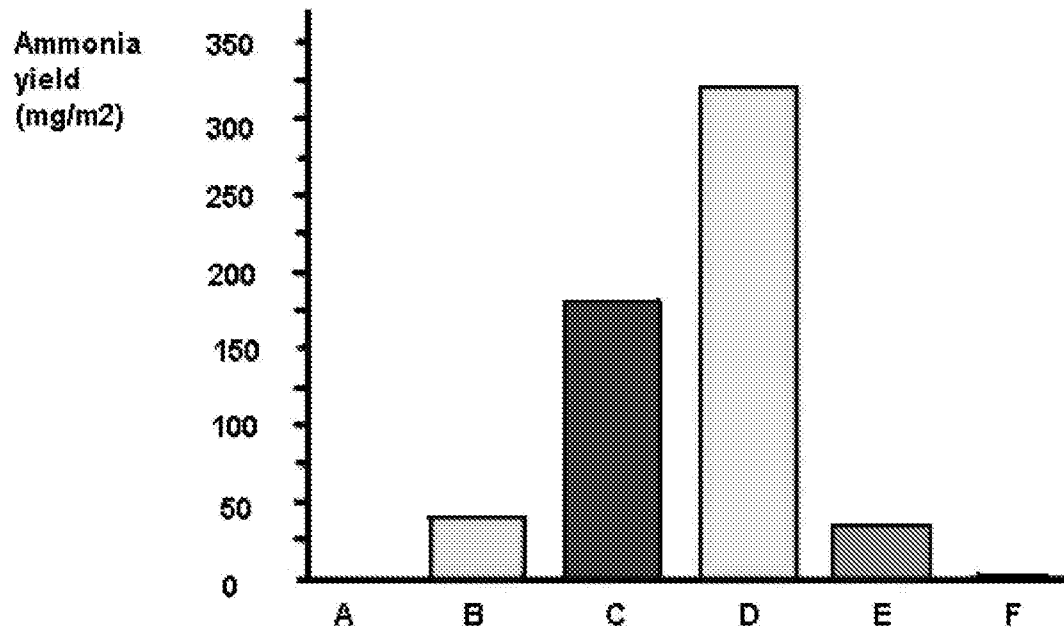


FIG. 6

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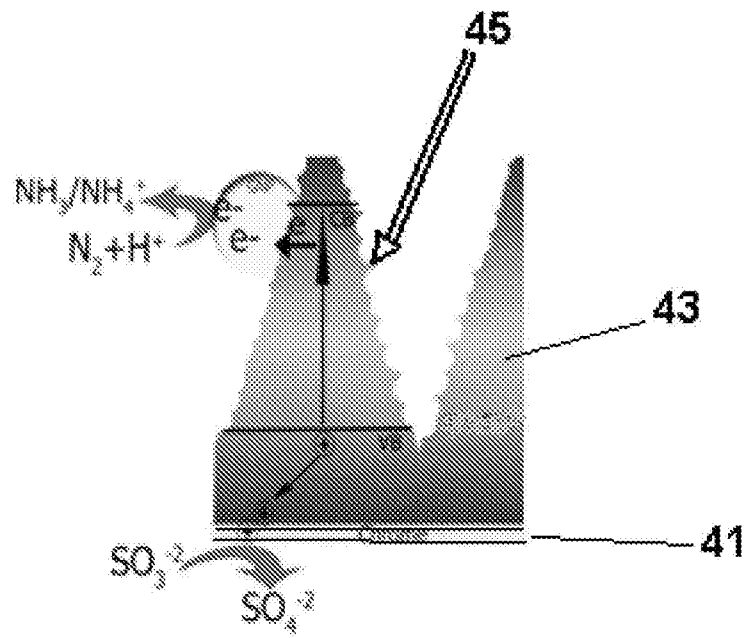


