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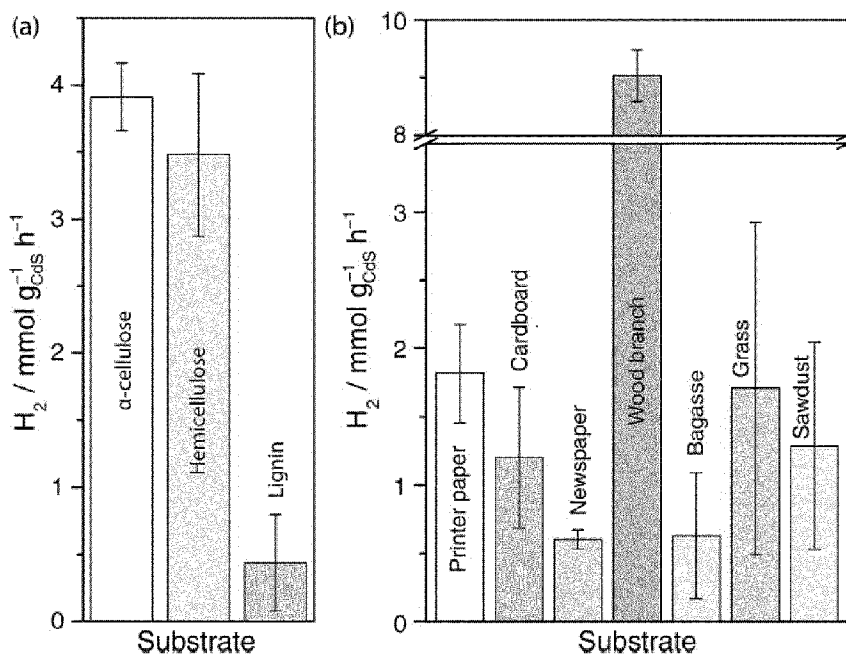
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Fig. 4



(57) Abstract: The present invention provides a method of producing hydrogen, the method comprising the step of exposing a photocatalyst to visible and/or ultraviolet light in the presence of an organic substrate, wherein the photocatalyst has a semiconductor core having an oxide- and/or hydroxide-functionalised surface, thereby to generate hydrogen from the organic substrate, and the hydrogen is optionally collected. The photocatalyst semiconductor core may be CdS having oxide- and/or hydroxide-functionality at its surface (CdS/CdOx). The organic substrate typically contains a component having a molecular weight of 50 or more, such as 500 or more.

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PHOTOCATALYST AND PHOTOCATALYTIC METHODS***Related Applications***

5 This application claims the benefit and the priority of GB 1619953.1 filed on 25 November 2016 (25/11/2016) and GB 1701130.5 filed on 23 January 2017 (23/01/2017), the contents of both of which are hereby incorporated by reference in their entirety.

Field of the Invention

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The present invention provides a photocatalyst and the use of the photocatalyst in photocatalytic methods for degrading an organic substrate, such as biomass or an organic polymer. Also provided is the use of the photocatalyst in photocatalytic methods for generating hydrogen.

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Background

As of 2016 the global consumption of fossil-derived oil has reached 1,100 barrels (10⁵ litres) per second and continues to climb annually. Low-cost fuel cannot be produced at this rate indefinitely, and securing and combusting crude oil is causing irreversible environmental damage.

Investigations into sustainable alternatives have consequently identified H₂ as a promising energy carrier, which can be used directly in an emission-free fuel cell, or as a hydrogenating agent in the synthesis of renewable liquid fuel. To date however, H₂ is almost exclusively attained through reforming/gasification of fossil-derived coal, gas or oil. It is also possible to produce H₂ by electrolysis. However, such methods are not regarded as renewable where the electrical power is ultimately sourced from coal, gas or oil.

25 Biomass conversion is one of the most affordable routes to generate sustainable H₂, but this process requires the demanding chemical transformation of lignocellulose. Lignocellulose is the main constituent of biomass and can be cultivated worldwide, even on unfertilised, marginal land. Lignocellulose conversion to H₂ has predominantly been realised through gasification, which uses high temperatures (> 750°C) to decompose its organic structure and release H₂, alongside other gases, such as CO, CO₂ and CH₄.

30 In the interest of increasing the selectivity and efficiency of this conversion, it is possible to replace the thermal input with sunlight. Solar light offers an essentially inexhaustible source of globally available energy and therefore the photoreforming of biomass-derived compounds is a fast growing field of research. A particular attraction of photoreforming is the ability to perform the reforming reaction at ambient temperature.

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Photoreforming requires a photocatalyst able to oxidise lignocellulose and use the resultant electrons to undertake the two-electron reduction of aqueous protons to H₂. Lignocellulose adopts the role of a hole scavenger, replacing the expensive sacrificial electron donors commonly used when studying photocatalytic proton reduction. Thus far, this field has

5 focused on H₂ evolution from substrates that could be derived from lignocellulose, such as methanol, glycerol or glucose, however lignocellulose refining is expensive and inefficient, usually requiring acid hydrolysis, enzymatic hydrolysis or pyrolysis to produce more manageable substrates.

10 These processes are followed by hydrogenation or fermentation depending on the desired product. Viable H₂ production systems must therefore reform lignocellulose directly to compete with thermochemical processes. This is a considerable challenge at ambient temperatures, as the structure of lignocellulose has evolved to prevent its consumption by microbial and animal life. Lignocellulose is mainly comprised of cellulose (> 40% in wood

15 stems), a crystalline polysaccharide of anhydroglucose monomers.

Cellulose is surrounded by branched polysaccharides, called hemicelluloses (20-40%), which are heteropolymers of pentose and hexose sugars. The two cellulosic polymers are further encased in the cross-linked phenolic polymer, lignin (< 35%), and the combined

20 structures form microfibrils that are resistant to chemical transformation. Examples of the direct photoreformation of lignocellulose or even purified cellulose to H₂ are consequently rare and until now have exclusively required a UV-light absorbing TiO₂ architecture loaded with expensive, non-scalable noble-metal catalysts, such as Pt and RuO₂.

25 Li *et al.* report the direct catalytic conversion of raw woody biomass into two groups of chemicals over a carbon supported Ni-W₂C catalyst (see *Energy Environ. Sci.* 2012, 5, 6383). The carbohydrate fraction in the woody biomass, principally cellulose and hemicellulose, was converted to ethylene glycol and other diols with a total yield of up to 75.6% (based on the amount of cellulose and hemicellulose), while the lignin component

30 was converted selectively into monophenols with a yield of 46.5% (based on lignin).

Matson *et al.* describe the quantitative catalytic conversion of wood and cellulosic solids to liquid and gaseous products (*J. Am. Chem. Soc.* 2011, 133, 14090). A single stage reactor is used, operating at 300–320°C and 160-220 bar. Little or no char is formed during this

35 process. The reaction medium is supercritical methanol (sc-MeOH) and the catalyst, a copper-doped porous metal oxide, is composed of earth-abundant materials. The major liquid product is a mixture of C₂-C₆ aliphatic alcohols and methylated derivatives of these alcohols, and these products are, in principle, suitable for applications as liquid fuels.

40 Photocatalysts have also been used to treat refined (or processed) biomass substrates. These methods are not necessarily desirable, as the biomass must be pre-treated to provide

the refined material. However, these methods may be suitable under some circumstances, for example where the pre-treatment (refining) process is not costly or time consuming.

5 Xia *et al.* describe the direct hydrodeoxygenation of raw woody biomass into liquid alkanes with mass yields up to 28.1 wt % using a multifunctional Pt/NbOPO₄ catalyst in cyclohexane (see *Nat. Commun.* 2016, 7, 11162). The reactions were conducted at 190°C and 5 MPa H₂ for 20 h and a total mass yield of liquid alkanes of greater than 20 wt % was achieved for all woods, among which birch wood gave the highest mass yield of 28.1 wt %. This method requires, however, hydrogen to be consumed in the degradation reaction.

10 Zhang *et al.* describe the photocatalytic conversion of cellulose to sugars and carbon dioxide with simultaneous production of hydrogen under UV or solar light irradiation (see *Chem. Commun.* 2016, 52, 1673). Here, degradation of the cellulose was achieved with immobilisation of the cellulose onto a platinised TiO₂ photocatalyst (P25, BET surface area 15 B50 m² g⁻¹, particle size B20–30 nm, loading of 0.5 wt % platinum for H₂ production).

Kawai *et al.* (*Nature*) have reported the reaction of aqueous mixtures of carbohydrates, including cellulose, in the presence of a RuO₂/TiO₂/Pt photocatalyst powder with irradiation from a 500 W Xe lamp (*Nature* 1980, 286, 474). The evolution of hydrogen was observed.

20 Kawai *et al.* (*Chemistry Lett.*) have also described photocatalytic production of hydrogen from water and synthetic and natural organic molecules (*Chemistry Lett.* 1981, 10, 81). The authors use a platinized TiO₂ photocatalyst to photoreform PVC, gelatine and turf, amongst others, under incident light generated from a Xe lamp.

25 Speltini *et al.* have described the evolution of hydrogen during the degradation of cellulose in an aqueous suspension together with Pt/TiO₂ under irradiation at 366 nm (UV-A) or under natural light (*Photochem. Photobiol. Sci.* 2014, 13, 1410).

30 The present inventors have identified an alternative class of photocatalysts having use in methods of degrading biomass, and also more generally in methods of degrading organic substrates.

35 **Summary of the Invention**

The present inventors have identified a particular class of catalysts that have useful reduction and oxidation properties when exposed to visible light, such as sunlight, or simulated visible light. These photocatalysts may be reliably used in photocatalytic methods for degrading organic substrates, such as biomass, and photocatalytic methods for 40 producing hydrogen.

The catalyst is therefore a photocatalyst. The photocatalyst of the invention is typically a particle, and the photocatalyst has a surface that is oxygen functionalised (which may be referred to as *passivated*), such as hydroxide- or oxide-functionalised. Exemplified in the present case is an oxygenated CdS photocatalyst (which may be referred to as CdS|CdO_x).

5 A photocatalyst may be obtained or is obtainable by treatment of a semiconductor with aqueous base, for example.

The photocatalysts of the invention have excellent catalytic activity in methods for degrading biomass, such as those biomasses having a high cellulose content, and this degradation
10 may be accomplished at ambient temperatures and pressures using natural light or simulated natural light. Thus, the photocatalyst may be used to degrade tree material, such as branches, as well as processed biomass products such as paper and cardboard, which may be obtained as waste materials. Advantageously, the photocatalyst is also capable of catalysing the degradation of lignin, which is also a component of many biomasses. Further,
15 the photocatalyst may also be used to degrade semi-refined biomass, for example the photocatalyst may be used to degrade cellulose extracted from a biomass. Here, degradation may refer to oxidative degradation or depolymerisation degradation.

