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(71) Applicant: **THE ROYAL INSTITUTION FOR THE
 ADVANCEMENT OF LEARNING/MCGILL UNI-
 VERSITY** [CA/CA]; 845 Sherbrooke Street West,
 Montreal, Québec H3A 0G4 (CA).

(72) Inventors: **LI, Chao-jun**; 3960 rue de Leningrad, Bross-
 ard, Québec J4Y 3J6 (CA). **MI, Zetian**; 368 rue des
 Roselins, Verdun, Québec H3E 1Y6 (CA). **LI, Lu**; 3484
 Hutchison, Montreal, Québec H2X 2G8 (CA).

(74) Agent: **NORTON ROSE FULBRIGHT CANADA
 LLP/S.E.N.C.R.L., S.R.L.**; Suite 2500, 1 Place Ville-
 Marie, Montréal, Québec H3B 1R1 (CA).

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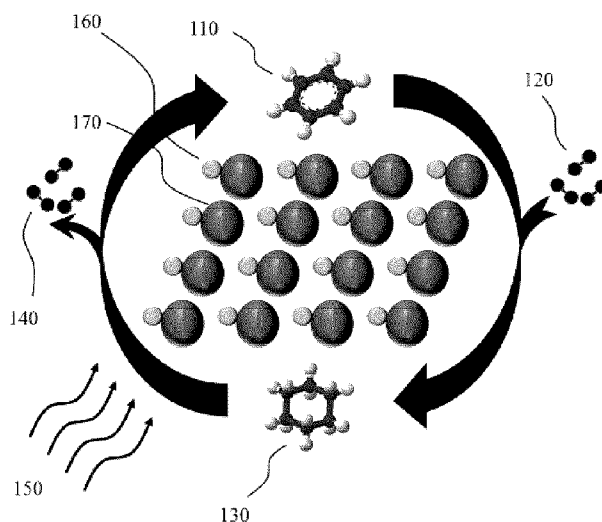


Fig. 1A

(57) Abstract: The present disclosure relates to a reversible hydrogen transfer process and storage system using visible light to photocatalytically generate hydrogen from compounds comprising saturated or partially saturated carbocyclic residue and catalytically hydrogenate compounds comprising at least one carbocyclic aromatic residue.

SOLAR ENERGY HARVESTING AND REVERSIBLE HYDROGEN STORAGE
METHODS AND SYSTEMS

FIELD OF THE DISCLOSURE

[001] The present disclosure relates to a reversible hydrogen transfer process and storage system using visible light to photocatalytically generate hydrogen from compounds comprising saturated or partially saturated carbocyclic residue and catalytically hydrogenate compounds comprising at least one carbocyclic aromatic residue.

BACKGROUND OF THE DISCLOSURE

[002] Since the initial discovery of water photolysis on titanium dioxide (TiO_2 or titania) in the early 1970s the utilization of solar energy to either produce renewable fuels or trigger valuable transformations has become one of the most sustainable and promising strategies to solve the growing global concerns on energy supply and environmental issues, which are among the biggest challenges facing our society today. Hydrogen (H_2) is an attractive energy source, however, the problem of hydrogen storage and transportation is a major obstacle to employing hydrogen as a universal fuel since hydrogen has a very low volumetric density at ambient conditions. Storage and transportation of hydrogen currently requires using compressed hydrogen gas (30 – 70MPa) or liquid hydrogen ($-253^\circ C$) in tanks.

[003] Therefore, a technical problem resides in the design of a process and/ or system that can both generate hydrogen or “store” hydrogen under practical conditions.

[004] Other aspects and features of the present disclosure will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the disclosure in conjunction with the accompanying figures.

SUMMARY OF THE DISCLOSURE

[005] In one aspect, there is provided a process comprising at least one step of:

- a photo-driven catalyzed hydrogen (H_2) generation by dehydrogenation of a compound comprising at least one saturated or partially saturated carbocyclic residue; wherein said

dehydrogenation is providing a compound comprising at least one carbocyclic aromatic residue;
and

- a catalyzed hydrogenation of a compound comprising at least one carbocyclic aromatic residue,
wherein said hydrogenation is providing a compound comprising at least one saturated or
partially saturated carbocyclic residue;

wherein said catalyzed dehydrogenation and hydrogenation are conducted in the presence of a
noble metal (metal) supported on semiconductor nanoparticles (NP) illustrated by the formula:

metal@NP

and wherein said photo-driven catalyzed dehydrogenation is conducted in the presence of visible
light.

[006] In one aspect, there is provided a process comprising a photo-driven catalyzed hydrogen
(H₂) generation by dehydrogenation of a compound comprising at least one saturated or partially
saturated carbocyclic residue; wherein said dehydrogenation is providing a compound
comprising at least one carbocyclic aromatic residue;

wherein said catalyzed dehydrogenation is conducted in the presence of a noble metal (metal)
supported on semiconductor nanoparticles (NP) illustrated by the formula:

metal@NP

and wherein said photo-driven catalyzed dehydrogenation is conducted in the presence of visible
light.

[007] In one aspect, there is provided a process comprising a catalyzed hydrogenation of a
compound comprising at least one carbocyclic aromatic residue, wherein said hydrogenation is
providing a compound comprising at least one saturated or partially saturated carbocyclic
residue;

wherein said catalyzed hydrogenation is conducted in the presence of a noble metal (metal)
supported on semiconductor nanoparticles (NP) illustrated by the formula:

metal@NP.

[008] In one aspect, there is provided a process for preparing a noble metal (metal) supported
on semiconductor nanoparticles (NP) illustrated by the formula:

metal@NP

said process comprising chemically reducing a noble metal precursors of said noble metal, in the
presence of semiconductor nanoparticles (NPs) in aqueous solution.

[009] In one aspect, there is provided a noble metal (metal) supported on semiconductor nanoparticles (NP) illustrated by the formula:

metal@NP

wherein said metal of said metal@NP is gold, silver, platinum, ruthenium, rhodium, palladium, osmium, iridium and combinations thereof.

[0010] In accordance with an aspect of the disclosure there is provided a method comprising:
providing a device comprising:

a plurality of first nanostructures having a first predetermined geometry and formed from a first predetermined material composition, each first nanostructure having disposed upon its exterior surface or surfaces a plurality of second nanostructures having a second predetermined geometry and formed from a second predetermined material composition;
and

providing within the device a predetermined fluid comprising at least a predetermined hydrocarbon; and
at least one of:

storing hydrogen within the predetermined fluid under first predetermined conditions (such as in an absence of visible light) such that the hydrogen is absorbed through a hydrogenation process with respect to the predetermined hydrocarbon; and

releasing hydrogen from the predetermined fluid under second predetermined conditions (such as in the presence of visible light) such that the hydrogen is released through a dehydrogenation process with respect to the predetermined hydrocarbon (such as an aromatic hydrocarbon).

[0011] In accordance with an embodiment of the disclosure there is provided a device comprising:

a plurality of first nanostructures having a first predetermined geometry and formed from a first predetermined material composition, each first nanostructure having disposed upon its exterior surface or surfaces a plurality of second nanostructures having a second predetermined geometry and formed from a second predetermined material composition;
and

providing within the device a predetermined fluid comprising at least a predetermined hydrocarbon (such as an aromatic hydrocarbon); wherein

the device under first predetermined conditions (such as in the absence of visible light) stores hydrogen within the predetermined fluid such that the hydrogen is absorbed through a hydrogenation process with respect to the predetermined hydrocarbon; and the device under second predetermined conditions releases (such as in the presence of visible light) hydrogen from the predetermined fluid such that the hydrogen is released through a dehydrogenation process with respect to the predetermined hydrocarbon.

[0012] Other aspects and features of the present disclosure will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the disclosure in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Embodiments of the present disclosure will now be described, by way of example only, with reference to the attached Figures, wherein:

[0014] Fig. 1A depicts schematically a catalyzed hydrogen addition and release to an organic cyclic hydrocarbon according to an embodiment of the disclosure;

[0015] Fig. 1B depicts the efficiencies of different noble metal catalyst activated nanoparticles for catalytic dehydrogenation of cyclohexane to benzene;

[0016] Fig. 2A depicts a low resolution TEM image showing Pt species dispersed on the surface of the TiO_2 ;

[0017] Fig. 2B depicts a high resolution TEM image showing Pt species dispersed on the surface of the TiO_2 ;

[0018] Fig. 2C depicts the Pt size distribution derived from TEM measurements;

[0019] Fig. 2D depicts powder X-ray diffraction (XRD) measurements of an embodiment of the disclosure;

[0020] Fig. 3A depicts the visible light driven dehydrogenation reactions of cyclohexane providing hydrogen and benzene using different embodiments of the disclosure;

[0021] Fig. 3B depicts the X-ray photoelectron spectroscopy (XPS) spectra for different embodiments of the disclosure;

[0022] Fig. 3C is a schematic representation of the possible mechanism involved in a process of the present disclosure;

[0023] Fig. 3D depicts the wavelength dependence of photocatalytic activity of embodiments of the disclosure;

[0024] Fig. 4 depicts a photocatalytic dehydrogenation mechanism for the dehydrogenation reactions of cyclohexane according to an embodiment of the disclosure; and

[0025] Fig. 5A depicts kinetic studies of hydrogen addition for certain organic cyclic hydrocarbons according to an embodiment of the disclosure;

[0026] Fig. 5B depicts kinetic studies of hydrogen release for certain organic cyclic hydrocarbons according to an embodiment of the disclosure; and

[0027] Fig. 5C depicts kinetic isotope effects in the dehydrogenation and hydrogenation processes.

DETAILED DESCRIPTION

[0028] The ensuing description provides exemplary embodiment(s) only, and is not intended to limit the scope, applicability or configuration of the disclosure. Rather, the ensuing description of the exemplary embodiment(s) will provide those skilled in the art with an enabling description for implementing an exemplary embodiment. It is being understood that various changes may be made in the function and arrangement of elements.