FIG. 7

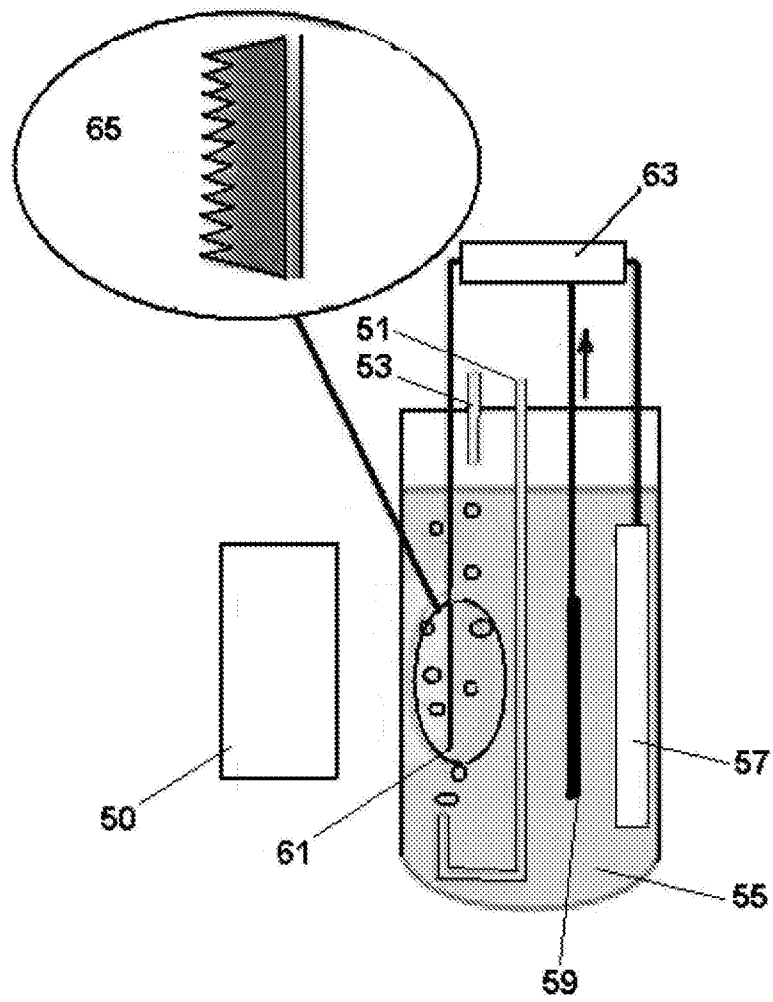


FIG. 8

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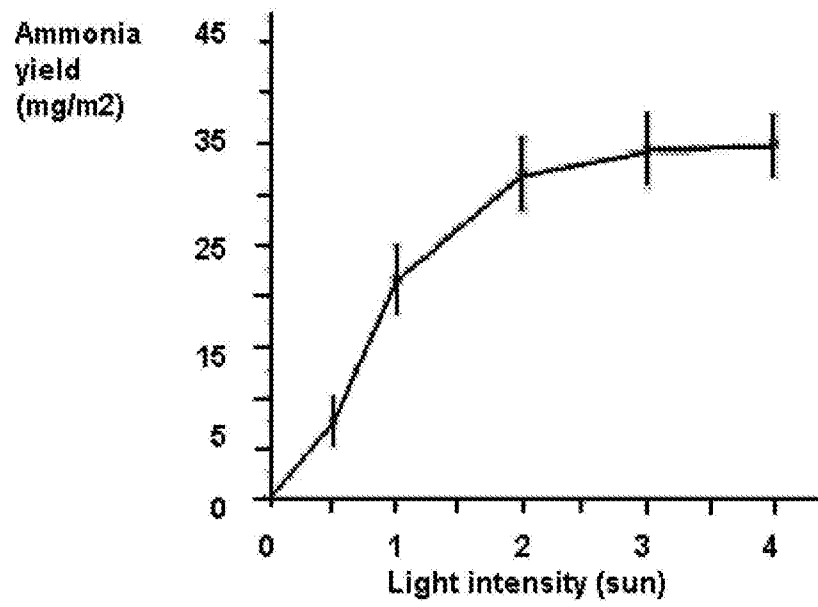