The photocatalyst of the invention may be used in a photocatalytic method for the generation
20 of hydrogen, for example from biomass. Thus, the photocatalyst is therefore capable of producing a useful fuel from abundant raw and waste biomasses. The methods of the invention may also allow hydrogen to be produced that is substantially free of carbon dioxide.

25 The photocatalyst of the invention is active under incident visible light, and may be used for sustained periods, for example for more than two days, without appreciable loss in activity. The photocatalyst may also be regenerated with ease, for example by simple changes to the pH of a catalyst mixture.

30 The rate of substrate degradation, such as biomass degradation, is remarkably high, and the hydrogen evolution that is observed is comparable to that observed for catalysts using purified monosaccharides. However, the photocatalyst of the invention has a significant advantage in that no substrate processing is required in order to obtain the hydrogen
35 product.

A photocatalyst may be used to generate hydrogen without photocorrosion and without the need to use noble metal co-catalysts.

In a general aspect there is provided a photocatalyst and the use of the photocatalyst to
40 degrade organic materials and/or to generate hydrogen. The photocatalyst has a semiconductor core with a hydroxide- and/or oxide-functionalised surface, which may be referred to as an oxygenated surface.

Accordingly, in a first aspect of the invention there is provided a method for degrading an organic substrate, the method comprising the step of exposing a photocatalyst of the invention to visible and/or ultraviolet light in the presence of the organic substrate. The degradation of the organic substrate may produce hydrogen, and the hydrogen is optionally collected.

In a second aspect of the invention there is provided a method for producing hydrogen, the method comprising the step of exposing a photocatalyst of the invention to visible and/or ultraviolet light in the presence of the organic substrate. The method may also comprise the step of collecting the hydrogen. Carbon dioxide or an organic compound, such as a carboxylic acid, is optionally produced in this method.

In the methods of the invention, the photocatalyst and the organic substrate may be provided as an aqueous mixture, and typically a basic aqueous mixture. The aqueous mixture may have a pH of at least pH 10, such as at least pH 11, such as at least pH 12. Where carbon dioxide is produced, it may be provided as carbonate in the aqueous mixture. Any hydrogen that evolves in the methods of the invention is therefore substantially free of carbon dioxide.

The organic substrate may be or comprise a hydroxyl-functionalised compound, such as a hydroxyl-functionalised compound having a molecular weight of 50 or more, such as 500 or more. The organic substrate may be or comprise a polyol.

The organic substrate may be or comprise an oligosaccharide or a polysaccharide, such as cellulose, and preferably the organic substrate may be or comprise a polysaccharide.

The organic substrate may be a biomass, such as wood, paper, cardboard or grass. The organic substrate may contain cellulose and lignin.

The organic substrate may be selected from the group consisting of general waste, plastics, packing materials, waste food, aliphatic polyols, algae, sugars, starches, biomass, sewage and/or domestic waste.

The organic substrate may be mechanically processed, such as chopped (including chipped), prior to use in the methods of the invention. However, in the preferred method of the invention no mechanical processing is required, and the organic substrate may be used directly.

The organic substrate may be pre-treated, for example with an aqueous base, to at least partially degrade the organic substrate and/or to improve the aqueous solubility of the organic substrate. Such a pre-treatment is associated with an increased hydrogen evolution rate in the subsequent photocatalytic reaction.

Additionally or alternatively, the organic substrate may be an organic polymer, such as a polymer having hydroxyl, ester, amide, ether, carbonate, and/or urethane functionality, either in the backbone chain or a side chain.

The organic polymer may be selected from polyester, substituted polyethylene, polyether, polycarbonate, and polyurethane.

5 The organic substrate may be a polymer selected from the group consisting of poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), poly(vinyl pyrrolidone) (PVP), and poly(ethylene glycol) (PEG). Additionally or alternatively, the organic substrate may be selected from the group consisting of polyurethane (PUR), a polypeptide and a polysaccharide. Optionally the polymer may be further selected from low density polyethylene (LDPE), polyvinyl chloride (PVC), poly(methyl methacrylate), polystyrene (PS) and polycarbonate. Here, the polymers
10 may require pre-treatment, such as with aqueous base, prior to the photocatalytic reaction.

The organic polymer may have a molecular weight of 500 or more, such as 1,000 or more, such as 5,000 or more.

15 The incident light may be ultraviolet light, such as light having a wavelength in the range from 100 to less than 400 nm, and it may be visible light, such as natural light (such as sunlight), such as light having a wavelength in the range from 400 to 700 nm, or a combination of visible and ultraviolet light, such as natural light (such as sunlight, which has visible and UV components). The incident light may be a combination of natural and non-natural light.

20 The intensity of the light may be in the range 1 to 150 mW/cm², such as 10 to 150 mW/cm², such as 50 to 150 mW/cm², such as 90 to 150 mW/cm², such as 130 to 145 mW/cm². The light intensity may be around 100 mW/cm².

In yet another aspect of the invention there is provided a photocatalyst, which may be used in the methods of the invention. The photocatalyst has a passivated surface, such as an
25 oxygenated surface, typically in the form of hydroxide and/or oxide functionality, which is present as a thin layer on the surface of a photocatalytic core material, such as CdS. The core material is a semiconductor material.

30 In a further aspect of the invention there is provided the use of the photocatalyst as a photocatalyst. The photocatalyst may be for use under incident visible light, including natural light.

The photocatalyst may have a passivated surface.

35 The photocatalyst may have an at least partially oxygenated, surface, such as a surface that is at least partially functionalised with hydroxide- or oxide-functionality.

The core material may generally consist essentially of one or more metals with one or more chalcogenides. Thus, the core may have a mixed metal combination.

The core material of the photocatalyst may consist essentially of a metal sulfide or a metal selenide, such as CdS or CdSe. The core material of the photocatalyst may consist
40 essentially of a mixed metal, such as CdTe or ZnTe.

The photocatalyst may be a CdS|CdO_x photocatalyst. The photocatalyst is obtained or obtainable by oxygenation of the surface of CdS, for example under basic aqueous conditions

5 The photocatalyst may be substantially free of precious metals, such as substantially free of Pt, Au, Ag and Pt. The photocatalyst may be substantially free of Ni, Zn and Pt.

Also provided by the present invention is a method of preparing a photocatalyst, the method comprising the step of oxygenating the surface of a semiconductor material, thereby to provide a photocatalyst of the invention.

10 The method may comprise the step of treating the semiconductor material with aqueous base having a pH of at least pH 10, thereby to provide a photocatalyst of the invention. The photocatalyst is typically retained within a basic aqueous mixture having a pH of at least pH 10.

15 In a further aspect of the invention there is provided a method for regenerating a photocatalyst, where the photocatalyst is provided in an aqueous mixture, such as a basic aqueous mixture, the method comprising the step of increasing the acidity of the mixture (lowering the pH), and then subsequently increasing the basicity of the mixture (increasing the pH), thereby to provide the photocatalyst.

Summary of the Figures

25 Figure 1 shows (a) a schematic of lignocellulose showing cellulose surrounded by the less crystalline polymers hemicellulose and lignin; (b) a schematic of photocatalytic degradation of lignocellulose to H₂ on a photocatalyst of the invention, where semiconducting CdS is coated with CdO_x (the CdO_x surface is believed to contain some -OH functionality, but H atoms are omitted for clarity); (c) images of biomass substrates degraded in the presence of a photocatalyst of the invention.

30 Figure 2 shows (a) a TEM image of ligand-free CdS particles (quantum dots); (b) the size distribution (counts per particle size (nm)) of the ligand-free CdS particles shown in (a); (c) the change in binding energy (eV) for CdS particles untreated and treated with aqueous KOH (M); (d) the Raman spectra of ligand-free CdS particles with 514 nm excitation at different KOH concentrations, which is shown as change in normalised Raman intensity with change in Raman shift (cm⁻¹). The peaks at 305 cm⁻¹ and 604 cm⁻¹ are attributed to LO and 2LO phonon scattering of CdS; (e) the Raman spectra of ligand-free CdS in 10 M KOH and in water, which is shown as change in normalised Raman intensity with change in Raman shift (cm⁻¹). In 10 M KOH an interfering spectral signature of CdO can be identified. The
35 reference spectrum of CdO is shown in purple; (f) a TEM image of CdS|CdO_x particles obtained from treatment of CdS particles with 10 M KOH; (g) the size distribution (counts per particle size (nm)) of the CdS|CdO_x particles of (f); (h) the change in Zeta potential (mV) for
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CdS particles with change in pH, when particles untreated and treated with aqueous KOH; (i) the change in relative photoluminescence with change in wavelength (nm) for a range of CdS particles untreated and treated with aqueous KOH (M).

- 5 Figure 3 shows (a) the H₂ evolution ($\mu\text{mol H}_2/\text{nmol catalyst}$ after 18 h.) in a cellulose degradation reaction using a photocatalyst, where the photocatalyst was generated from CdS particles untreated and treated with aqueous KOH at different concentrations (M); (b) the H₂ evolution ($\text{mmol H}_2/\text{g catalyst}$) over time (days) with and without the presence of the substrate cellulose, in the presence of a photocatalyst of the invention; (c) the ¹³C-NMR
- 10 spectra of the supernatant from a suspension of ¹³C-labelled cellulose (after 3 days irradiation) with and without a photocatalyst of the invention. Photocatalysis was carried out under simulated solar light (AM 1.5G, 100 mW cm⁻²).

- 15 Figure 4 shows (a) the H₂ evolution ($\text{mmol H}_2/\text{g catalyst h}^{-1}$) in a biomass degradation reaction using a photocatalyst of the invention, where the substrate was, from left to right, α -cellulose, hemicellulose (xylan) and lignin; (b) the H₂ evolution ($\text{mmol H}_2/\text{g catalyst h}^{-1}$) in a biomass degradation reaction using a photocatalyst of the invention, where the substrate was, from left to right, printing paper, cardboard, newspaper, wooden branch, bagasse, grass and sawdust. All values are background corrected by the activity without substrate.

- 20 Figure 5 is a schematic showing the proposed mechanism of lignocellulose reforming on a photocatalyst of the invention, illustrating lignocellulose degradation to carbonate (CO₃²⁻) and H⁺ reduction to H₂ upon irradiation.

- 25 Figure 6 are X-ray photoelectron spectra of CdS untreated and treated with aqueous KOH (0.1 M and 10 M KOH), in the region of (a) O (1s) and (b) S (2p). The spectra show the change in normalised intensity with change in binding energy (eV).