[0029] As used herein, the visible light is comprising (or consisting of) a wavelength greater than about 400nm or greater than about 420nm. Alternatively said visible light is comprising (or consisting of) a wavelength of from about 380 to about 800 nm, preferably about 420 to 700nm, still more preferably about 420 to 600nm.

[0030] As used herein, the aromatic residue (of “compound comprising at least one carbocyclic aromatic residue”) refers generally to a conjugated system comprising alternating single and double bonds in a ring allowing for the electrons in the molecule's pi system to be delocalized around the ring and wherein the number of said pi delocalized electrons meets the equation $4n + 2$, where n is an integer (such as 1, 2, 3,...).

[0031] In one embodiment, said carbocyclic aromatic residue is comprising a monocarbocyclic or polycarbocyclic aromatic ring, preferably a monocarbocyclic aromatic ring.

[0032] In one embodiment, the aromatic residue is comprising a benzo-fused residue such as benzofuran, isobenzofuran, indole, isoindole, indazole, benzimidazole, benzoxazole, benzisoxazole ect.

[0033] In one embodiment, said compound comprising at least one carbocyclic aromatic residue is comprising benzene, toluene, o, m and p-xylene, ethylbenzene, mesitylene, cumene, cymene or a mixture thereof.

[0034] In one embodiment, said “compound comprising at least one saturated or partially saturated carbocyclic residue” is in a substantially liquid state between about 5 to about 80°C, or from about 10 to 70 °C or from about 20 to about 50 °C or from about 20 to about 25 °C.

[0035] In one embodiment, said “compound comprising at least one carbocyclic aromatic residue” is in a substantially liquid state between about 5 to about 80 °C, or from about 10 to 70 °C or from about 20 to about 50 °C or from about 20 to about 25 °C.

[0036] As used herein, the “compound comprising at least one saturated or partially saturated carbocyclic residue” are compounds corresponding to those obtained by saturating or partially saturating a “compound comprising at least one carbocyclic aromatic residue” as defined herein. Examples of these include cyclohexane/ cyclohexene/ cyclohexadiene (from benzene), methylcyclohexane/ methylcyclohexene/ methylcyclohexadiene (from toluene), 1,2-, 1,3- and 1,4-dimethylcyclohexane/ dimethylcyclohexene/ dimethylcyclohexadiene (from o-, m- and p-xylene). In one embodiment, said “compound comprising at least one saturated or partially saturated carbocyclic residue” is saturated, and preferably cyclohexane, methylcyclohexane, dimethylcyclohexane, or a mixture thereof. More preferably the compound is cyclohexane.

[0037] In one embodiment, said metal of said metal@NP is gold, silver, platinum, ruthenium, rhodium, palladium, osmium, iridium and combinations thereof.

[0038] In one embodiment, said metal of said metal@NP is gold, platinum, ruthenium, palladium, iridium and combinations thereof.

[0039] In one embodiment, said NP is comprising (or consisting of, or consisting essentially of) TiO_2 , GaN, Al_2O_3 or a combination thereof. In one embodiment, said NP is comprising (or consisting of, or consisting essentially of) TiO_2 .

[0040] In one embodiment, the wt% amount of said noble metal to said NP is from about 0.1 to 10%, or 0.1 to 5% or about 5%.

[0041] In one embodiment, said catalyzed dehydrogenation is conducted at a temperature lower than the boiling point and higher than the melting point of said “compound comprising at least one saturated or partially saturated carbocyclic residue”. In one embodiment, the temperature is from about 5 to about 80 °C, or from about 10 to 70 °C or from about 20 to about 50 °C or from about 20 to about 25 °C.

[0042] In one embodiment, said catalyzed hydrogenation is conducted at a temperature lower than the boiling point and higher than the melting point of said “compound comprising at least one carbocyclic aromatic residue”. In one embodiment, the temperature is from about 5 to about 80 °C, or from about 10 to 70 °C or from about 20 to about 50 °C or from about 20 to about 25 °C.

[0043] In one embodiment, said catalyzed hydrogenation is conducted in a reactor, wherein at least a portion of the reactor wall is a quartz wall. In one embodiment, said catalyzed hydrogenation is conducted in a photocatalytic glass reactors. In one embodiment, said catalyzed hydrogenation is conducted in a quartz reactor.

[0044] In one embodiment, said hydrogenation is conducted substantially in absence of visible light.

[0045] In one embodiment, said chemical reduction of said noble metal precursors is comprising a borohydride mediated reduction using a borohydride reagent. In one embodiment, said borohydride reagent is NaBH_4 .

[0046] In one embodiment, said noble metal precursors and said nanoparticles (NPs) are contacted together in absence of light for a period of time before chemically reducing said precursor.

[0047] In one embodiment, said chemical reduction of said noble metal precursors comprising said borohydride reagent is conducted at an alkaline pH.

[0048] In one embodiment, said chemical reduction of said noble metal precursors comprising said borohydride reagent is conducted in the presence of an inorganic hydroxide-containing base, such as LiOH, NaOH, KOH etc.

[0049] In one embodiment, said NP of said metal@NP is comprising TiO_2 , GaN, Al_2O_3 or a combination thereof. In one embodiment, said NP is comprising (or consisting of, or consisting essentially of) TiO_2 .

[0050] In one embodiment, the wt% amount of said noble metal to said NP is from about 0.1 to 5% or about 5%.

[0051] A “catalyst” as used herein refers to, but is not limited to, a substance that starts or speeds up a chemical reaction while undergoing no permanent change itself although the catalyst may react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process regenerating the catalyst. The chemical nature of catalysts is as diverse as catalysis itself although, for example, proton acids may be employed in many reactions involving water, including hydrolysis and its reverse. Other catalysts may include multifunctional solids, e.g. zeolites, alumina, higher-order oxides, graphitic carbon, nanoparticles, nanodots, and the facets of bulk materials; transition metals to catalyze reduction-oxidation (redox) reactions such as oxidation, hydrogenation; “late transition metals”, such as palladium, platinum, gold, ruthenium, rhodium, or iridium for example; and pre-catalysts which convert to catalysts in the reaction.

[0052] A “semiconductor” or “compound semiconductor” as used herein refers to, but is not limited to, a material having an electrical conductivity value falling between that of a conductor and an insulator wherein the material may be an elemental materials or a compound material. Semiconductors may include, but are not limited to:

Elements, such as certain group IV and group VI elements, e.g. silicon (Si) and germanium (Ge), and binary group IV alloys, e.g. silicon germanium (SiGe) and silicon carbide (SiC);
III-V semiconductors, such as those between aluminum (Al), gallium (Ga), and indium (In) with nitrogen (N), phosphorous (P), arsenic (As) and tin (Sb), including for example GaN, GaP, GaAs, InP, InAs, AlN and AlAs;

II-VI semiconductors, such as cadmium selenide (CdSe), zinc oxide (ZnO), and zinc selenide (ZnS), for example;

I-VII semiconductors, IV-VI semiconductors, IV-VI semiconductors, V-VI semiconductors, II-V semiconductors, I-III-VI₂ semiconductors;

Oxides, layered semiconductors, magnetic semiconductors;

Organic semiconductors, which may include single molecules oligomers, organic polymers, and polycyclic aromatic hydrocarbons, for example; and,

Charge-transfer complexes, either organic or inorganic.

[0053] A “metal” as used herein refers to, but is not limited to, a material (an element, compound, or alloy) that have good electrical and thermal conductivity as a result of readily losing outer shell electrons which generally provides a free flowing electron cloud. This may include, but not be limited to, gold, chromium, aluminum, silver, platinum, nickel, copper, rhodium, palladium, tungsten, palladium, and combinations of such materials.

[0054] A “nanostructure” or “nanoparticle” as used herein refers to, but is not limited to, a structure having one or more dimensions at the nanometer level, which is typically between the lower and upper dimensions of 0.1nm and 100nm. Such structures, may include, nanotextured surfaces having one dimension on the nanoscale, nanotubes having two dimensions on the nanoscale, and nanoparticles having three dimensions on the nanoscale. Nanotextured surfaces may include, but not be limited, nano-grooves, nano-channels, and nano-ridges. Nanotubes may include structures having geometries resembling, but not be limited to, tubes, solid rods, whiskers, and rhomboids with square, rectangular, circular, elliptical, and polygonal cross-sections perpendicular to an axis of the nanotube. Nanoparticles may include structures having geometries representing, but not limited to, spheres, pyramids, and cubes. The cross-sectional geometry of nanotubes and nanoparticles may not be constant such that a nanostructure may taper in one or two dimensions.

[0055] A “nanowire” as used herein refers to, but is not limited to, a structure within the category of nanotubes by virtue of being nanoscale on two dimensions and solid cross-sectionally formed from one or more materials.

[0056] In order to achieve economical and high-density hydrogen storage it would be beneficial, preferable even, to provide a process, a noble metal supported catalyst or system providing a direct reversible hydrogen storage system. In this regard, the inventors have considered that a

promising strategy is to add hydrogen to unsaturated aromatic hydrocarbons that contain only carbon and hydrogen atoms. For instance, benzene, the simplest aromatic, can “absorb” six hydrogen atoms to form cyclohexane through a metal catalyzed hydrogenation reaction. As benzene is one of the most widely used industrial petrochemicals, with 2012 production of approximately 43 million tons and expected to rise to 51 million tons in 2017, the bulk market price of benzene at $< \$1/\text{kg}$ is highly competitive with other hydrogen storage materials. Furthermore, both benzene and the cyclohexane produced as the hydrogen carrier, see Fig. 1A, are very stable and readily available for transportation using current liquid fossil fuel distribution infrastructure. However, this potential hydrogen storage system suffers from a severe limitation that the dehydrogenation of cyclohexane is highly endothermic. Owing to the large positive Gibbs free energy, an elevated temperature, $> 300^\circ\text{C}$, has been required for hydrogen release, which is not suitable for practical commercial and consumer applications and also inevitably results in the formation of coke.