FIG. 9

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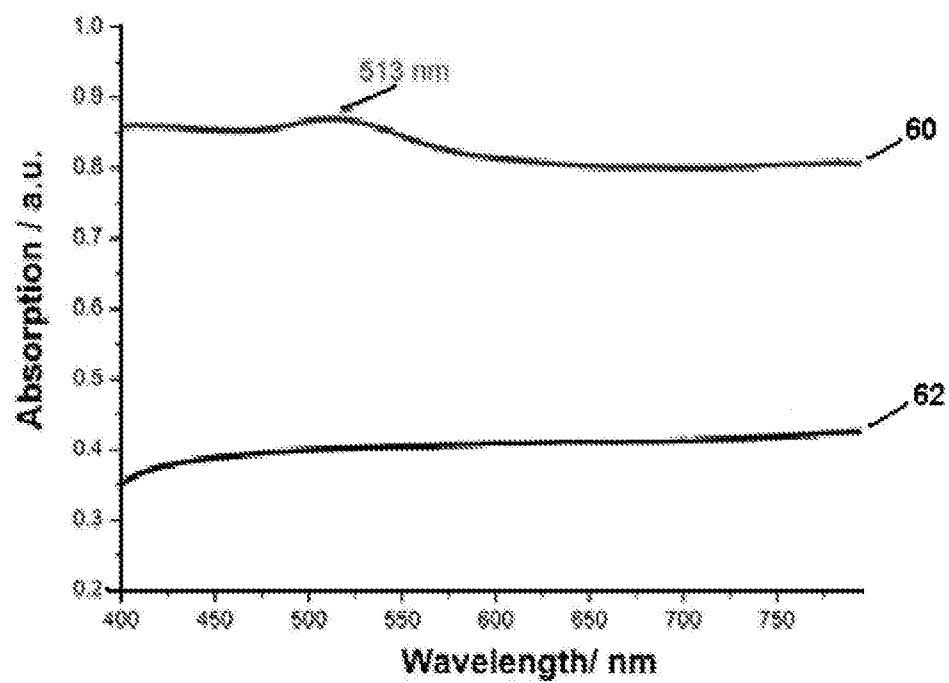


FIG. 10

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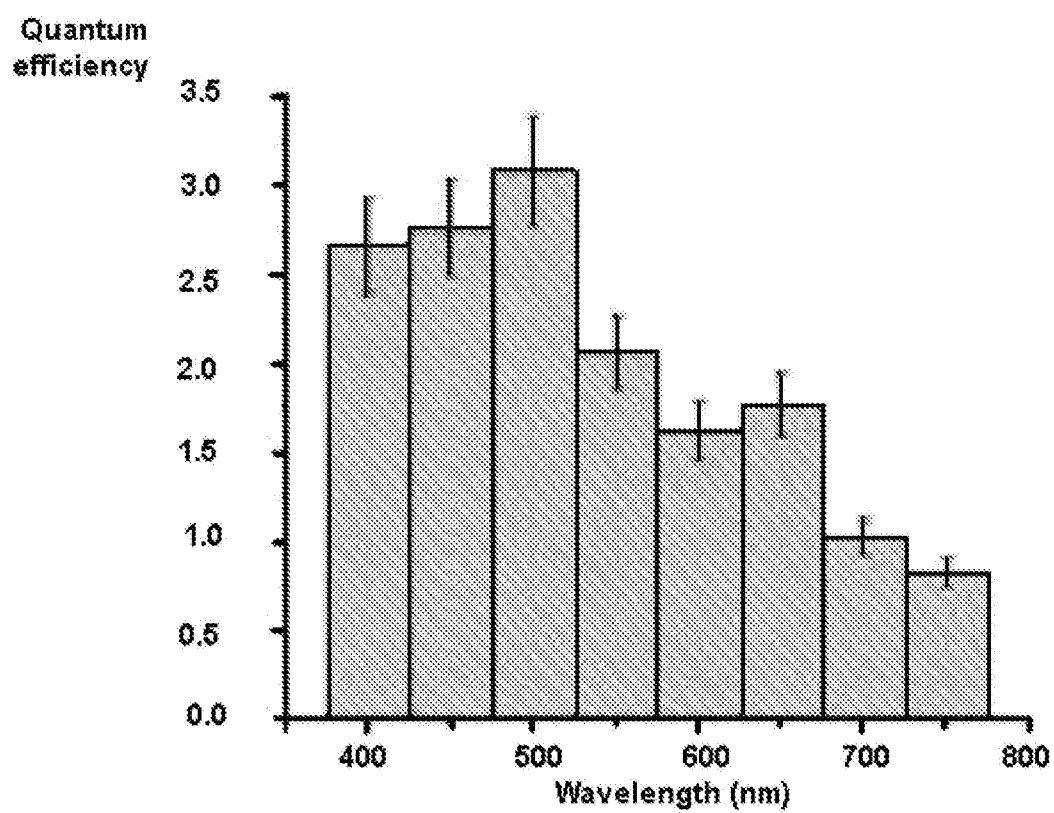