- 30 Figure 7 is a series of Raman spectra where (a) is the Raman spectra of ligand-free CdS QDs (10 μM) under 514 nm excitation at different concentrations of KOH and reference spectra of Cd(OH)₂, CdO and KOH (wet and dry). Overlapping bands of CdO in the reference spectrum and in the spectrum of CdS in 10 M KOH are denoted by the dashed lines; and the band deconvolution of the LO band at 305 cm⁻¹ (highlighted in red) of CdS in different media are presented in (b) at 0 M KOH, (c) at 0.1 M KOH and (d) at 10 M KOH.
- 35 Arising bands with increasing KOH concentration are indicated with arrows (frequencies are 260 cm⁻¹; 292 cm⁻¹; 365 cm⁻¹, blue lines) and associated with the presence of CdO. The Raman spectra show the change in normalised Raman intensity (a.u.) with change in Raman shift (cm⁻¹).

- 40 Figure 8 shows the X-ray diffraction patterns for CdS QDs after isolation from pH 7 (bottom) and pH 15 (top) solutions, alongside the diffraction pattern expected from cubic CdS. The spectra show change in intensity with change in 2θ (°).

Figure 9 is a series of UV-visible and photoluminescence emission spectra where (a) is the spectra for CdS in DMF (0.72 μM , lower line) and CdS|CdO_x (0.72 μM in 10 M KOH, upper line), as recorded at room temperature; (b) is the spectra for CdS|CdO_x QDs in 10 M KOH (0.72 μM) and photoluminescence emission spectra (excitation/emission bandwidth = 5 nm) at an excitation wavelength of 360 nm of CdS QDs (0.5 μM) at room temperature. The UV-visible spectra show the change in normalised absorbance with change in wavelength (nm). The photoluminescence emission spectra show the change in photoluminescence intensity with change in wavelength (nm).

Figure 10 shows the mass spectra of headspace gases collected after a 24 h treatment of α -cellulose (50 mg/mL) with CdS|CdO_x (0.5 μM) in aqueous NaOH (2 mL, 9.75 M) or NaOD (2 mL, 9.75 M) in D₂O, under an anaerobic atmosphere. The incident light was simulated solar light (AM 1.5G, 100 mW cm⁻²). The background trace was collected by opening the sampling inlet to air. The spectra show change in normalised intensity with change in m/z.

Figure 11 shows H₂ evolution (μmol) over time (h) for photocatalytic experiments using suspended cellulose (top line) or the supernatant of a cellulose suspension (bottom line) using CdS|CdO_x QDs (0.5 μM) under an anaerobic atmosphere at 25°C with 50 mg mL⁻¹ suspended α -cellulose or suspension free α -cellulose in 1 mL aqueous 10 M KOH.

Figure 12 is a series of NMR spectra where (a) is the ¹H NMR spectrum of a filtered sample collected from a mixture of α -cellulose (100 mg/mL) and CdS|CdO_x (1 μM) in 10 M NaOD/D₂O (2 mL) following a 3 day irradiation (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere; (b) is a ¹³C NMR reference spectrum of NaCO₂H in 10 M NaOD/D₂O; (c) is a ¹³C NMR reference spectrum of Na₂¹³CO₃ in 10 M NaOD /D₂O; (d) is a ¹³C NMR reference spectrum of 5-(hydroxymethyl)furfural in 10 M NaOD in D₂O; and (e) is a ¹³C NMR spectrum of ¹³C-cellulose in ZnCl₂ (1.00 g), LiCl (200 mg) and D₂O (360 μL) after 12 hours irradiation (AM 1.5G, 100 mW cm⁻²) either with or without CdS|CdO_x QDs (1 nmol) at 25°C under an anaerobic atmosphere. New peaks are indicated by the shaded regions. The spectra show changes in relative intensity with change in chemical shift (δ , ppm).

Figure 13 shows (a) the H₂ evolution ($\mu\text{mol H}_2$) over time (h) from a mixture of α -cellulose (50 mg/mL) and CdS|CdO_x (0.5 μM) in aqueous KOH (2 mL, 10 M) following irradiation (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere. The reactions were conducted in the absence or presence of different concentrations of Co(BF₄)₂ (0.17 to 1.4 mM); and (b) the H₂ evolution (mmol_{H₂}/g_{CdS}) over time (days) from a mixture of α -cellulose (50 mg/mL) and CdS|CdO_x (0.5 μM) in aqueous KOH (2 mL, 10 M) following irradiation (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere. The reactions were conducted in the absence (squares) or presence of Co(BF₄)₂ (0.34 mM, circles). A control experiment with the co-catalyst and without α -cellulose was also performed (triangles).

Figure 14 is the X-ray photoelectron spectrum of CdS|CdO_x (3.15 μM) and Co(BF₄)₂ (0.34 mM) in aqueous KOH (10 M, 2 mL) following irradiation with monochromatic light (450 nm, 5 mW cm⁻²) for 5 min under an anaerobic atmosphere. The spectrum is of the Co (2p) region. The spectrum shows the change in normalised intensity with change in binding energy (eV).

Figure 15 is the UV-visible spectra of CdS|CdO_x (0.5 μM) in aqueous KOH (2 mL, 10 M, top line), and lignin (0.25 mg/mL) in aqueous KOH (2 mL, 10 M, bottom line). The spectra show the change in normalised absorbance (a.u.) with change in wavelength (nm).

Figure 16 shows (a) the UV-visible spectra of lignin (0.25 mg mL⁻¹) in aqueous KOH (10 M, 2 mL) without (blue and pink traces) or with (red and black traces) CdS|CdO_x (0.5 μM) after various periods of irradiation (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere. The mixtures were filtered before the measurement to remove CdS|CdO_x; (b) the change in absorbance at 300 nm over time (days) for the mixtures in (a) with and without CdS|CdO_x; and (c) the change in absorbance at 350 nm over time (days) for the mixtures in (a) with and without CdS|CdO_x. The absorbances in (b) and (c) were calculated by subtracting the peak absorbance by the absorbance at the base of the peaks.

Figure 17 shows (a) the photoluminescence emission spectra (bandwidth 2 nm) at an excitation wavelength of 315 nm (bandwidth 2 nm) for 10 mM terephthalic acid solution (2 mL) with CdS (0.5 μM) at various pH (adjusted by adding 0 to 5 M KOH) after 18 hours of irradiation (AM 1.5G, 100 mW cm⁻², λ > 420 nm). The background spectrum of 10 mM terephthalic acid was taken at pH 5.2 after 18 hours of irradiation without CdS. The emission at 420-430 nm arises from 2-hydroxyterephthalic acid; and (b) selected spectra from (a) relative to 1 mM 2-hydroxyterephthalic (2 μmol) at various pH values (pH 5.2, 12.9 and 13.9).

Figure 18 is a series of photoluminescence emission spectra (bandwidth 2 nm) at an excitation wavelength of 315 nm (bandwidth 2 nm) of a 10 mM terephthalic acid solution (2 mL) before and after exposure to ·OH through the photolysis of 0.5 mM H₂O₂ where the spectra show the recorded intensity for reactions conducted in (a) 1 mM KOH (pH 5.2); (b) 0.1 M KOH (pH 12.9); and (c) 5 M KOH (pH 14.7). Photolysis was induced during each measurement by the excitation beam. A 100% photolysis yield would generate a maximum of 2 μmol of ·OH, but the actual yield will be much lower than this value. A peak from 2-hydroxyterephthalic at 430 nm arises after addition of H₂O₂ in all cases. This does not differ significantly from the background of terephthalic acid (410 nm) as only minimal amounts of the 2-hydroxyterephthalic are present, but the peak is clearly distinguishable. These controls confirm that even minimal ·OH formation is detectable by the probe.

Figure 19 is (a) a TEM image of an α -cellulose film obtained from a mixture of α -cellulose (50 mg/mL) with CdS|CdO_x (0.5 μ M) in 10 M KOH (2 mL) after 18 hours of photocatalysis (AM 1.5G, 100 mW cm⁻²) under an anaerobic atmosphere; and (b) a close up of (a) showing CdS|CdO_x embedded in the film. The scale bars are 100 nm (a) and 20 nm (b).

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Figure 20 shows the hydrogen evolved (μ mol H₂) from different polymers (between 20 to 200 mg) in the presence of CdS|CdO_x (0.5 μ M) in aqueous KOH (2 mL, 10 M) following irradiation (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere after 24 hours. Error bars assume 10% error in the measurement.

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Figure 21 is the hydrogen evolution (μ mol H₂) from different polymers (around 100 mg) in the presence of CdS|CdO_x (0.5 μ M) in aqueous KOH (2 mL, 10 M) following irradiation (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere after 24 hours, with and without the addition of Co(BF₄)₂ (0.25 mM).

15

Figure 22 is the hydrogen evolution (μ mol H₂) from different substrates (100 mg PVP or α -cellulose) in the presence of CdS|CdO_x (0.5 μ M) and Co(BF₄)₂ (0.25 mM) in aqueous KOH (2 mL, 10 M) following irradiation (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere after 24 hours, with and without heat-treatment of the substrate prior to photocatalysis (1 h stirred at 100°C in 10 M aqueous KOH).

20

Figure 23 is the hydrogen evolution (μ mol H₂ after 4 h irradiation) from different substrates (100 mg for each) in the presence of CdS|CdO_x (0.5 μ M) in aqueous NaOH (10 M) or following irradiation (AM 1.5G, 100 mW cm⁻²). Hydrogen evolution is shown without and with pre-treatment of the substrate prior to irradiation (24 h stirring in 10 M NaOH at 40°C, followed by centrifugation and removal of the precipitate).

25

Figure 24 is the hydrogen evolution (μ mol H₂ after 4 h irradiation) from different substrates (100 mg for chitin, chitosan, casein and BSA) in the presence of CdS|CdO_x (0.5 μ M) and in aqueous NaOH (10 M) following irradiation (AM 1.5G, 100 mW cm⁻²).

30

Figure 25 is the hydrogen evolution (μ mol H₂ after 4 h irradiation) from different substrates (100 mg for chitin and chitosan) in the presence of CdS|CdO_x (0.5 μ M) and in aqueous NaOH (10 M) following irradiation (AM 1.5G, 100 mW cm⁻²). The organic substrates are pre-treated prior to irradiation (24 h stirring in 10 M NaOH at 40°C, followed by centrifugation and removal of the precipitate).