[0057] However, the inventors have demonstrated that photoenergy is effective to overcome the intrinsic thermodynamic constraint of activating the $C-H$ bonds of cyclic alkanes and provide easy stable hydrogen release under ambient conditions. Accordingly, referring to Figure 1A there is depicted a reversible hydrogen storage/release cycle based on the metal-catalyzed hydrogenation and photoinduced dehydrogenation of organic cyclic hydrocarbons reactions at room temperature.

[0058] Referring to Fig. 1A benzene 110 is catalyzed in the presence of hydrogen 120 to form cyclohexane 130 at room temperature. This catalysis employing transition metal catalysts 160, for example, bound to titania nanoparticles 170, for example. Subsequently, under visible light irradiation 150 thereby releasing hydrogen 140 and yielding the original benzene 110. Importantly, the cleavage of six covalent C-H bonds of cyclohexane to form hydrogen and benzene stores comparable amount of energy as that of the water splitting reaction given in Equations (1) and (2), indicating a new approach to the concept of solar energy harvesting.



[0059] In order to develop an efficient catalyst for the hydrogen release process under visible light, the inventors synthesized a series of noble metal, e.g. gold (Au), platinum (Pt), palladium (Pd), iridium (Ir), and rubidium (Ru) modified titania (TiO_2) nanoparticles (NPs). They were

formed by chemically reducing the corresponding metal precursors in a sodium borohydride (NaBH_4) aqueous solution in the presence of commercial titania particles. These had a particle size of approximately 25 nm with Brunauer-Emmett-Teller (BET) surface area of approximately $55.2 \text{ m}^2 \text{ g}^{-1}$ and an anatase - rutile phase ratio of approximately 4/1 at room temperature.

Materials and Methods

[0060] Degussa P25 TiO_2 (particle size, ~25 nm; Brunauer-Emmett-Teller (BET) surface area, $55.2 \text{ m}^2 \text{ g}^{-1}$; anatase/rutile phase ratio, 4/1) were purchased from Sigma-Aldrich and used without further treatment. All commercially available compounds were purchased from Sigma-Aldrich, Strem and Across Company, and used without further purification.

Chemical Reduction

[0061] The metallic Au^0 , Pt^0 , Pd^0 , Ir^0 and Ru0-modified TiO_2 (or GaN, Al_2O_3) catalysts were obtained through chemically reducing the corresponding metal precursors in a NaBH_4 aqueous solution. In a typical synthesis, 0.2 g of TiO_2 powders was added into 50 mL of aqueous solution (1-10 wt % metal) of H_2AuCl_6 , H_2PtCl_6 , PdCl_2 , H_2IrCl_6 and RuCl_3 , respectively, followed by stirring under darkness overnight. Then, 5 mL of NaBH_4 (0.02-0.2 M) and NaOH (0.02-0.2 M) solution was slowly added into the gel mixture under vigorous stirring at 20°C . After one hour reduction, the materials were washed in deionized water and dried in an oven at 110°C for 5 hrs.

Photo-Reduction

[0062] A certain amount of chloroplatinic acid (H_2PtCl_6 , Sigma Aldrich), 0.2 g of TiO_2 , 12 mL of CH_3OH , and 60 mL of water were added in a 460 mL Pyrex chamber (Kimble Chase) with quartz lid. The chamber was evacuated for 10 min in order to remove the dissolved O_2 , and subsequently irradiated using 300 W xenon lamp (PerkinElmer, PE300BF) for 30 min under vigorous stirring for photoassisted deposition of metallic Pt species. After reduction, the materials were washed in deionized water and dried in an oven at 110°C for 5 hrs.

Hydrogen Release and Storage

[0063] Photo-Driven Alkane Dehydrogenation Reaction (Hydrogen Release) 10 mg of the metal-modified substrate was spread evenly on the bottom of a closed quartz reactor and then evacuated at 250°C for 1 h to remove the water and other molecules adsorbed on the surface of the sample. Afterwards, the reactor was cooled slowly to room temperature under vacuum ($P < 1$

Pa), followed by the reaction with 100 μ mol of pure cyclohexane (or other cyclic alkanes) under visible irradiation from a 300 W xenon lamp.

Aromatic Hydrogenation Reaction (Hydrogen Storage)

[0064] 10 mg of the metal-modified substrate was spread evenly on the bottom of a closed quartz reactor and then evacuated at 250 °C for 1 h to remove the water and other molecules adsorbed on the surface of the sample. Afterwards, the reactor was cooled slowly to room temperature (or 50 °C) under vacuum ($P < 1$ Pa), followed by the introduction of 300 μ mol of hydrogen gas and 100 μ mol of benzene (or other aromatics) under darkness.

General Characterization

[0065] The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced Diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). High resolution bright field transmission electron microscope (TEM) images were obtained using FEI Tecnai G2 F20 S/TEM at accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured from the adsorption of N₂ at 77 K by using a Micromeritics ASAP 2020M system. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromated X-ray source (Al K $\cdot$ h $\cdot$ = 1486.6 eV). The energy scale of the spectrometer was calibrated using Au4f7/2, Cu2p3/2, and Ag3d5/2 peak positions. The standard deviation for the binding energy (BE) values was 0.1 eV.

Carbon Balance

[0066] The calculation of the carbon balance during the photocatalytic cyclohexane dehydrogenation reaction was carefully performed based on the ratio of carbon output (methane, benzene, CO₂, recovered cyclohexane) to carbon input (cyclohexane), see equation ES1:

$$\text{Carbon balance} = \frac{\text{Moles of products in terms of carbon}}{\text{Moles of converted cyclohexane in terms of carbon}} \times 100 \% \text{ (ES1)}$$

Calculation of Conversion and Selectivity

[0067] The conversion of cyclohexane is defined as the ratio of moles of cyclohexane consumed in the reaction to the total moles of cyclohexane initially added (Eq. ES2). The selectivity to benzene is defined as the ratio of moles of benzene produced to the total moles of all hydrocarbon products in terms of carbon (Eq. ES3).

$$\text{Conversion of cyclohexane} = \frac{\text{Moles of cyclohexane consumed}}{\text{Moles of cyclohexane initially added}} \times 100 \% \text{ (ES2)}$$

$$\text{Selectivity of benzene} = \frac{\text{Moles of benzene produced in terms of carbon}}{\text{Moles of all hydrocarbon products in terms of carbon}} \times 100 \% \text{ (ES3)}$$

[0068] Methane, ethane, cyclohexene and benzene were the only products observed. Therefore, we calculated the conversion and selectivity using the GC traces without the internal standard in order to avoid the error originated from the internal standard.

Calculation of Apparent Quantum Efficiency

[0069] In principle, it takes two photons to produce each hydrogen molecule from cyclohexane molecules. Thus, in turn, six photons are needed to produce one benzene molecule.

[0070] The as-synthesized metal@TiO₂ hybrid materials were tested as photocatalysts for the non-oxidative dehydrogenation of cyclohexane under visible light ($420\text{nm} \leq \lambda \leq 700\text{nm}$) from a 300W xenon lamp. To eliminate photo-thermal effects, a cooling system was employed to keep the reaction temperature constant at 20°C. Amongst the noble metal @TiO₂ hybrid materials synthesized and tested Pt@TiO₂ NPs gave the highest photocatalytic activity for the dehydrogenation reaction among all the samples tested under identical conditions as evident from Fig. 1B.

[0071] The inventors then proceeded to further optimize Pt@TiO₂ NPs by altering the Pt content, NaBH₄ concentration and pH value during the preparation procedure. The results of varying these parameters can be seen in Table 1.

Entry	TiO ₂ (mg)	Pt Loading (wt%)	NaBH ₄ (Equiv.) [†]	NaOH (μmol)	Reaction Time (hour)	Conversion (%)	TOF (h ⁻¹)
1	200	0.1 (1 μmol)	10	100	24	4	3.3
2	200	0.2 (2 μmol)	10	100	24	12	5.0
3	200	0.5 (5 μmol)	10	100	24	40	6.7
4	200	1 (10 μmol)	10	100	24	69	5.8
5	200	2 (20 μmol)	10	100	24	71	3.0
6	200	5 (50 μmol)	10	100	24	80	1.3
7	200	5 (50 μmol)	10	100	2	7	1.5
8	200	5 (50 μmol)	10	125	2	43	8.5
9	200	5 (50 μmol)	10	200	2	83	17
10	200	5 (50 μmol)	20	200	2	91	18
11	200	5 (50 μmol)	20	250	2	99	20
12 [‡]	200	5 (50 μmol)	20	250	2	NP	0

Table 1: Pt@TiO₂ Optimization for Photocatalytic Dehydrogenation of Cyclohexane

*Reaction conditions: 10 mg of Pt@TiO₂-N and 100 μmol of cyclohexane were used under visible light irradiation at 20 °C.

[†]in terms of Pt loading

[‡]Dark Reaction.

TOF = turnover frequency (based on the amount of Pt).

NP = no product.

[0072] Finally, the optimized *Pt@TiO₂* NPs with a platinum content of 5 wt% were carefully prepared by using 20 equiv. of NaBH₄ (in terms of platinum) at pH 10, designated as *Pt@TiO₂ - N*. Transmission electron microscopy (TEM) images, such as those depicted in first and second images A and B in Fig. 2 at low and high resolution respectively revealed that Pt species were highly dispersed on the surface of the TiO₂ NPs with an exposed (111) facet. The Pt size distribution derived from TEM measurements fits well in a logarithmic normal distribution with a mean diameter of 3.2 nm as evident from first graph C in Fig. 2. Further, powder X-ray diffraction (XRD) measurements confirmed the formation of metallic *Pt*⁰ species with a high degree of crystallinity since three characteristic peaks of *Pt*⁰ at 2θ = 41°, 46°, 67° were clearly observed as evident with second graph D in Fig. 2.