FIG. 11

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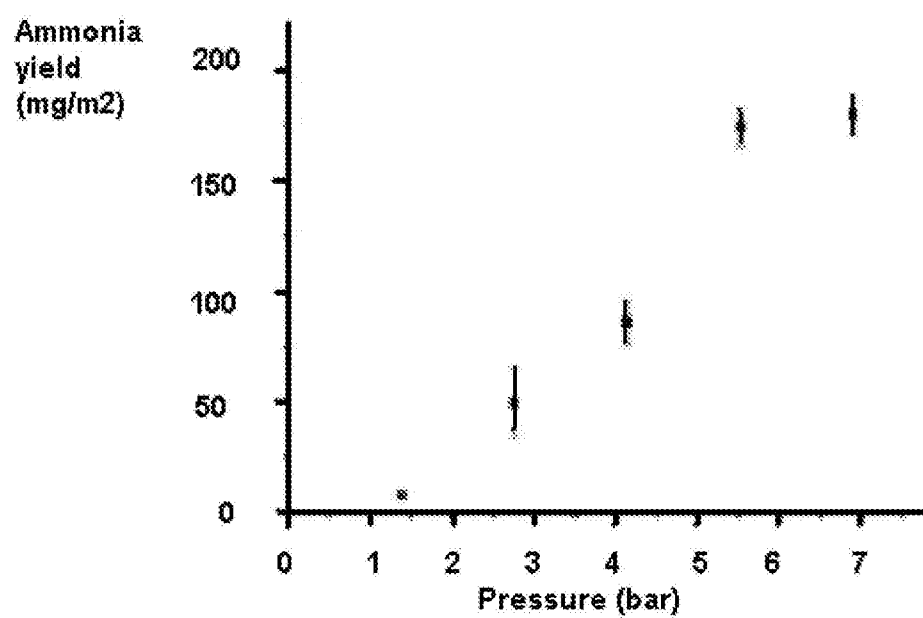


FIG. 12

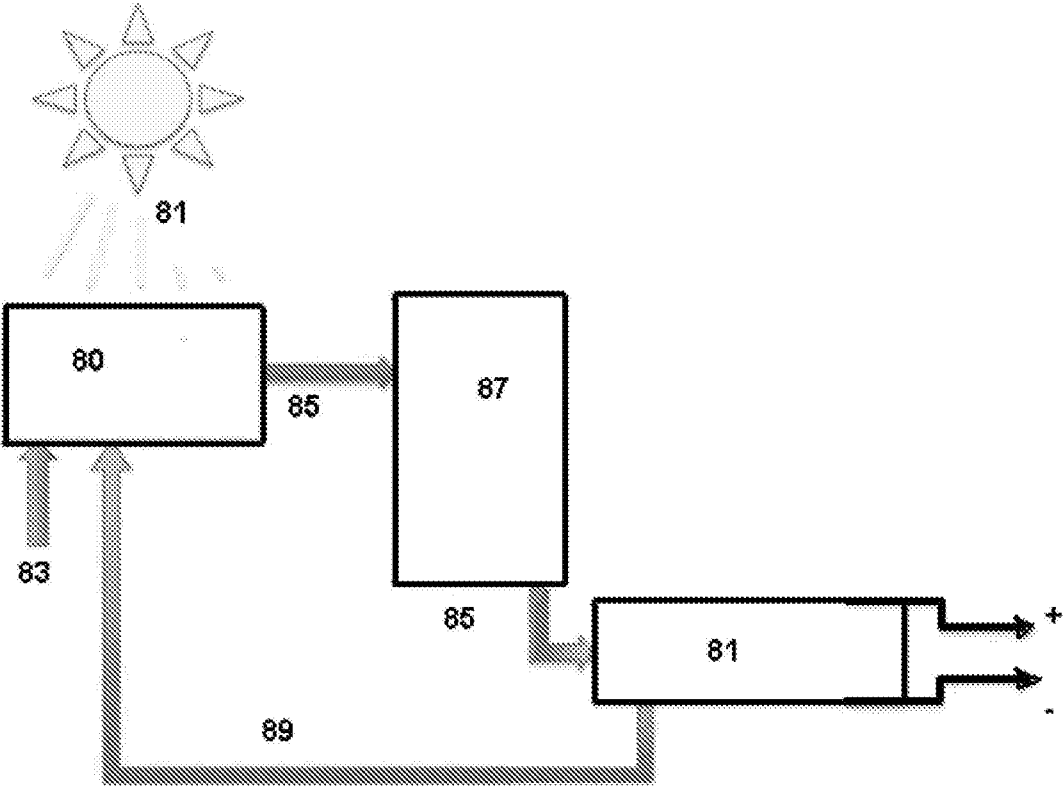


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2016/000151

A. CLASSIFICATION OF SUBJECT MATTER

B01J 21/06 (2006.01) C01C 1/04 (2006.01) B01J 19/12 (2006.01) B01J 35/00 (2006.01) B01J 37/02 (2006.01)
C01B 3/04 (2006.01) C25B 1/00 (2006.01) C25B 5/00 (2006.01) C25B 11/04 (2006.01) H01M 8/0606 (2016.01)
H01M 8/22 (2006.01) H01M 8/18 (2006.01) B82Y 30/00 (2011.01)