35

Figure 26 is a series of ¹H NMR spectra for (a) polylactic acid (PLA) and the intermediate degradation product, lactic acid (LA), (b) PET and its intermediate degradation products terephthalic acid (TA) and ethylene glycol (EG), and (c) polyurethane, where each polymer sample is shown before and after photoreforming (PR) of that sample. The photoreforming

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was carried out for 24 hours in 10 M NaOD in D₂O under simulated solar light (AM 1.5G, 100 mW cm⁻²).

5 Figure 27 is the hydrogen evolution (μmol H₂ after 4 h irradiation) from PET that has been pre-treated with base under conditions A to F or not pre-treated, prior to photoreforming in the presence of CdS|CdO_x (0.5 μM) in aqueous NaOH (10 M) following irradiation (AM 1.5G, 100 mW cm⁻²).

10 Figure 28 is the hydrogen evolution (μmol H₂ after 4 h irradiation) from different substrates (100 mg PET or α-cellulose) in the presence of CdS|CdO_x (0.5 μM) in aqueous KOH (10 M) or aqueous NaOH (10 M) following irradiation (AM 1.5G, 100 mW cm⁻²).

Detailed Description of the Invention

15 The present inventors have found that a particular class of photocatalysts may be used to degrade organic substrates under visible light, such as to provide hydrogen and optionally other products, including carbon dioxide, such as in the form of a carbonate.

20 Generally, a photocatalyst of the invention comprises a semiconductor core, such as a metal- or metal-containing core, which may be a mixed metal-containing core, the outer surface of which is oxygenated (passivated), and more specifically may have metal hydroxide and/or metal oxide functionality. The photocatalyst may be prepared from a metal-containing substrate by oxygenation (passivation) of the metal surface. The photocatalyst may be regarded as having an at least partial oxide and/or hydroxide coating.
25 Typically the core consists essentially of a metal sulfide or a metal selenide.

The oxygenation of the surface alters the catalytic activity of the material, such as to provide or improve the photocatalytic activity. The worked examples in the present case show that incorporating oxide- and hydroxide-functionality into CdS surfaces provides an oxygenated
30 material, referred to herein as CdS|CdO_x, having excellent photocatalytic activity against a broad range of organic substrates, including unreformed biomass.

The passivation of metal sulfides has previously been described, though these materials are not shown to be useful for the treatment of biomass.

35 For example, Kalisman *et al.* (*Nano Lett.* 2016, 16, 1776) have described the preparation of nanoparticle photocatalysts having CdSe embedded within CdS, with a Pt-reduction catalyst located on a tip of the material. The photocatalyst is used at high pH, and this is observed to shift the valance band of the CdS material. The use of the photocatalyst at high pH
40 exponentially increases the catalytic activity. The photocatalyst is used to generate hydrogen, with isopropyl alcohol provided as an electron donor in the reaction mixture.

Simon *et al.* (*Nat. Mater.* 2014, 13, 1013) described the use of cadmium sulfide nanorods that are decorated with Ni nanoparticles. The nanorods were dispersed into basic hydroxide solutions of varying pH together with ethanol. The photocatalytic generation of hydrogen from the resulting mixture was seen to increase significantly with increases in pH.

5

Petrov *et al.* (*J. Phys. Chem. B* 2002, 106, 5325) describe the preparation of CdS nanocrystals which optionally contain Zn. The CdS surfaces of the nanocrystals were passivated by treatment with aqueous base. The use of the nanocrystals as a photocatalyst is not described.

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CN 102181283 describes the preparation of nanowires from CdS/CdO nanocrystals, which is treated in order to generate hydroxyl functionality. This document does not apparently describe the use of the photocatalyst for degrading organic substrates or for generating hydrogen.

15

Anku *et al.* describe the use of a ZnS/ZnO composite as a photocatalyst. However, Anku *et al.* use such materials doped with Ni. The photocatalyst of the present invention typically does not include materials that are doped with metals such as Ni. Anku *et al.* do describe the use of the ZnS/ZnO composite to catalyse the degradation of an organic dye under visible light. There is no mention by Anku *et al.* that the photocatalyst could be used to degrade biomass, or that they could be used specifically to generate hydrogen.

20

Emin *et al.* describe the preparation of ZnS microspheres that are subsequently heat treated to give ZnO microspheres. Intermediate mixed products, of the type ZnS/ZnO, were also formed and studied. These materials are shown to have use as photocatalysts for the degradation of an organic dye under incident UV light. Emin *et al.* do not suggest that the catalysts could or would be useful for generating hydrogen, nor for degrading biomass.

25

30 *Photocatalyst*

The photocatalyst of the invention is a material, which may be in the form of a particle, having an oxygenated surface. Typically the material is a semiconductor material, and the properties of the semiconductor are modified by the oxygenation of that surface, which introduces oxide and/or hydroxide functionality to the surface. The treatment of the semiconductor material (or precursor material) may have the effect of altering the surface charge of the material, such as to increase the negative surface charge.

35

The oxygenation of the surface may result in other changes. For example, the electron binding energy of the precursor material at the surface of the material (for example, as measured by XPS) may change. Here, the electron binding energy may refer to that of a metal, such as Cd, that is present within the material, and is present within the surface layer,

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for example present within 10 nm of the surface. Typically, the oxygenation of the surface may be associated with a reduction in the binding energy for the metal. This is observed in the present case where the electron binding energies for Cd decrease with oxygenation.

- 5 Spectral characterisation of the material may show evidence for oxygenated metal on the surface, for example through its identification using Raman spectroscopy. In the worked examples of the present case the oxygenation of CdS is seen to result in a product having CdO bonds.
- 10 Also observed on oxygenation of the surface is an alteration in the photoluminescent properties of the semiconductor, particularly within the visible range, with the development of emissions within this range.

15 The photocatalyst of the invention is typically a particle, such as a nanoparticle. Thus, the average largest dimension, such as the diameter, of the photocatalyst may be at most 7, at most 10, at most 25, at most 50, at most 100, or at most 250 nm.

The average largest dimension, such as the diameter, of the photocatalyst may be at least 0.1, at least 0.5, at least 1, or at least 5 nm.

20 The average largest dimension, such as the diameter, of the photocatalyst may be within a range with the upper and lower limits selected from the values given above. For example, the average largest dimension, such as the diameter, of the photocatalyst may be in the range 1 to 100 nm.

The particle size may be about 4 nm or about 5 nm.

25 The size of a particle may be determined by, for example, measurements taken from the transmission electron microscopy imagery of the particle or measurements based on the UV-visible absorption spectrum of the particle. Such measurements are described in the worked examples. Particle size may also be determined by dynamic light scattering (DLS).

30 The photocatalyst particle may have a low size distribution. For example, the standard deviation may be at most 0.5%, at most 1%, at most 2%, at most 3%, at most 4%, at most 5%, at most 10%, at most 15%, at most 20%, or at most 25%.

35 The worked examples in the present case show that a photocatalyst of the invention may be prepared from a precursor material, such as CdS, having a low size distribution (such as a distribution with the limits set out above), resulting in a photocatalyst product having a substantially unaltered size distribution. Thus, the methods of preparation are not associated with a significant loss of homogeneity in the material.

40 The inventors have found that the size of the particles may be altered very slightly by the passivation treatments described herein. However, the change in size, which is typically a

reduction in size, is very small and is uniform cross the population. Consequently the homogeneity in the sample is retained.

5 The photocatalyst has a negatively charged surface, which is formed by the oxygenation, of the surface of the precursor material.

10 The photocatalyst has an oxygenated surface that may be generated under basic conditions. The surface may contain metal hydroxide and/or metal oxide functionality, and the recorded zeta potential is negative. The inventors have found that the zeta potential of the photocatalyst of the invention is relatively large (that is, large and negative). Increasing the surface metal hydroxide and/or metal oxide content increases the magnitude of the zeta potential.

15 In the worked examples of the present case a significant increase in the zeta potential is observed during the treatment of CdS particles with strong aqueous base. Where the basic aqueous mixture has a pH of 11 or more, there is a significant alteration in the zeta potential, which becomes considerably more negative at higher pH values.

20 The photocatalyst may be regarded as having a surface that is oxygenated (passivated). As noted above, the surface may contain hydroxide and/or oxide groups, such as metal hydroxide and/or metal oxide groups. The hydroxide and/or oxide functionality may be present across at least part of the available surface area, and it may be present across the entire surface.

25 The oxygenated surface need not, and typically does not, extend far into the bulk of the metal substrate. The oxide and/or hydroxide functionality may be a thin layer, perhaps a few atoms only, that is provided at the surface of the photocatalyst. In one embodiment, the oxygenated surface is not more than 10 nm deep, and may be no more than 5 nm deep, such as no more than 1 nm deep.

30 The extent of the oxygenated surface may be determined in part from XPS analysis of the photocatalyst. Here, the presence of the oxygenated surface may be seen from the change in the electron binding energies observable in the XPS spectrum. The presence of a relatively thin oxygenated surface layer may be inferred from the presence of binding energy peaks associated with the core, bulk material, such as the metal. Such signals are observable only when the oxygenated surface layer is thin, as XPS experiments can generally only provide information regarding the uppermost (such as within 1 to 10 nm) surface of the tested material.

40 Direct study of the oxygen environment by XPS (for example O 1s) may be difficult: the inventors have found that the use of hydroxide base as the oxide source generates residual hydroxide at the sample surface, and this residual hydroxide dominates the signal.

Whilst the XPS analysis may focus on the metal environment of the photocatalyst, other environments may be analysed, where such are present. For example, many photocatalysts of the invention have a core that contains both metal and sulfur as a metal sulfide, and the sulfur environment at the surface may be considered.

Raman spectroscopy may also be used to analyse the surface of a photocatalyst. Vibrational bands that are associated with oxide- and/or hydroxide-functionality, such as metal oxide and/or metal hydroxide, at the surface of the photocatalyst may be visible in the Raman spectrum.

In the worked examples of the present case, a photocatalyst having a CdS core and an oxygenated surface is prepared and used to degrade cellulose and cellulose-containing biomass. Here, the oxygenated surface comprises Cd-OH and/or Cd-O (which may be Cd-O⁻) functionality (metal hydroxide and metal oxide functionality respectively). Raman measurements of the photocatalyst give rise to vibrational bands associated with Cd-O (for example in comparison to a reference spectrum of CdO (bulk)).

The photocatalyst may comprise a material that is selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, CuI₃GaS, Cd_(1-x)Zn_(x)S_(1-y)Se_(y), CuGa₃S₅, ZnO_(1-x)S_(x), FeS₂, SiC, CuO, SnS₂, SnSe and carbon nanoparticles. The surface of these materials is oxygenated. Here, the material may be regarded as core material, with a coating that is the oxygenated surface. The oxygenated surface may comprise hydroxide and oxide functionality bonded with the metal or other atoms at the surface. Thus, the surface may have metal hydroxide and/or metal oxide groups. Where S and Se is present within the material, these may be displaced by O at the surface.