[0073] The photocatalytic cyclohexane dehydrogenation reaction over the optimal $Pt@TiO_2 - N$ led to the formation of benzene with nearly stoichiometric amounts of H_2 (3 equiv.). Using 10mg of $Pt@TiO_2 - N$ and 100 μ mol of cyclohexane, a conversion of 99% and a benzene selectivity of nearly 100% was achieved after 2 hour visible light irradiation as evident from first graph A in Fig. 3. The carbon mass balances during the conversion were close to 100% and only a trace amount of methane and carbon dioxide by-products were detected by gas chromatography. The control experiments have shown that the reaction does not proceed at all in the dark or in the absence of the Pt species (exemplified by using pure TiO_2), confirming that the dehydrogenation of cyclohexane to benzene by $Pt@TiO_2 - N$ is a photocatalytic process and the Pt species behave as the active sites for reaction.

[0074] To gain a better understanding of the nature of the catalytic active sites, the inventors also prepared another Pt modified TiO_2 through the photo-reduction of $PtCl_6^{2-}$ precursor in a mixture of methanol/water solution (designated as $Pt@TiO_2 - M$). Here, although the content, shape and size of Pt species in $Pt@TiO_2 - M$ are similar to those in $Pt@TiO_2 - N$, as confirmed by TEM and XRD measurements, the photoactivity of $Pt@TiO_2 - M$, however, was very low for cyclohexane dehydrogenation under the same reaction conditions, first graph A in Fig. 3. As evident from X-ray photoelectron spectroscopy (XPS) spectra presented in second graph B in Fig. 3, the Pt^{4f} peaks of $Pt@TiO_2 - N$ are negatively shifted (70.4eV) compared to the standard binding energies of metallic Pt^0 (71.1eV), indicating that the Pt species in $Pt@TiO_2 - N$ possess a fraction of negative charge which may be caused by the strong reducing ability of $NaBH_4$; whereas the Pt^{4f} peaks of $Pt@TiO_2 - M$ remain almost unchanged (71.0eV). These results imply that the Pt species with high electron density, which can act as Lewis base sites, are highly beneficial to the dehydrogenation process.

[0075] Besides TiO_2 , GaN and Al_2O_3 were also used as supporting-substrates for the cyclohexane dehydrogenation reaction. The performance of the tested $Pt@GaN - N$ and $Pt@Al_2O_3 - N$ catalyst is shown in first graph A in Fig. 3. Although the conversion was lower than for $Pt@TiO_2 - N$, under visible light irradiation, (despite the fact that the band gap and band position of GaN are similar to TiO_2), the use of GaN and Al_2O_3 may be justified in certain circumstances, or their respective performances may still be optimized. The binding energy of Pt deposited on GaN or Al_2O_3 is also higher than that on TiO_2 , as evidenced by the

XPS results presented in second graph B in Fig. 3. These results indicate that the interaction between metal and support could significantly alter the electronic and catalytic properties of loaded *Pt* species.

[0076] Nanosized *Pt* are visible-light-active species due to intra-band electron transitions whereas *TiO₂* substrate can only absorb photons in the ultraviolet region. Therefore, the metallic *Pt* species essentially act as both sensitizers to absorb resonant photons, and active sites to facilitate the dehydrogenation reactions. As illustrated in schematic C in Fig. 3, upon visible light irradiation, the photoexcited hot electrons of *Pt* species can be temporarily added to an empty *C*–*H* σ^* -antibonding orbital of the adsorbed cyclohexane to actively and homolytically cleave its *C*–*H* bond, followed by the formation of an *H* atom which then couples with another *H* atom to produce *H₂*. It is worth noting that the alkane dehydrogenation process does not consume extra electrons and thus, the photoexcited electrons will finally fall back to *Pt*. This mechanism is consistent with the experimental and XPS results that the *Pt* species with high electron density (low electron binding energy), which can offer electrons efficiently, are critical to access a high reactivity to the cyclohexane dehydrogenation reaction under visible light.

[0077] In order to identify the effective spectral range and quantum efficiency, wavelength dependence experiments were carried out using a series of filters. As shown in third graph D in Fig. 3, the photocatalytic activity still remains at a high level around $\lambda \approx 600nm$, but decreased dramatically when the wavelength of light irradiation was longer than $\lambda > 700nm$. The apparent quantum efficiency (*H₂* produced per photon consumed) between $420nm \leq \lambda \leq 600nm$ was calculated to be approximately 6.0%, which rivals previously reported best performing solar water splitting devices without any external bias voltage by one of the inventors.

[0078] During the cyclohexane dehydrogenation reaction, only the cyclohexene intermediate was observed, whereas 1,3-cyclohexadiene was not detected. The control experiments indicate that 1,3-cyclohexadiene can either directly lose hydrogen to form benzene or react with cyclohexene to form benzene and cyclohexane over *Pt@TiO₂*–*N* under visible light irradiation. Both reactions are extremely fast (within few seconds). Taken together, a proposed mechanism is depicted in Fig. 4. The reaction starts with the activation of cyclohexane *C*–*H* bonds on the exposed *Pt* facets. Upon visible light irradiation, cyclohexane loses two hydrogen atoms to form cyclohexene. 1,3-cyclohexadiene produced from the further dehydrogenation of

cyclohexene can quickly go through the dehydrogenation process or react with cyclohexene to form benzene.

[0079] After the dehydrogenation reaction, the produced hydrogen can very slowly add back into benzene to form cyclohexane again under no illumination at room temperature in the presence of $Pt @ TiO_2 - N$. In contrast, no hydrogenation product was obtained in the absence of $Pt @ TiO_2 - N$. The hydrogenation process can be accelerated dramatically at slightly higher temperatures. As depicted in first graph A in Fig. 5 a hydrogenation conversion of 97% can be achieved within one hour at $50^\circ C$. Furthermore, toluene/methylcyclohexane and xylene/1,4-dimethylcyclohexane systems also work well for hydrogen storage and release as evident from the results depicted in first and second graphs A and B respectively in Fig. 5 under the same conditions, indicating a wide applicability of embodiments of the disclosure for a reversible hydrogen storage system exploiting low cost hydrocarbons.

[0080] As depicted in first graph A in Fig. 5 the time curves of hydrogen addition ($300 \mu mol$) onto different aromatics ($100 \mu mol$) over $Pt @ TiO_2 - N$ under dark conditions at $50^\circ C$ are plotted. Corresponding hydrogen release curves for these different cyclic alkanes ($100 \mu mol$) as a function of time over $Pt @ TiO_2 - N$ under visible light irradiation ($\lambda > 420 nm$) at $20^\circ C$ are depicted in second graph B in Fig. 5. Schematic C in Fig. 5 depicts kinetic isotope effects in the dehydrogenation and hydrogenation processes.

[0081] To gain the mechanistic insights of different hydrogen transfer steps, the deuterium kinetic isotope effects (KIE) for both dehydrogenation and hydrogenation processes were determined comprehensively, as depicted in schematic C in Fig. 5. In the case of the dehydrogenation reaction, a high KIE (k_H/k_D) of 5.8 was determined through parallel reactions by using the same amount of cyclohexane and cyclohexane- d_{12} (C_6D_{12}), indicating that the $C-H$ bond cleavage is the rate-determining step. In contrast, kinetic studies for the hydrogenation reaction were performed by using four different combinations including benzene/ H_2 , benzene/ D_2 , benzene- d_6 / H_2 and benzene- d_6 / D_2 . The hydrogenation rate of benzene/ D_2 was much lower than that of benzene/ H_2 ($k_H/k_D = 3.5$), whereas a large inverse secondary isotope effect was observed in benzene- d_6 / D_2 ($k_H/k_D = 0.59$) since the hybridization of carbon changes from sp^2 to sp^3 during the reaction. In benzene- d_6 / D_2 case,

the overall KIE value is close to one since both primary isotope and inverse secondary isotope effects exist in the system which can neutralize each other to a certain extent.

[0082] Accordingly, embodiments of the invention described *supra* show that abundant and low-cost petrochemicals can form the basis of large scale reversible hydrogen storage/release without any external requirements. Accordingly, a reversible hydrogen storage/release assembly may be employed in conjunction with a visible light based hydrogen generator. Importantly, such a stable and scalable hydrogen storage/release system can be seamlessly integrated with solar energy harvesting under practical conditions, i.e., with the use of only visible light at ambient temperature. The apparent quantum efficiency for solar-to-hydrogen conversion can reach 6% under white light illumination, which can be further improved by optimizing the photon absorption. Embodiments of the disclosure provide for an entirely new strategy to effectively address the twin problems associated with the emerging hydrogen economy, including hydrogen storage and solar-to-hydrogen conversion.

[0083] Within the embodiments of the disclosure described and depicted *supra* noble metal catalysts were employed in conjunction with nanoparticles (such as TiO_2).

[0084] It would be evident to one of skill in the art that in other embodiments of the disclosure other noble metals that those listed above may be used. Such catalysts may be formed, for example, as nanoparticles upon TiO_2 nanoparticles or as other structures upon or as part of the TiO_2 nanoparticles or other material nanoparticles, 2D nanostructures, and 3D nanostructures without departing from the scope of the disclosure.