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)

EPODOC, WPIAP, TXTE, CAPLUS, INSPEC, REGISTRY, Espacenet, Google Scholar: IPC/CPC marks B01J19/122, B01J21/06, B01J35/004, B01J37/0215, B01J37/0244, C01C1/-, C25B1/003, C25B5/-, C25B11/0421, C25B11/0473, H01M8/06, H01M8/222, B01J2523/-, C01B3/047, C25B11/0478, H01M8/18, H01M2250/10, Y02E60/364, Y02E60/528, Y02E70/20, Y02E70/30, Y02P20/135, Y02P70/56 (in applicable databases); Keywords (photo-electrochemical, photocatalyst, ammonia synthesis, nitrogen reduction, semiconductor, black silicon, nanoparticle coating, plasmon, integrated, electricity generation, fuel cell) and like terms.

CAPLUS, INSPEC, Espacenet: Applicant/Inventor name search.

Applicant(s)/Inventor(s) name searched in internal databases provided by IP Australia.

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

* "A"	Special categories of cited documents: 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 31 May 2016		Date of mailing of the international search report 31 May 2016	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Tien Ngo AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832243	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2016/000151
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0215276 A1 (VERECKEN et al.) 27 August 2009 Abstract, paragraphs [0006]–[0010], [0029], [0037], [0040], [0057], [0068], [0083], Figs. 7 & 8	1–5, 7–11
X	KENNEY, M. J. et al., ‘High-Performance Silicon Photoanodes Passivated with Ultrathin Nickel Films for Water Oxidation’, SCIENCE, 2013, Vol 342, pages 836–840 Abstract, pages 837–838, Fig. 1	1–5, 7–11
X	OH, J. et al., ‘An 18.2%-efficient black-silicon solar cell achieved through control of carrier recombination in nanostructures’, NATURE NANOTECHNOLOGY, 2012, Vol. 7, pages 743–748 Methods on page 747	1–5, 7, 8
X	YUAN, H.-C. et al., ‘Efficient black silicon solar cell with a density-graded nanoporous surface: Optical properties, performance limitations, and design rules’, APPLIED PHYSICS LETTERS, 2009, Vol. 95, pages 123501-1–123501-3 Page 123501-1, right column	1–5, 7, 8
X	OSHIKIRI, T. et al., ‘Plasmon-Induced Ammonia Synthesis through Nitrogen Photofixation with Visible Light Irradiation’, Angew. Chem. Int. Ed. 2014, Vol. 53, pages 9802–9805 Abstract, Figure 1, pages 9802–9803, Experimental Section	1, 2, 4–16
A	US 2012/0068471 A1 (ROBERTSON) 22 March 2012 Abstract, Fig. 5, [0131]–[0132], [0197]–[0221]	1–16
A	WO 2012/037571 A2 (ROBERTSON) 22 March 2012 Abstract, Fig. 1, page 19 lines 1–30, page 28 pages 4–11	1–16
P,X	ALI, M. et al., ‘Nanostructured photoelectrochemical solar cell for nitrogen reduction using plasmon-enhanced black silicon’, NATURE COMMUNICATIONS, 2016, Vol. 7, pages 1–5, DOI: 10.1038/ncomms11335 [published 20 April 2016] Whole document	1–16
Form PCT/ISA/210 (fifth sheet) (July 2009)		

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2016/000151	
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
US 2009/0215276 A1	27 August 2009	US 2009215276 A1	27 Aug 2009
		US 8148188 B2	03 Apr 2012
US 2012/0068471 A1	22 March 2012	US 2012068471 A1	22 Mar 2012
		EP 2272110 A1	12 Jan 2011
		US 2009257940 A1	15 Oct 2009
		US 2013252120 A1	26 Sep 2013
		US 2016006066 A1	07 Jan 2016
		WO 2009117118 A1	24 Sep 2009
		WO 2012037571 A2	22 Mar 2012
WO 2012/037571 A2	22 March 2012	WO 2012037571 A2	22 Mar 2012
		EP 2272110 A1	12 Jan 2011
		US 2009257940 A1	15 Oct 2009
		US 2012068471 A1	22 Mar 2012
		US 2013252120 A1	26 Sep 2013
		US 2016006066 A1	07 Jan 2016
		WO 2009117118 A1	24 Sep 2009
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			