The photocatalyst may have an oxygenated surface containing a material that is selected from the group consisting of ZnO, TiO₂, Al₂O₃, and SnO₂, and combinations thereof. These materials may be provided onto a core material, such as a semiconductor, in the form of a precursor material that is subsequently oxygenated to give the ZnO, TiO₂, Al₂O₃, and SnO₂ forms, for example. For example, ZnO may be obtained from ZnS and TiO₂ may be obtained from TiCl₄.

The photocatalyst of the invention may be substantially free of additional metals, such as Pt, Zn and Ni. The beneficial photocatalytic effects may be achieved without the need for the addition of such metals. However, additional metals, such as Pt, Zn, Co and Ni, may be present to enhance the photocatalytic effect. Thus, in one embodiment, the photocatalyst of the invention, such as a CdS-based photocatalyst, is doped with such metals.

Other metals may be use in place of Cd, in alternative sulfur-based systems. For example, the photocatalyst may be based on CdS, ZnS, PbS, or FeS₂. Mixed-metal sulfur-based

systems may also be used, for example the photocatalyst may be based on CuInGaS , CuGa_3S_5 or $\text{ZnO}_{(1-x)}\text{S}_{(x)}$, where x is typically in the range 0 to 1.

5 Sulfur may be replaced with selenium in the photocatalyst, or the photocatalyst may contain a mixture of both sulfur and selenium. For example the photocatalyst may be based on CdSe , ZnSe , or PbSe , or combinations thereof.

10 Mixed metal sulfides and selenides may be used. For example, $\text{Cd}_{(1-x)}\text{Zn}_{(x)}\text{S}_{(1-y)}\text{Se}_{(y)}$ may be used, where x is typically in the range 0 to 1 and y is in the range 0 to 1, such as where x is 0.5, and such where y is 0.5.

15 As an alternative to the systems described above, which are based on metal sulfides and/or metal selenides, a mixed metal material may be used as the photocatalyst core. For example, the photocatalyst may be based on CdTe , ZnTe , or PbTe , or combinations thereof.

20 As a further alternative, non-metal-based materials may also be used, including in particular SiC and carbon nanoparticles (also known as carbon quantum dots). Additionally or alternatively, the non-metal-based material may be selected from carbon nitride and silicon nanoparticles.

25 In each case, the photocatalyst has a core of one or more of the materials described above, the surface of which is passivated, or oxygenated. In a preferred embodiment, the core of the material consists essentially of a material as described above. Thus, additional components, such as additional metals, are preferably not present.

30 The photocatalyst of the invention may be prepared directly from the base material by treating the surface of that material, such as oxygenating the surface thereby to provide the oxygen functionality. The surface is typically hydroxide- and/or oxide-functionalised.

35 In one embodiment the photocatalyst has a band gap of 3.0 eV or less, such as 2.7 eV or less, such as 2.5 eV or less. The band gap of the photocatalyst may be determined by standard methods.

40 The photocatalyst of the invention has catalytic activity when exposed to visible light. The photocatalyst is capable of catalysing the degradation of cellulose under aqueous conditions under incident visible light, for example to generate hydrogen, such as to generate hydrogen at a rate of at least 0.1, at least 0.5, at least 1.0, at least 2.0 or at least 5 $\text{mmol g}_{\text{cat}}^{-1}\text{h}^{-1}$.

45 The photocatalyst may not have a ligand bound to its surface. Ligands may be present on the semiconductor material from which the photocatalyst is prepared, but these are displaced in the oxygenation of the material.

Without wishing to be bound by theory, it is thought that the photocatalyst coating - the oxidation layer at the surface of the semiconductor material - reduces photocorrosion and extends the lifetime of the photocatalyst. The photocatalyst coating is preferably equal to or less than 1 nm in thickness.

5

Basic Aqueous Mixture

The photocatalyst is typically provided and used in a basic aqueous mixture. The photocatalyst is suspended in the mixture.

10

A basic aqueous reaction mixture may be used to form the oxygenated surface on the photocatalyst, and retaining the product photocatalyst in that basic aqueous mixture can maintain that oxygenated surface, for example during the use of the photocatalyst in the methods of the invention.

15

The aqueous mixture is basic and the aqueous mixture may have a pH of 10 or more, such as 11 or more, such as 12 or more, such as 13 or more, such as 14 or more.

A high basicity (high pH) is associated with extensive oxide/hydroxide formation, and a higher degradation rate in the degradation reaction described herein, and a higher hydrogen evolution rate. The inventors have found that the highest rates of degradation are generally achieved when the pH of the aqueous mixture is pH 11 or more, and most preferably pH 12 or more, such as pH 14 or more. The degradation and evolution reactions may occur when the aqueous mixture is less basic (lower pH), however the rate is significantly lower than the rates achieved at higher pH values.

25

The increase in pH is associated with an increase in the surface passivation of the photocatalyst.

The inventors have also found that the increase in pH is associated with an increase (larger negative value) in the Zeta potential of the photocatalyst. Unexpectedly, there is a large increase (toward more negative values) in the Zeta potential at around pH 11, such as for a photocatalyst based on CdS. The changes in Zeta potential here show a substantial increase in the negative surface charge of the photocatalyst, and this is associated with a substantial increase in the photocatalytic activity of the material.

35

A reduction in the basicity of the aqueous mixture may be associated with a reduction or loss of the oxygenated surface, therefore the pH of the aqueous basic mixture may be maintained at a level sufficiently high to maintain the oxygenated surface and therefore to maintain the beneficial photocatalytic activity.

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The pH of the aqueous mixture may be adjusted as required, such as the pH increased, for example by the addition of further base to the aqueous mixture.

5 In the methods of the invention, an organic substrate may be degraded with the resulting production of a carbon dioxide product and/or an organic product, such as a low molecular weight organic compound. Here, where carbon dioxide is generated, the carbon dioxide product may be dissolved into the aqueous mixture as carbonate. As such, the carbon dioxide may be regarded as sequestered in the aqueous mixture. This may result in a change in the pH of the aqueous mixture. Suitable adjustment of the pH level may be
10 required.

In the worked examples of the present case the amount of carbon dioxide generated in the degradation reaction (as carbonate) was not of a level sufficient to significantly alter the pH of the basic aqueous mixture, therefore it was not necessary to make any adjustments to the
15 pH of the basic aqueous mixture during the course of the degradation reaction.

The use of high pH may also promote the dissolution of the organic substrate, thereby promoting the interaction between the photocatalyst and the substrate. This is shown in the worked examples, where high pH solutions promote the dissolution of lignocellulose. As described herein, a pre-treatment of the organic substrate with, for example, aqueous base,
20 may improve the dissolution of the organic substrate.

A reduction in basicity may be used to deliberately remove the oxygenated surface in a regeneration method. After removal of the oxygenated surface, the photocatalyst may be regenerated by an increase in basicity, which provides a new oxygenated surface. The
25 photocatalytic activity may be restored in this way.

The basic solution contains the photocatalyst, which may be present at a concentration selected for an appropriate rate of reaction for the degradation reaction.

30 The inventors have found that the photocatalyst of the invention may be used at relatively low concentrations with a sufficiently high rate of substrate degradation and a sufficiently high rate of hydrogen evolution and/or carbon dioxide (which may be carbonate generation) or organic product generation.

35 The photocatalyst may be used at relatively low concentrations and at relatively low levels with respect to the organic substrate. At these concentrations and levels the rate of organic substrate degradation and the rate of hydrogen evolution and/or product generation, such as carbon dioxide generation (for example as carbonate), is relatively high. Minimising the amount of photocatalyst required in the methods of the invention will clearly minimise the
40 processing cost.

The photocatalyst may be present in the basic aqueous mixture at a concentration of at least 1.0, at least 5.0, at least 10, at least 50 or at least 100 nM. The photocatalyst may be present in the basic aqueous mixture at a concentration of at most 0.5, at most 1.0, at most 5.0, at most 10, at most 50, at most 100, at most 500 at most 1,000 or at most 5,000 μM .

- 5 The photocatalyst may be present in the mixture at a concentration within a range where the lower and upper limits are selected from the values given above. For example, the photocatalyst may be present at a concentration in the range 50 nM to 1.0 μM .
The photocatalyst may be present in the mixture at a concentration of around 0.5 μM .
For the values given above, concentration refers to nanomoles of photocatalyst particles per
10 litre.

The photocatalyst may be present in the basic aqueous mixture at a concentration of at least 0.01 wt %, at least 0.05 wt %, or at least 0.1 wt % with respect to the total amount of organic substrate in the basic aqueous mixture.

- 15 The photocatalyst may be present in the basic aqueous mixture at a concentration of at most 0.5 wt %, at most 1.0 wt %, at most 5.0 wt %, at most 10 wt %, or at most 20 wt % with respect to the total amount of organic substrate in the basic aqueous mixture.
The photocatalyst may be present in the mixture at a concentration within a range where the lower and upper limits are selected from the values given above. For example, the
20 photocatalyst may be present at a concentration in the range 0.1 to 10 wt %, such as 0.1 to 1.0 wt %.

- The amount of photocatalyst present in the basic aqueous mixture may be based on the amount of precursor material that is added to the basic aqueous mixture during the method
25 of preparation.

The photocatalyst may be used with organic substrates across a wide concentration range. The organic substrate may be provided in the basic aqueous mixture, together with the photocatalyst, at a concentration of at most 50, 75, 100, 150, 200 or 500 mg/mL.

- 30 The organic substrate may be provided in the basic aqueous mixture, together with the photocatalyst, at a concentration of at least 1, 5, 10, 15, 20 or 25 mg/mL.
The organic substrate may be provided in the basic aqueous mixture at a concentration in a range with upper and lower limits selected from the values given above. For example, the organic substrate may be present at a concentration in the range 15 to 100 mg/mL.
35 The organic substrate may be provided in the basic aqueous mixture at a concentration of around 50 mg/mL. The inventors have found that the use of an organic substrate, such as cellulose, at this concentration provides the highest catalytic activity, for example where a CdS|CdO_x photocatalyst is used.

- 40 When the photocatalyst and the organic substrate are present together in the amounts given above, it is possible to degrade the organic substrate under incident visible light, and the degradation rate is sufficiently high as to allow for an efficient degradation of the substrate.

The degradation rate of the organic substrate may be determined from the amount of hydrogen evolved and/or carbon dioxide generated (for example as carbonate) from the reaction mixture during the time course of the degradation reaction.