[0085] It would be evident to one of skill in the art that rather than nanoparticles that other types of TiO_2 substrates in the form of nanorods, nanotubes and films may also be applied to form supporting structures for catalysts and provide good activities towards both the hydrogen addition and release processes. In addition, besides TiO_2 , graphene oxide, graphene sheets and graphene nanoribbons may also be employed as supporting materials for the cyclohexane dehydrogenation and benzene hydrogenation reactions, especially in liquid solutions. Within other embodiments of the disclosure semiconductors may be employed to form the nanostructures supporting catalysts.

[0086] In one embodiment of the method described herein, said method is further comprising performing a cyclic process of storing hydrogen and releasing hydrogen such the predetermined

hydrocarbon is initially converted to another hydrocarbon on the basis of the hydrogenation reaction during the storing sequence and then the another hydrocarbon is converted back to the predetermined hydrocarbon on the basis of the dehydrogenation reaction during the releasing sequence.

[0087] In one embodiment of the method described herein, said method is performing a cyclic process of storing hydrogen and releasing hydrogen, wherein the hydrogen store within the device is generated though visible light splitting of water.

[0088] In one embodiment of the method described herein,
at least one of:

the plurality of first nanostructures are at least one of a two-dimensional (2D) nanostructure and a three-dimensional (3D) nanostructure;

the plurality of second nanostructures are at least one of a two-dimensional (2D) nanostructure and a three-dimensional (3D) nanostructure;

the plurality of first nanostructures are formed from a catalyst selected in dependence upon at least the predetermined hydrocarbon and another hydrocarbon such that the predetermined hydrocarbon and another hydrocarbon are either the results of the hydrogenation and dehydrogenation reactions respectively or the dehydrogenation and hydrogenation reactions respectively;

the second predetermined material composition is a noble metal, a transition metal, a combinations of noble metals, a combination of transition metals, and a noble metal – transition metal combination;

the first predetermined material composition is at least one of titania, graphite, graphene, and semiconductor.

[0089] The foregoing disclosure of the exemplary embodiments of the present disclosure has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the disclosure to the precise forms disclosed. Many variations and modifications of the embodiments described herein will be apparent to one of ordinary skill in the art in light of the above disclosure. The scope of the disclosure is to be defined only by the claims appended hereto, and by their equivalents.

[0090] Further, in describing representative embodiments of the present disclosure, the specification may have presented the method and/or process of the present disclosure as a

particular sequence of steps. However, to the extent that the method or process does not rely on the particular order of steps set forth herein, the method or process should not be limited to the particular sequence of steps described. As one of ordinary skill in the art would appreciate, other sequences of steps may be possible.

CLAIMS

1. A process comprising at least one of:
 - a photo-driven catalyzed hydrogen (H₂) generation by dehydrogenation of a compound comprising at least one saturated or partially saturated carbocyclic residue; wherein said dehydrogenation is providing a compound comprising at least one carbocyclic aromatic residue; and
 - a catalyzed hydrogenation of a compound comprising at least one carbocyclic aromatic residue, wherein said hydrogenation is providing a compound comprising at least one saturated or partially saturated carbocyclic residue;wherein said catalyzed dehydrogenation and hydrogenation are conducted in the presence of a noble metal (metal) supported on semiconductor nanoparticles (NP) illustrated by the formula:
metal@NP
and wherein said photo-driven catalyzed dehydrogenation is conducted in the presence of visible light.
2. The process of claim 1, wherein said visible light is comprising a wavelength greater than about 400 nm.
3. The process of claim 1 or 2, wherein said carbocyclic aromatic residue is comprising a monocarbocyclic or polycarbocyclic aromatic ring.
4. The process of any one of claims 1 to 3, wherein said compound comprising at least one carbocyclic aromatic residue is in a substantially liquid state between about 5 to about 80°C.
5. The process of any one of claims 1 to 4, wherein said compound comprising at least one carbocyclic aromatic residue is comprising benzene, toluene, o-, m- or p-xylene, ethylbenzene, mesitylene, cumene, cymene or a mixture thereof.
6. The process of any one of claims 1 to 5, wherein said compound comprising at least one saturated or partially saturated carbocyclic residue is in a substantially liquid state between about 5 to about 80°C.

7. The process of any one of claims 1 to 6, wherein said compound comprising at least one saturated or partially saturated carbocyclic residue is cyclohexane, cyclohexene, cyclohexadiene methylcyclohexane, methylcyclohexene, methylcyclohexadiene, 1,2-, 1,3- and 1,4-dimethylcyclohexane, dimethylcyclohexene, dimethylcyclohexadiene or a combination thereof.
8. The process of any one of claims 1 to 7, wherein said compound comprising at least one saturated or partially saturated carbocyclic residue is a saturated carbocyclic compound.
9. The process of any one of claims 1 to 8, wherein said metal of said metal@NP is gold, silver, platinum, ruthenium, rhodium, palladium, osmium, iridium or a combination thereof.
10. The process of any one of claims 1 to 9, wherein said NP is comprising TiO_2 , GaN, Al_2O_3 or a combination thereof.
11. The process of any one of claims 1 to 10, wherein said catalyzed dehydrogenation is conducted at a temperature of from about 5 to about 80°C.
12. The process of any one of claims 1 to 10, wherein said catalyzed hydrogenation is conducted at a temperature of from about 5 to about 80°C.
13. A process for preparing a noble metal (metal) supported on semiconductor nanoparticles (NP) illustrated by the formula:
metal@NP
said process comprising chemically reducing a noble metal precursors of said noble metal, in the presence of semiconductor nanoparticles (NPs) in aqueous solution.
14. The process of claim 13, wherein said noble metal precursors and said nanoparticles (NPs) are contacted together in absence of light for a period of time before chemically reducing said precursor.
15. The process of claim 13 or 14, wherein said chemical reduction of said noble metal precursors comprising said borohydride reagent is conducted at an alkaline pH.

16. A noble metal (metal) supported on semiconductor nanoparticles (NP) illustrated by the formula:

metal@NP

wherein said metal of said metal@NP is gold, silver, platinum, ruthenium, rhodium, palladium, osmium, iridium and combinations thereof.

17. The process of claim 16, wherein said NP of said metal@NP is comprising TiO_2 , GaN, Al_2O_3 or a combination thereof.