5 In the worked examples of the present case hydrogen evolution rates determined from the degradation of biomass, such as wood, and α -cellulose and hemicellulose is high. For example, the amount of hydrogen evolved over time with respect to the amount of photocatalyst may be 1 or more, 2 or more, or 5 or more $\text{mmol g}_{\text{cat}}^{-1}\text{h}^{-1}$, such as measured over a 24 h photocatalytic reaction period, where the photocatalyst is used at $0.5 \mu\text{M}$, and
10 the organic substrate is present at 50 mg/mL .

The inventors have found that the quantum yield for the photocatalysts of the invention is relatively high, at around 1.2 %, at 430 nm, which is comparable to the reported efficiencies for the Pt/TiO_2 photocatalyst. It is noted that higher quantum yields are known, but these
15 yields are reported for incident light having a wavelength less than 400 nm, and therefore within the UV-range, and not the visible range.

The present photocatalysts achieve these efficiencies when used to degrade a complex organic substrate, such as cellulose, under visible light, whereas the Pt/TiO_2 photocatalyst
20 achieves the reported efficiencies only when used under UV light.

The pH of the basic aqueous mixture may be determined by standard analytical techniques. Alternatively, the pH of the basic aqueous mixture may be estimated from the amount of base present in (or added to) the aqueous mixture.
25

Use of the Photocatalyst

The present invention provides for the use of the photocatalyst as such, for example in the degradation of an organic substrate. The degradation may also be referred to as
30 reformation or reforming, and more specifically as photoreformation or photoreforming.

Accordingly, the invention provides a method for degrading an organic substrate, the method comprising the step of exposing a photocatalyst of the invention to visible and/or ultraviolet light in the presence of the organic substrate. The photocatalyst and the organic substrate
35 may be provided in an aqueous mixture, and preferably a basic aqueous mixture.

Degradation may refer to a reduction in the molecular weight of the organic substrate due, for example, to the oxidative cleavage of bonds within the organic substrate. The degradation may be accompanied by the formal loss of hydrogen and/or carbon dioxide from
40 the organic substrate.

The methods of the invention also provide for the generation of hydrogen and/or a product such as carbon dioxide (for example as carbonate) or an organic product such as formic acid, the method comprising the step of exposing a photocatalyst of the invention to visible and/or ultraviolet light in the presence of the organic substrate.

5

The photocatalyst and the organic substrate may both be provided in an aqueous mixture. The aqueous mixture may be a basic aqueous mixture, such as a mixture having a pH of 10 or more, such as 11 or more, such as 12 or more, such as 13 or more, such as 14 or more.

10 In the methods for generating hydrogen, the source of hydrogen may be the organic substrate, the basic aqueous mixture or both. The present inventors have found from deuterium experiments that the predominant source of hydrogen is water.

15 In the methods for generating carbon dioxide (or carbonate) the source of carbon is the organic substrate. Similarly, in the methods for generating an organic product, the source of carbon is the organic substrate.

Carbon dioxide may be retained in the reaction mixture, such as the aqueous reaction mixture, for example as the carbonate form. Where carbon dioxide is produced together with hydrogen this ensures that the hydrogen evolved from the mixture is substantially free of carbon dioxide. The methods of the invention therefore provide the possibility of preparing clean hydrogen.

20 The organic product may be retained in the reaction mixture, such as the aqueous reaction mixture, and the organic product may be in ionic form. Example organic products produced in the methods of the invention include formic acid, acetic acid, pyruvic acid, and terephthalic acid, and the ionic, such as anionic, forms thereof.

25 The method may include the subsequent step of collecting the hydrogen and/or a product, such as carbon dioxide or the organic product. Hydrogen may be removed from the headspace over the reaction mixture as it is evolved. Carbon dioxide may be recovered from the basic aqueous mixture, as its carbonate form or as gaseous form, after appropriate processing of the basic aqueous mixture. The organic products may be recovered by standard work-up and purification techniques. This may include recovery of an aqueous solution of the organic product after filtration to remove insoluble components of the reaction mixture.

30 The photocatalyst is active ("excited") under incident light in the visible or ultraviolet range, and preferably the photocatalyst is used under incident visible light. Here, visible light refers to light having a wavelength in the range 400 to 700 nm, and ultraviolet light refers to light having a wavelength in the range 100 to 400 nm, such as 315 to 400 nm.

40

The incident light may be natural light, such as sunlight. Natural light may include light in both the visible and ultraviolet ranges.

The incident light may be artificial light, such as provided by a solar simulator, or light from a xenon or mercury lamp, or an LED. Examples of simulated solar light include AM1.5D,
5 AM1.5G and AM0.

The incident light may be monochromatic.

The incident light may be a combination of natural and artificial light.

10 The methods of the present invention may be performed under light having an intensity that is similar to that of natural light. Thus, in the methods of the invention it is not necessary to expose the photocatalyst to intense light.

The intensity of the incident light may be at most 140, at most 150, at most 160 or at most 200 mW/cm².

15 The intensity of the incident light may be at least 1, at least 10, at least 20, at least 50, at least 70, at least 80, at least 90, or at least 100 mW/cm².

The incident light maybe of an intensity within a range where the upper and lower limits are selected from the values given above. For example, the intensity of the incident light may be in the range 1 to 150 mW/cm², such as 10 to 150 mW/cm², such as 50 to 150 mW/cm², such as 90 to 150 mW/cm², such as 130 to 145 mW/cm².

20 The light intensity may be around 100 mW/cm². In the worked examples of the present case, artificial light of 100 mW/cm² is used (AM 1.5G).

The methods of the invention may be conducted at ambient temperatures, for example at a temperature in the range 5 to 30°C. Accordingly, it is not necessary to apply heat to the
25 reaction mixture in order to promote the reaction. Photocatalytic reactions previously reported in the art described heating the reaction mixture, and such is not required in the methods of the present invention.

30 However, if needed, the methods of the invention may be performed at an elevated temperature, such as a temperature greater than 30°C, and for example at a temperature no more than 60°C, such as no more than 50°C, such as no more than 40°C.

35 Additionally or alternatively, the organic substrate may be pre-heated prior to its contact with the photocatalyst or prior to irradiation, and preferably prior to its contact with the photocatalyst. Typically, the organic substrate is provided in the basic aqueous mixture, for example at a pH of at least 10, such as at least pH 11, and the mixture is heated to a temperature above room temperature, for example a temperature greater than 30°C. The mixture may be a heated to a temperature that is no more than 100°C, such as no more than 80°C, such as no more than 60°C, such as no more than 50°C, such as no more than 40°C

40 The heating of the mixture may be maintained during and after the addition of the photocatalyst, and throughout the catalytic reaction. Alternatively, the heating of the mixture

may be discontinued during or after the addition of the photocatalyst. Indeed, the mixture may be allowed to cool, for example to a temperature in the range 5 to 30°C, prior to the addition of the photocatalyst.

- 5 The present invention also provides the use of the photocatalyst in a method of synthesising a carboxylic acid, the method comprising the step of exposing a photocatalyst of the invention to visible and/or ultraviolet light in the presence of an alcohol, thereby to generate a carboxylic acid.
- 10 The inventors have found that the photocatalyst may be used more generally to generate organic products, such as carboxylic acids, from organic substrates. The present invention therefore also provides the use of the photocatalyst in a method of synthesising an organic product, the method comprising the step of exposing a photocatalyst of the invention to visible and/or ultraviolet light in the presence of an organic substrate, thereby to generate an
- 15 organic product, such as a carboxylic acid. For example, the organic product may be selected from the group consisting of formic acid, acetic acid, pyruvic acid, terephthalic acid, ethylene glycol, glycolic acid, ethanol, diaminotoluene, lactic acid. The method may also yield a combination of organic products, including those listed.
- 20 For example, the photodegradation of polylactic acid is associated with the production of lactic acid and pyruvic acid. The photodegradation of polyethylene terephthalate terephthalic acid is associated with the production of terephthalic acid (and its salts), ethylene glycol, glycolic acid, acetic acid, formic acid and ethanol. The photodegradation of polyurethane is associated with the production of diaminotoluene, formic acid, acetic acid,
- 25 lactic acid and pyruvic acid.

The methods of the invention may be performed as a batch process, or as a flow process where the organic substrate is permitted to flow across the photocatalyst, which may be immobilised to a support.

- 30 After a degradation reaction is deemed complete the photocatalyst may be recovered for future further use. Here, the photocatalyst may be separated from remaining unreacted organic substrate and any reaction intermediates, such as partially degraded organic substrate. If appropriate, the recovered photocatalyst may be rejuvenated prior to reuse,
- 35 such as described in further detail below.

- The method of the invention may additionally comprise the step of pre-treating the organic substrate prior to its use in a photocatalysed hydrogen production method or degradation reaction. Such a treatment may at least partially degrade the organic substrate as a
- 40 preliminary step. Additionally or alternatively, such a treatment may increase the aqueous dissolution of the organic substrate prior to photocatalytic degradation.

The pre-treatment step may subsequently include the step of separating insoluble materials from the pre-treatment mixture, such as by filtration or centrifugation. The solubilised components may then be used in the photocatalysed hydrogen production method or degradation reaction.

5

The pre-treatment step is a treatment to reduce the molecular weight, such as weight or number average molecular weight, of the organic substrate. The pre-treatment step may be the treatment of the organic substrate with base, such as inorganic base. The base may be an aqueous base.

10

Preferably, the base used in the pre-treatment step is the same base for use in the subsequent photocatalytic reaction, which base is used to provide the photocatalyst and the organic substrate in an aqueous mixture having a pH of 10 or more. Thus, the pre-treatment reaction mixture may be used directly in the photocatalytic reaction after the pre-treatment is deemed complete. Here, the pre-treatment reaction mixture may be optionally separated to remove solids, and it may then be mixed with the photocatalyst components. The base may be used in the pre-treatment step at a concentration that is suitable for the later photocatalytic reaction.

15

20 Preferably, the organic substrate is treated with a basic aqueous mixture having a pH of 10 or more, such as a pH of 11 or more, such as a pH of 12 or more. Thus, most preferably the organic substrate is pre-treated with aqueous NaOH or aqueous KOH, such as aqueous NaOH.

25 The pre-treatment step may include heating the organic substrate in the presence of the base. The organic substrate may be heated to a temperature of at least 30°C, at least 40°C or at least 50°C. The organic substrate may be heated to a temperature of at most 60°C, at most 70°C, at most 80°C, or at most 90°C.

The organic substrate may be heated to a temperature of around 40°C.

30

The organic substrate may be treated with base for at least 1 hour, at least 2 hours, at least 12 hours, or at least 24 hours. The organic substrate may be treated with base for at most 26 hours, at most 48 hours, or at most 96 hours.

The organic substrate may be treated with base for around 24 hours.

35

Preferably, the mixture of the organic substrate with the base is agitated, such as stirred, to promote any degradation of the organic substrate.

40 The at least partial degradation of the organic substrate, and the treatment of the organic substrate with base, may result in a product mixture having insoluble materials, and these materials may be separated from solubilised components, for example by filtration or centrifugation. The solubilised components may then be used in the photocatalytic reaction.

The inventors have found that pre-treatment of the organic substrate may cause degradation of the polymer substrate, and this degradation is associated with an increase in the amount of material that is solubilised in the reaction mixture, which is typically an aqueous basic mixture. This at least partial degradation of the polymer is associated with an increase photoreforming rate, as is seen from the collection of hydrogen over a set time period.

Associated with an improvement in substrate solubility is an increase in the reaction mixture transparency. An increased transparency allows for great light penetration into the mixture, and thereby greater exposure of the photocatalyst to the incident light. An increase in the photoreforming rate is thereby provided.

The pre-treatment step often produces insoluble material, and such may be beneficially removed from dissolved organic substrate. Solid materials are thereby prevented from contacting the photocatalyst, and this means there is no contamination of unreacted material.

Organic Substrate

The photocatalyst of the invention may be used to degrade, or reform, an organic substrate, and preferably the degradation reaction yields hydrogen and/or carbon dioxide. The methods of the invention may be used to degrade waste material as part of the disposal process of that material. Alternatively, the methods of the invention may be intended for the generation of a fuel material, such as hydrogen, for downstream use. Advantageously the methods of the invention may be used to dispose of unwanted biomass and also to generate commercially relevant fuels or commercially useful organic products, such as formic acid, acetic acid, pyruvic acid, and terephthalic acid.

The organic substrate typically contains both hydrogen and carbon atoms, and most typically contains multiple carbon-carbon and multiple carbon-hydrogen bonds. The photocatalyst is most useful in the degradation of higher molecular weight organic substrates, and is also most useful in the degradation of hydroxyl functionalised organic substrates. The photocatalyst may also be used to directly degrade biomass without any prior refining of the biomass. Thus, the photocatalyst is suitable for use with relatively simple organic materials as well as complex biomass mixtures, which contain a wide variety of different chemical structures, often with a wider distribution of molecular weights.

The photocatalyst has tolerance to a range of substrates, and such tolerance has not previously been reported in the art. The ability to use the photocatalyst with unrefined substrates therefore provides flexibility for the process, which may be used anywhere where there is a source of biomass materials, such as wood and grass. In contrast, many of the

degradation and hydrogen evolution reactions reported to date rely on the use of refined substrates for use in the photocatalytic reaction, and therefore the methods can only be performed where there is the ability to refine biomass materials, or where there is a ready commercial source of the refined material.

5

The degradation of the organic substrate may yield hydrogen, which has use as a commercial fuel and a chemical feedstock. Accordingly, the degradation reaction allows for the valorisation of the organic substrate.

10 The ability to generate hydrogen from any organic substrate, including wood and cardboard as well as refined cellulose and lignin, is highly advantageous, as the methods of the invention are not limited to locals where refined materials are available, which is a clear limitation of the prior art methods.

15 It is possible that other degradation products are also produced, such as carbon dioxide. The inventors have also found that the degradation of an organic substrate may yield formic acid (or formate) as a product, which product also has commercial value. The production of formic acid therefore provides an additional or alternative pathway for creating value from the organic substrate.

20

The production of ethanol from cellulose has been described previously as a route to preparing a fuel stock. However, in many cases cellulose-derived ethanol requires purification of glucose from lignocellulose, followed by the subsequent fermentation of that glucose to yield ethanol. As noted above, the present invention allows for the production of
25 hydrogen or formic acid directly from any source of unprocessed lignocellulose.

The organic substrate typically has hydroxyl functionality. Without wishing to be bound by theory, the present inventors believe that the hydroxyl functionality of an organic substrate strongly interacts with the surface of the photocatalyst, and more particularly the oxygenated
30 portions of the photocatalyst. This is seen from TEM images of a photocatalyst with an organic substrate after a degradation reaction: the photocatalyst is clearly closely associated with organic substrate.

The organic substrate may contain one or more, such as two or more, hydroxymethyl groups (-CH₂OH). For example, cellulose, hemi-cellulose and lignin contain a plurality of
35 hydroxymethyl groups within their core structures (see, for example, Figure 1(a)).

The organic substrate may be a polyol, for example a polyol having two or more, such as five or more, such as ten or more hydroxyl groups.

40 The photocatalyst of the invention may be used to degrade a high molecular weight component within the organic substrate. In the worked examples of the present case, the photocatalyst is shown to be useful in degrading cellulose, hemi-cellulose and lignin.

Indeed, the photocatalyst may be used to degrade biomass directly, and without any refining.

Thus, the photocatalyst may be used to degrade an organic substrate that is or contains a component having a molecular weight of 70 or more, such as 100 or more, such as 200 or
5 more, such as 500 or more, such as 1,000 or more. Here, the organic substrate may have a molecular weight of at most 1,500.

The photocatalyst may be used to degrade an organic substrate that is or contains a component having a molecular weight of 2 kDa or more, 5 kDa or more, 10 kDa or more, 20 kDa or more, 25 kDa or more, 30 kDa or more, or 50 kDa or more.

10 In the worked examples of the present case, the molecular weight of the cellulose used (see also Figure 4(a)) is believed to be around 30 kDa.

It is noted that Kalisman *et al.* only describe the reaction of the small molecular weight substrate isopropyl alcohol in the presence of a passivated photocatalyst. Similarly,
15 Simon *et al.* describe the reaction of ethanol in the presence of a passivated CdS material. Zhensheng also describes the use of CdS materials to photocatalytically dehydrogenate alcohols. There is no suggestion that the photocatalysts could or would be useful in the treatment of larger molecular weight substrates or biomass.

20 The organic substrate may be a biomass or a refined biomass. In the preferred embodiments of the invention, refining of the biomass is not required, and a biomass may be used directly (or after mechanical processing). Here, refining refers to a process where components of the biomass, such as lignin, cellulose and hemicellulose are separated from each other, or from other components of the biomass. Refining may refer to a thermal,
25 chemical or biochemical processes for achieving this separation.

The organic substrate may be or comprise a polysaccharide.

In the preferred methods of the invention, the organic substrate is a cellulose, such as α -cellulose.

30

The organic substrate may be or comprise a polypeptide.

A mixture of different organic substrates, such as those described above, may be present. In the worked examples of the present case, the organic substrate is a complex biomass
35 material, such as paper or wood. The organic substrate may contain many different types of biomass in a mixture.

In one embodiment, a mixture of lignin, cellulose and hemicellulose may be present as organic substrates. Such materials typically feature within biomasses such as paper and
40 wood or a biomass that is plant matter.

The organic substrate may be wood, paper, cardboard, bagasse, grass and/or sawdust.

The organic substrate can be general waste, plastics, packing materials, waste food, aliphatic polyols, algae, sugars, starches, biomass, sewage and/or domestic waste. The organic substrate preferably comprises lignocellulose or one or more of its constituent components.

5

A biomass for use in a method of the invention may be mechanically treated prior to used, for example to reduce the size of the biomass and optionally to provide the biomass in a uniform size distribution. Such mechanical treatments are for optimal processing of the biomass in the methods of the invention, for example to increase the available surface area of the substrate or simply to ensure that the organic substrate can be handled and distributed within a processing facility.

10

The inventors have found that the photocatalyst of the invention can be used directly to catalyse the reaction of biomass, and each of the major components of lignocellulose is reactive in the presence of the photocatalyst when it is exposed to light. Accordingly, the methods of the invention do not require the biomass to be chemically treated prior to use. Many methods contained in the prior art have described the preparation of monosaccharides from cellulose components as a preliminary step, prior to the use of the photocatalyst.

15

20 *Additional Organic Substrates*

In addition to, or as an alternative to, the organic substrates described above, the present inventors have found that the photocatalyst of the invention has broad application in degrading, or reforming, organic substrates that are organic polymers, and preferably the degradation reaction yields hydrogen and/or carbon dioxide (for example as carbonate).

25

In their initial work, the inventors found that the photocatalyst could be used to degrade organic polymers such as polysaccharides, including cellulose and hemicellulose, and lignin. The photocatalyst is now found to have use in the degradation of other organic polymers, and may be used to generate hydrogen from those organic polymers.

30

Without wishing to be bound by theory, the inventors believe that the organic polymers are at least partially hydrolysed or solubilised under the reactions conditions. The hydrolysis of the polymer may result in the formation of dissolved hydrolysis products having hydroxyl functionality. From their earlier work, the inventors have established that hydroxyl-containing materials, such as hydroxyl-containing organic polymers, are substrates for the photocatalyst.

35

The standard reaction conditions for the use of the photocatalyst are aqueous basic conditions, and such are sufficient for the at least partial hydrolysis or at least partial dissolution of many organic polymers. For example, substituted polyesters, polyethers, polycarbonates, and polyurethanes are all degradable under aqueous basic conditions, and

40

are therefore shown or expected to be suitable substrates for the generation of hydrogen using the photocatalyst of the invention.

5 The organic polymers described here may be used in the same way as the organic substrates described in the section above. Thus, the organic polymers may be provided together with the photocatalyst in an aqueous mixture having a pH of 10 or more, such as pH 11 or more, such as pH 12 or more, optionally together with a co-catalyst.

10 An organic polymer may refer to a polymer that contains multiple monomer units, and typically each monomer unit contains at least one carbon-carbon bond in the backbone chain of the polymer. Where a monomer does not contain a carbon-carbon bond in the backbone chain of the polymer, it may contain a carbon-oxygen in the backbone, for example as seen with paraformaldehyde polymers.

15 The monomer units may be covalently linked by carbon-carbon bonds, such as in a substituted polyethylene, but this is not necessary, and monomers may be linked by carbon-oxygen or carbon-nitrogen bonds. For example, carbon-oxygen bonds are present in polyethers.

20 The organic polymer may be a homopolymer or a copolymer. Typically each monomer (repeat) unit within the organic polymer contains one or more heteroatoms, such as one or more heteroatoms selected from oxygen, nitrogen and sulfur. A heteroatom may be present within the covalent bond connecting monomers, and/or a heteroatom may be present within a side chain of the monomer.