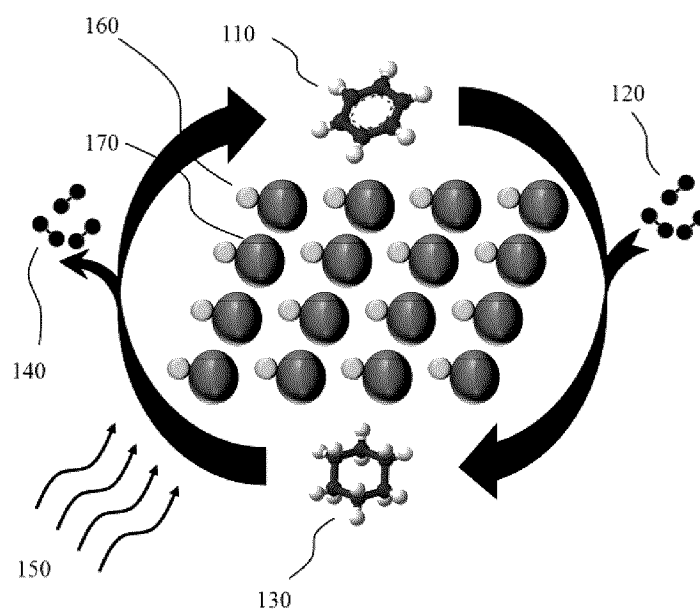


Fig. 1A

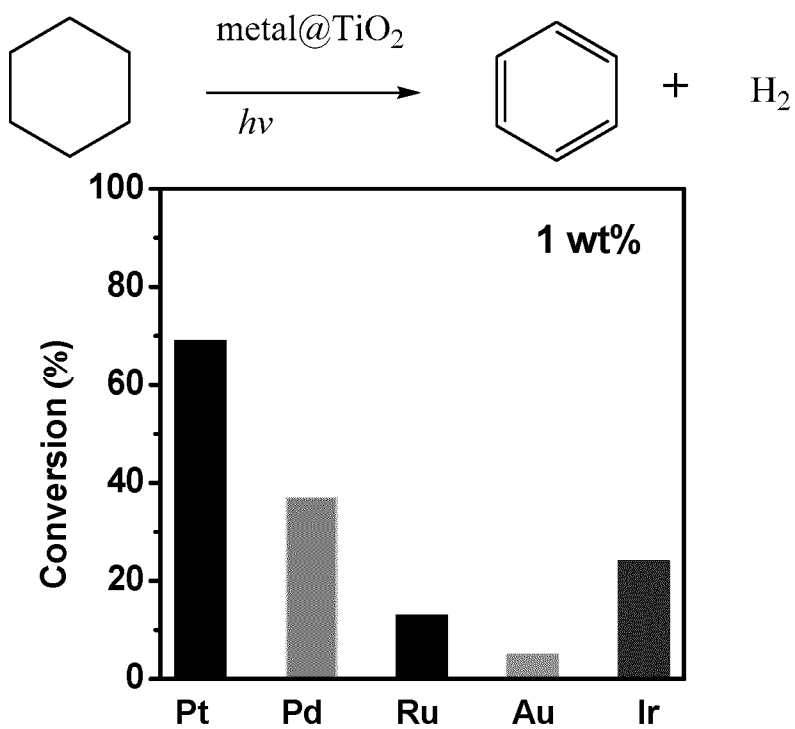


Fig. 1B

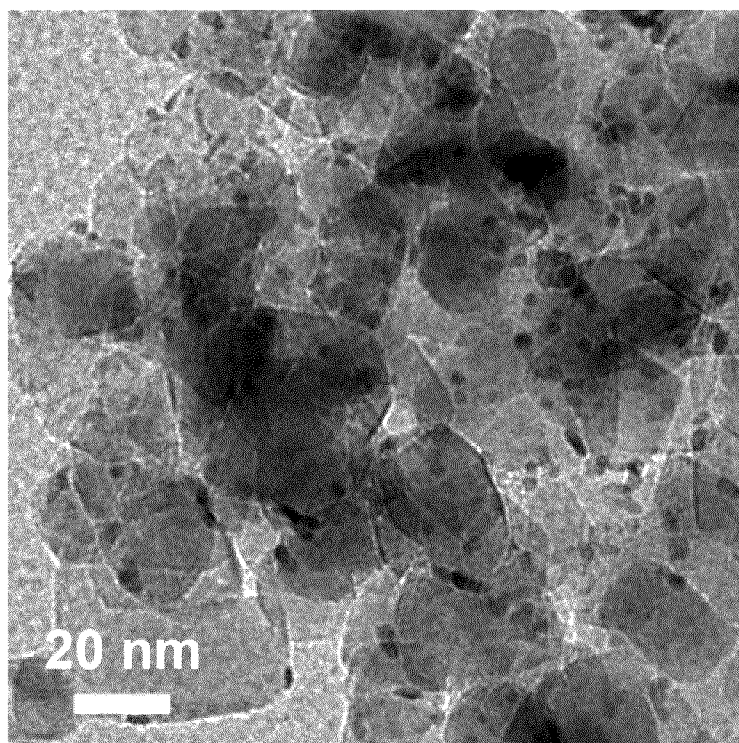


Fig. 2A

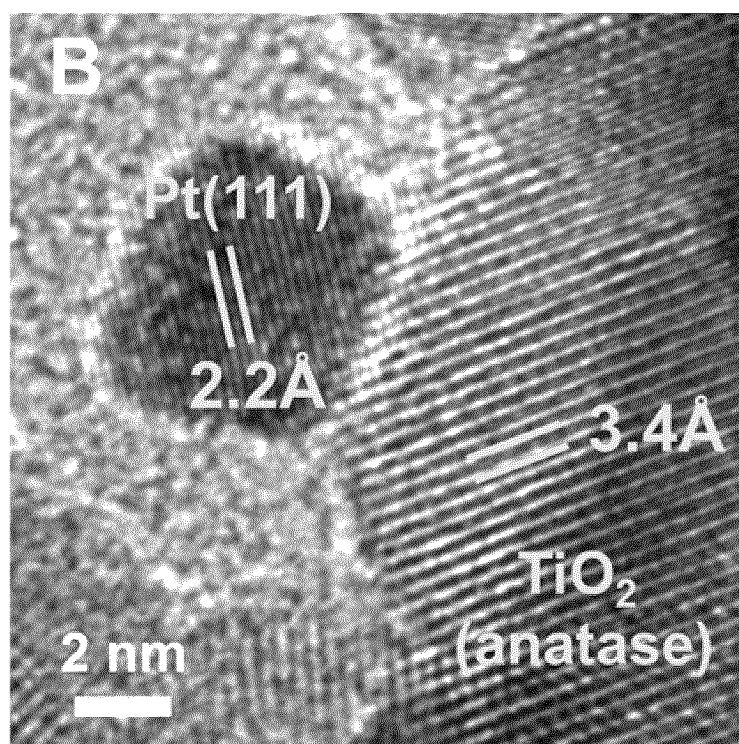


Fig. 2B

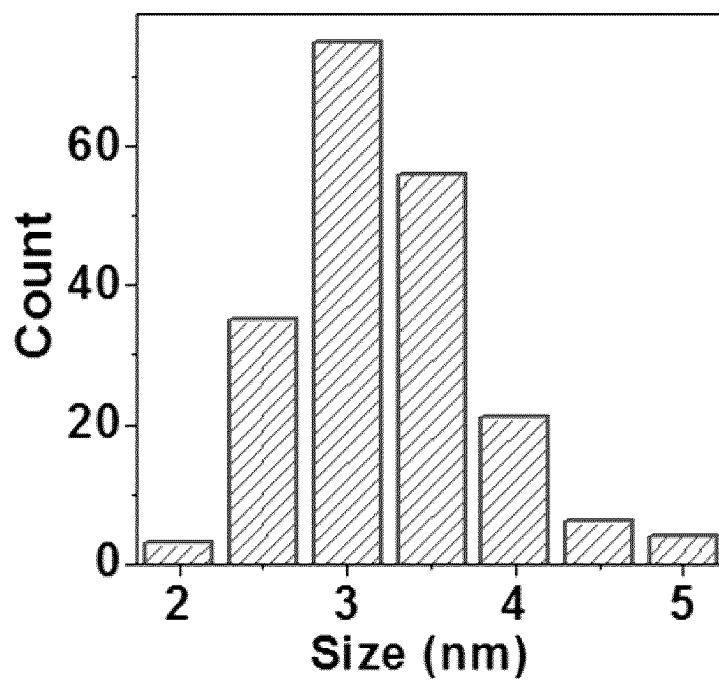


Fig. 2C

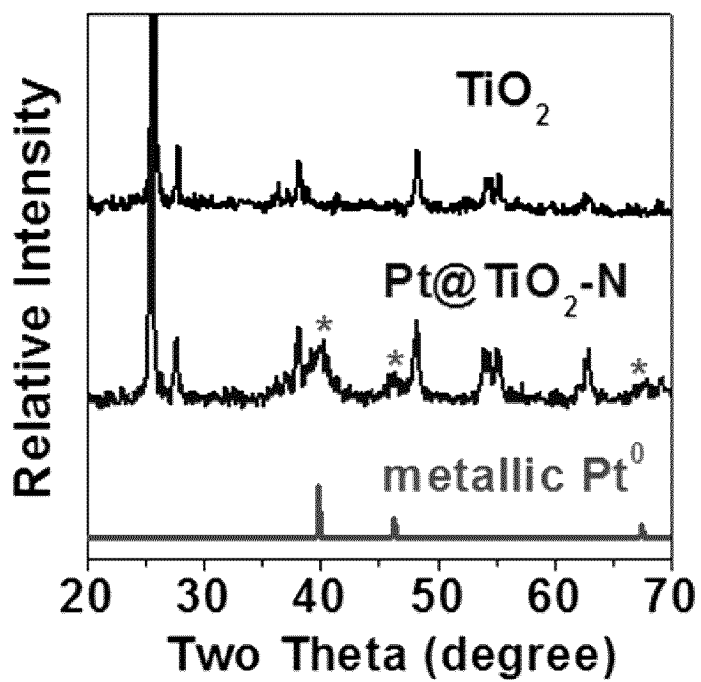


Fig. 2D

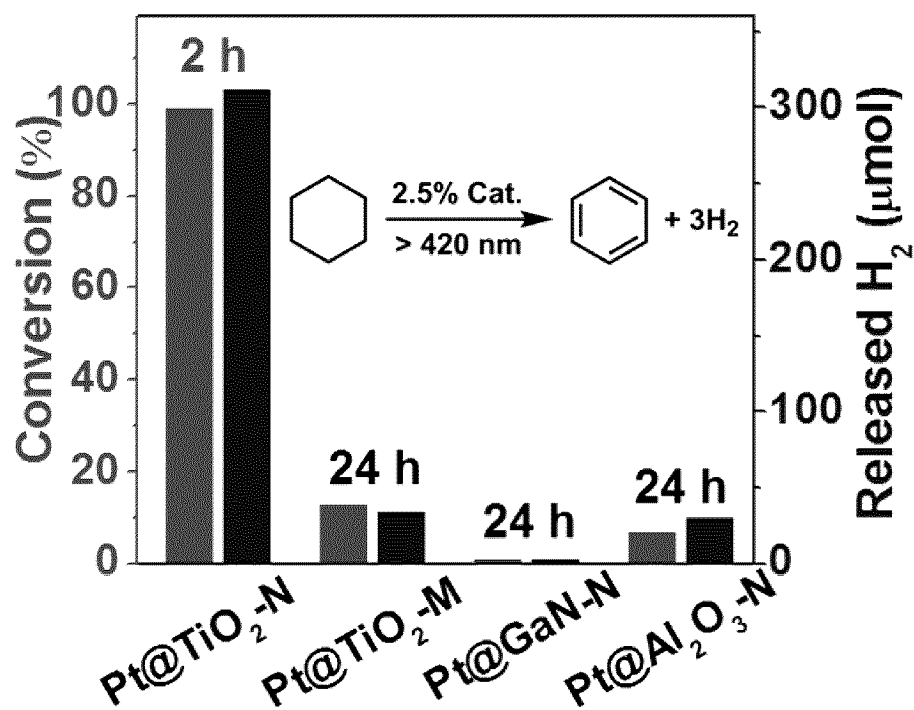


Fig. 3A

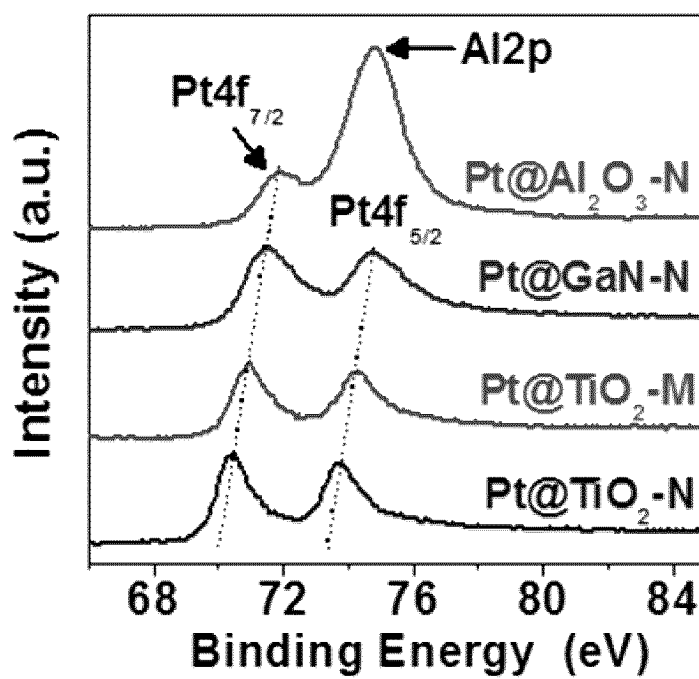


Fig. 3B

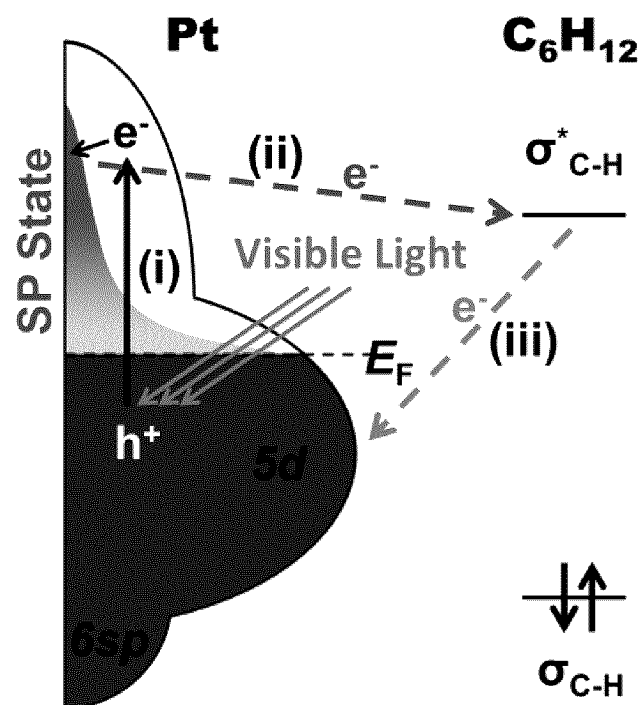


Fig. 3C

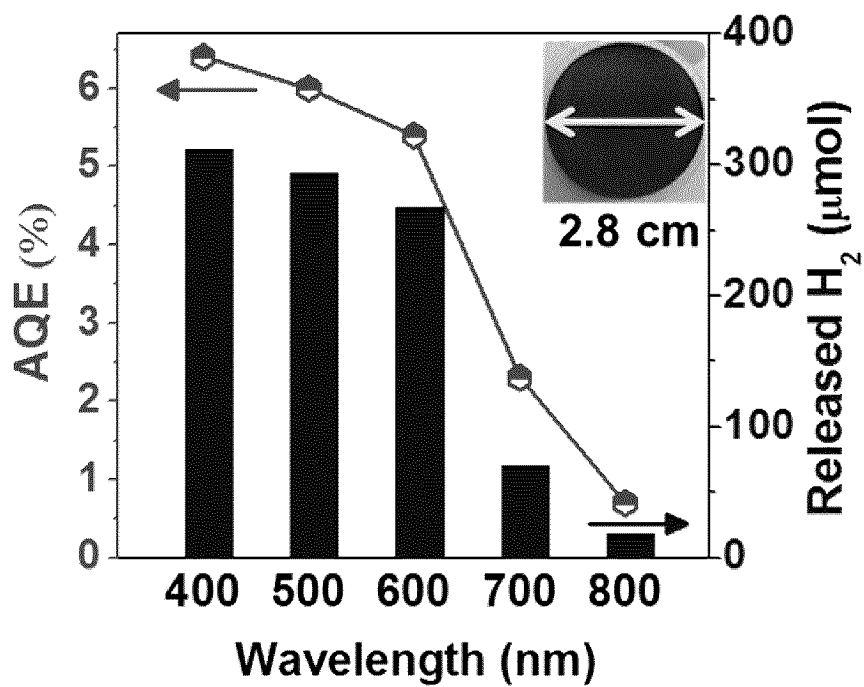


Fig. 3D

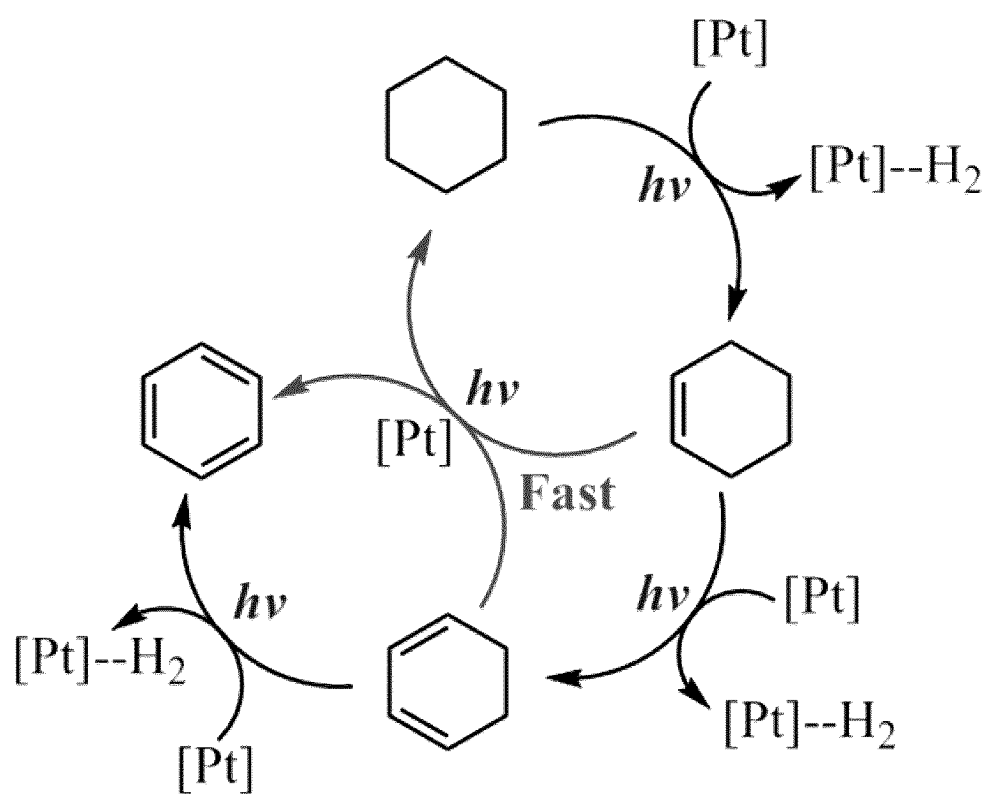


Fig. 4

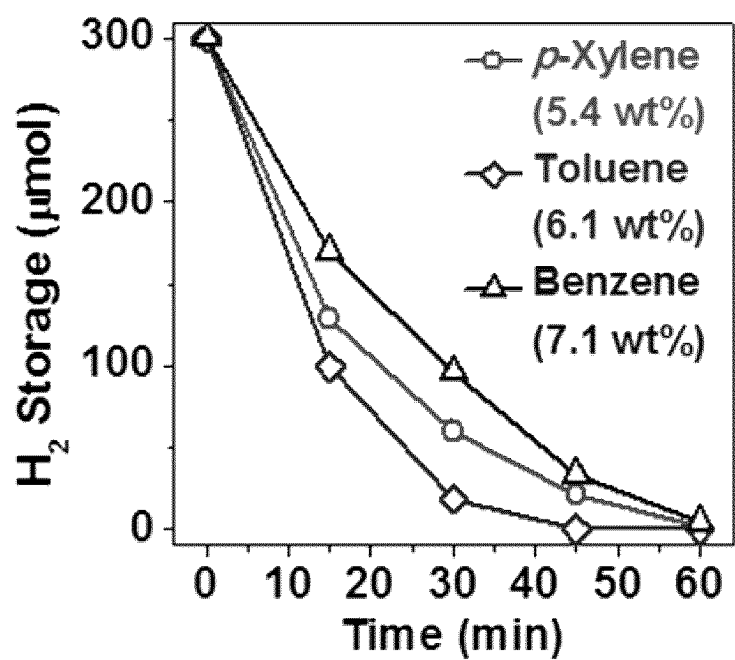


Fig. 5A

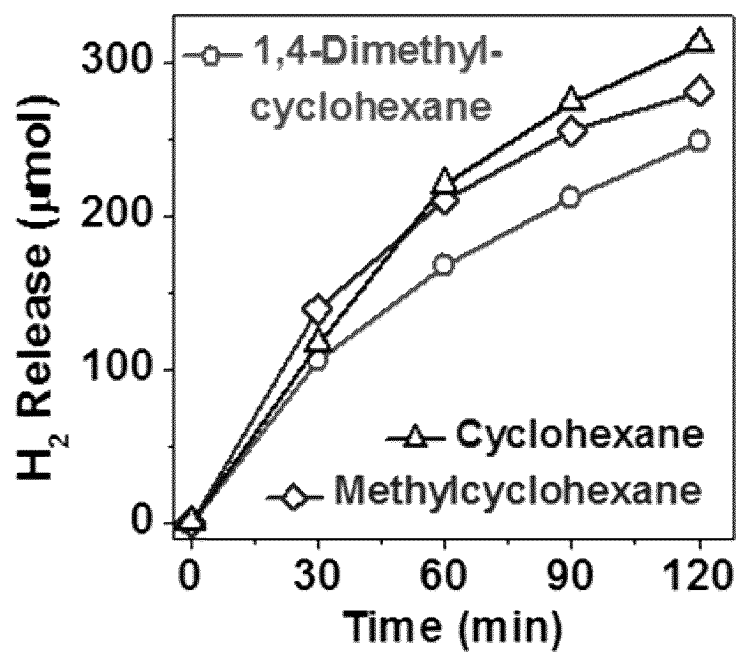


Fig. 5B

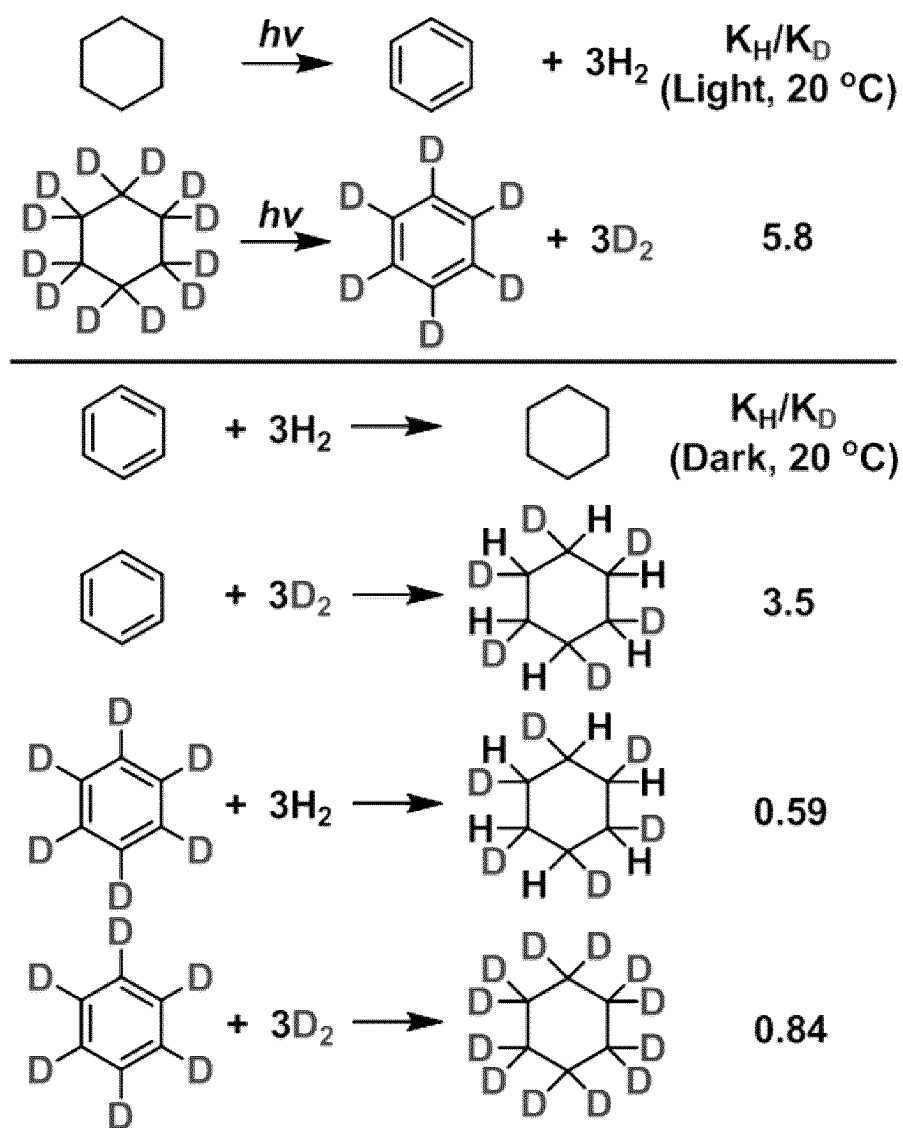


Fig. 5C

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050561

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C01B 3/22** (2006.01), **B01J 23/38** (2006.01), **B82Y 30/00** (2011.01), **C01B 3/02** (2006.01), **C07C 6/00** (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)
IPC (2006.01): C01B 3/22, C01B 3/02, B01J 23/38, C07C 6/00; IPC (2011.01): B82Y 30/00

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

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

Databases: QUESTEL, Canadian Patent Database, CIPO Library Discovery Tool

Keywords: hydrogen, hydrogenation, dehydrogenation, hydrocarbon, carbocyclic, cyclic hydrocarbon, aromatic, benzene, toluene, cyclohexane, cyclohexene, catalyst, nano+, nm, noble, silver, platinum, ruthenium, rhodium, palladium, osmium, iridium, semiconductor, titanium dioxide, TiO₂, GaN, alumina, Al₂O₃, photo+, visible light

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2011/0053020 A1 (NORTON et al.) 3 March 2011 (03-03-2011) *whole document*	1-12, 16-17 13-15
X A	KE et al., "Selective reductions using visible light photocatalysts of supported gold nanoparticles", <i>Green Chemistry</i> , Volume 15 (2013), Pages 236-244.	13-17 1-12
A	US 2004/0223907 A1 (PEZ et al.) 11 November 2004 (11-11-2004) *whole document*	1-17
A	US 9,005,571 B2 (BINIWALE et al.) 14 April 2015 (14-04-2015) *whole document*	1-17
A	WO 2015/035518 A1 (LI et al.) 19 March 2015 (19-03-2015) *whole document*	1-17

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	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 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 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 document member of the same patent family
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Date of the actual completion of the international search
27 July 2016 (27-07-2016)

Date of mailing of the international search report
29 July 2016 (29-07-2016)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 819-953-2476

Authorized officer

Philip Gbor (819) 639-8475

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050561**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the 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. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim 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. ☐ Claim 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:

Group A: Claims 1-12

Group B: Claims 13-15

Group C: Claims 16-17

Continued on extra sheet

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 claim 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 claim Nos.:

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.

PCT/CA2016/050561

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-110437 (ICHIKAWA et al.) 24 April 2001 (24-04-2001) * Abstract and Machine English Translation of Description*	1-17
A	MARCONI et al., "Nanostructured ruthenium on γ -Al ₂ O ₃ catalysts for the efficient hydrogenation of aromatic compounds", <i>Journal of Organometallic Chemistry</i> , Volume 689 (2004), Pages 639-646	1-17

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2016/050561

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US2011053020A1	03 March 2011 (03-03-2011)	US2011053020A1 CN101970104A CN101970104B EP2217371A1 EP2217371A4 WO2009062096A1	03 March 2011 (03-03-2011) 09 February 2011 (09-02-2011) 06 November 2013 (06-11-2013) 18 August 2010 (18-08-2010) 12 February 2014 (12-02-2014) 14 May 2009 (14-05-2009)
US2004223907A1	11 November 2004 (11-11-2004)	US2004223907A1 US7101530B2 CA2465555A1 CA2465555C CA2524846A1 CA2524846C CN1809505A CN100381351C CN101279222A CN101279222B EP1475349A2 EP1475349A3 EP1660404A2 EP1660404A4 EP1660404B1 EP2960204A1 JP2007515363A JP5431647B2 KR20060022651A KR101121819B1 MXPA05011850A US7351395B1 US2005002857A1 US7429372B2 US2005013767A1 WO2005000457A2 WO2005000457A3	11 November 2004 (11-11-2004) 05 September 2006 (05-09-2006) 06 November 2004 (06-11-2004) 16 March 2010 (16-03-2010) 06 January 2005 (06-01-2005) 22 July 2014 (22-07-2014) 26 July 2006 (26-07-2006) 16 April 2008 (16-04-2008) 08 October 2008 (08-10-2008) 15 February 2012 (15-02-2012) 10 November 2004 (10-11-2004) 08 December 2010 (08-12-2010) 31 May 2006 (31-05-2006) 25 August 2010 (25-08-2010) 05 August 2015 (05-08-2015) 30 December 2015 (30-12-2015) 14 June 2007 (14-06-2007) 05 March 2014 (05-03-2014) 10 March 2006 (10-03-2006) 21 March 2012 (21-03-2012) 25 May 2006 (25-05-2006) 01 April 2008 (01-04-2008) 06 January 2005 (06-01-2005) 30 September 2008 (30-09-2008) 20 January 2005 (20-01-2005) 06 January 2005 (06-01-2005) 07 July 2005 (07-07-2005)
US9005571B2	14 April 2015 (14-04-2015)	US2013142726A1 EP2598434A2 EP2620410A1 WO2012014225A2 WO2012014225A3	06 June 2013 (06-06-2013) 05 June 2013 (05-06-2013) 31 July 2013 (31-07-2013) 02 February 2012 (02-02-2012) 03 May 2012 (03-05-2012)
WO2015035518A1	19 March 2015 (19-03-2015)	None	
JP2001110437A	20 April 2001 (20-04-2001)	None	

Continuation of Box No. III

Group A:

Claims 1-12 are directed to a process comprising at least one of: a photo-driven catalyzed hydrogen generation by dehydrogenation of a compound comprising at least one saturated or partially saturated carbocyclic residue; wherein said dehydrogenation is providing a compound comprising at least one carbocyclic aromatic residue; and a catalyzed hydrogenation of a compound comprising at least one carbocyclic aromatic residue, wherein said hydrogenation is providing a compound comprising at least one saturated or partially saturated carbocyclic residue; wherein said catalyzed dehydrogenation and hydrogenation are conducted in the presence of a noble metal supported on semiconductor nanoparticles and wherein said photo-driven catalyzed dehydrogenation is conducted in the presence of visible light.

Group B:

Claims 13-15 are directed to a process for preparing a noble metal supported on semiconductor nanoparticles said process comprising chemically reducing a noble metal precursors of said noble metal, in the presence of semiconductor nanoparticles in aqueous solution.

Group C:

Claims 16-17 are directed to a noble metal supported on semiconductor nanoparticles wherein said metal is gold, silver, platinum, ruthenium, rhodium, palladium, osmium, iridium and combinations thereof.

Groups A, B and C are not linked by a single general inventive concept. The only feature that is common to Groups A to C is "a noble metal supported on semiconductor nanoparticle", however, this feature is well known in the prior art and as such cannot be relied upon to provide the single general inventive concept required to establish unity of invention.