25 The organic polymer may be a polymer that is hydrolysable or at least partially soluble under basic conditions, such as the aqueous basic conditions mentioned above, for example at aqueous pH 10 or more, such as aqueous pH 11 or more. Organic polymers that are not hydrolysable or partially soluble under basic aqueous conditions, such as polyethylene, 30 polypropylene or polystyrene, are not seen to evolve hydrogen under the reactions conditions described herein.

35 In certain methods of the invention, an organic substrate such as an organic polymer may be at least partially degraded or solubilised prior to its treatment with the photocatalyst. This pre-treatment of the organic substrate may be undertaken to improve the solubility of the substrate in the aqueous basic mixture.

40 The organic polymer may therefore comprise functionality, either in the backbone chain or the side chain, which is hydrolysable under basic conditions. For example, the organic polymer may contain ester, amide, ether, carbonate, and/or urethane (carbamate) functionality. The organic polymer may additionally or alternatively contain hydroxyl functionality, and such polymers are believed to be substrates for the photocatalyst.

As previously noted in the section above, the organic substrate may be a polyol, such as a polysaccharide, including cellulose, or lignin.

5 Additionally or alternatively, the organic polymer may be a polyester, such as polyethylene terephthalate (PET) or polylactic acid (PLA), a substituted polyethylene, such as polyvinyl pyrrolidone (PVP) and optionally also polyethylene, a polyether, such as polyethylene glycol (PEG), a polycarbonate (PC) or a polyurethane (PUR).

10 Additionally or alternatively, the organic polymer may be a polyamide, such as a protein.

For example, the organic polymer may be a polyester, a substituted polyethylene, or a polyether.

15 The photocatalyst may be used together with an organic polymer that is a polyester. The polyester may be an aryl-containing polyester (aromatic polyester) or an alkyl-containing polyester (aliphatic polyester). The polyester may contain both aryl and alkyl functionality.

20 Examples of aryl-containing polyesters include polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate and polytrimethylene terephthalate.

25 Examples of alkyl-containing polyesters include the homopolymers polylactic acid, polycaprolactone (PCL), polyglycolic acid, poly-3-hydroxyvalerate, poly-3-hydroxybutyrate, poly-4-hydroxybutyrate. Examples of alkyl-containing polyesters include the copolymer polybutylene succinate and poly(3-hydroxybutyrate-co-3-hydroxyvalerate).

The worked examples in the present case show that the photocatalyst can catalyse the oxidation of the polyesters PET and PLA.

30 The photocatalyst may be used together with an organic polymer that is a substituted polyethylene. Thus, the polyethylene has a side chain. Typically, the substituted polyethylene is a polymer having one or more heteroatoms, such as selected from oxygen, sulfur or nitrogen, within the side chain. The heteroatom functionally may be a component of a functional group that is hydrolysable under the reaction conditions, or it may assist in the dissolution of the polymer in the reaction mixture.

35 The polyethylene may be substituted with, for example, a heterocycle, such as a C₄₋₇ heterocycle having one ring heteroatom. The heterocycle may be pyrrolidone.

The polyethylene may be substituted with, for example, a cyano group. Thus, the polymer may be a polyacrylonitrile (PAN).

40 The polyethylene is typically not an acrylate polymer, for example the polyethylene is not a poly(methyl methacrylate).

The photocatalyst may be used together with an organic polymer that is a polyether, including for example polyethylene glycol.

5 A polyether may be an alkyl-containing polyether (aliphatic polyether) or an aryl-containing polyether (aromatic polyether). The polyether may contain both aryl and alkyl functionality.

10 Examples of alkyl-containing polyethers include polyethylene glycol, polypropylene glycol, paraformaldehyde (PFA) and poly(tetramethylene ether) glycol (also known as polytetrahydrofuran).

15 Examples of aryl-containing polyethers include polyphenyl ether and poly(p-phenylene ether) (PPE).

20 An example of a complex polyether containing both alkyl and aryl functionality, together with further substituent groups, is lignin. Here, lignin is a polymer of linked and crosslinked phenolic monomers. In one embodiment, a polyether is not lignin.

25 The organic polymer may be a component of a consumer product. For example, polyethylene terephthalate is found in fibres for clothing and containers for foods and liquids.

For the purposes of the present case, a polysaccharide may not be considered a polyether.

30 An example of a polyamide is a polypeptide. Example polypeptides include bovine serum albumin and casein.

35 As with the organic substrates previously described, the organic polymer may have a molecular weight that 500 or more, such as 1,000 or more. The photocatalyst may be used to degrade an organic substrate that is or contains a component having a molecular weight of 2 kDa or more, 5 kDa or more, 10 kDa or more, 20 kDa or more, 25 kDa or more, 30 kDa or more, or 50 kDa or more.

40 As previously noted, the organic substrate, such as the organic polymer, may be pre-treated prior to its mixing with the photocatalyst. For example, the organic substrate may be pre-heated to assist the hydrolysis or dissolution of the organic polymer. In a further example, the organic polymer may be pre-treated with base to assist the hydrolysis or dissolution of the organic polymer.

45 The organic polymer may also be mechanically treated, for example by cutting, grinding and milling and other such techniques. The mechanical treatment may be particularly advantageous where the organic polymer is a component of a consumer product, and a size reduction in the product will assist in the rate of degrading the product and its organic polymer component.

5 The organic substrate, such as an organic polymer, may be used to generate hydrogen, optionally together with carbon dioxide and/or an organic product, such as formic acid, acetic acid, pyruvic acid, and terephthalic acid. The pre-treatment steps, which may include mechanical or chemically pre-treatment, may provide an increased production rate for these products.

10 *Methods of Preparation*

The present case provides methods for preparing a photocatalyst. Generally the methods include the step of modifying the surface of a base material, which is a semiconductor, such as a metal-containing semiconductor, to provide an oxygenated surface, which is typically a metal hydroxide or metal oxide surface.

15 The semiconductor may be a metal chalcogenide, such as a metal sulfide, metal selenide or a metal telluride, for example. Example materials for use as the core materials are described above in relation to the structure of the photocatalyst.

20 In one embodiment, the method for preparing a photocatalyst comprises the step of treating a semiconducting material, such as a particle of a semiconducting material, with aqueous base, where the pH of the aqueous base is 10 or more, such as pH 11 or more. The method may be performed in the substantial absence of ligands. In the worked examples of the present case CdS|CdO_x is prepared from ligand-free CdS quantum dots.

25 Annealing methods performed in air may also be used to generate an oxygenated surface, for example a CdO layer in a photocatalyst (see Zhensheng *et al. J. Mol. Catal.* **1989**, *50*, 315).

30 The present case also provides a method for rejuvenating a photocatalyst, where the photocatalyst is provided in an aqueous mixture, such as a basic aqueous mixture, the method comprising the step of increasing the acidity of the mixture (lowering the pH), and then subsequently increasing the basicity of the mixture (increasing the pH), thereby to provide the photocatalyst.

35 The photocatalyst for rejuvenation is a photocatalyst that has previously been used in a photocatalytic reaction, such as the degradation, hydrogen generation and carbon dioxide generation methods described herein. The photocatalyst may have reduced activity, for example due to poisoning of the catalyst, including the loss of functionality, or some other
40 change resulting in a loss of activity. Here reduced activity refers to a reduction in catalytic activity compared with the photocatalyst activity as first used, for example within the first hour of use.

The steps of decreasing then increasing the pH of the aqueous mixture has the effect of “stripping” the surface of the photocatalyst, then regenerating the active surface, thereby substantially restoring catalytic activity.

5

Other Preferences

Each and every compatible combination of the embodiments described above is explicitly disclosed herein, as if each and every combination was individually and explicitly recited.

10

Various further aspects and embodiments of the present invention will be apparent to those skilled in the art in view of the present disclosure.

15

“and/or” where used herein is to be taken as specific disclosure of each of the two specified features or components with or without the other. For example “A and/or B” is to be taken as specific disclosure of each of (i) A, (ii) B and (iii) A and B, just as if each is set out individually herein.

20

Unless context dictates otherwise, the descriptions and definitions of the features set out above are not limited to any particular aspect or embodiment of the invention and apply equally to all aspects and embodiments which are described.

25

Certain aspects and embodiments of the invention will now be illustrated by way of example and with reference to the figures described above.

Experimental and Results

30

Described below is a photocatalytic system based on semiconducting CdS quantum dots (QDs) that is capable of degrading cellulose, hemicellulose and lignin into H₂ at room temperature. CdS is an inexpensive, visible-light absorbing photocatalyst with a bulk electronic band gap of around 2.4 eV that can be increased through quantum confinement effects. The CdS conduction band has a potential of -0.5 V vs. the normal hydrogen electrode (NHE, pH 0), providing sufficient driving force for proton reduction and is responsible for several of the highest reported rates of photocatalytic H₂ evolution.

35

40

The CdS valence band is located at roughly +1.9 V vs. NHE, which is adequate for saccharide oxidation, however it is also sufficient for the photooxidation of its constituent sulfide. This photocorrosion has brought the viability of CdS as a sustainable photocatalyst into question, as H₂ evolution has depended on the use of easily-oxidised sacrificial reagents to outcompete sulfide oxidation.

To circumvent these issues CdS is treated under highly alkaline conditions, and typically under ligand free conditions, that promote Cd(OH)₂/CdO (henceforth CdO_x) formation on the CdS surface (Fig. 1b). The resultant CdS|CdO_x material is able to undertake demanding photocatalytic reactions without photocorrosion, such that light-driven H₂ evolution is achievable through the oxidation of completely unprocessed lignocellulosic substrates. Beneficially, the use of highly alkaline conditions may also solubilise the organic substrate, such as lignocellulose, thereby providing highly accessible substrate for the photocatalyst. The synergistic interplay between the active photocatalyst formation and the increase in dissolved lignocellulosic substrate produces a system with previously unmatched rates of H₂ evolution.

Reagents

Ligand-free CdS quantum dots were synthesised as reported previously (see *J. Mater. Chem. A* **2016**, 4, 2856). α-Cellulose, hemicellulose (xylan from beechwood), CdO and CdSO₄ and lignin (alkali) were purchased from Sigma Aldrich and used without further processing.

Semiconductor-grade KOH (99.99%) was used to ensure impurities were not present during photocatalysis. Cobalt(II) tetrafluoroborate hydrate, 96% (assumed to be Co(BF₄)₂·6H₂O) was purchased from Alfa Aesar. NaOD (40 wt % in D₂O, 99% atom% D) and D₂ (99.8% atom D) were purchased from Sigma-Aldrich.

¹³C cellulose was purchased from IsoLife. Wood from the branch of a London plane tree was obtained from a tree on Lensfield Road, Cambridge, UK. Sawdust was obtained from a local sawmill (B&Q, Cambridge, UK) and grass was attained from a garden in north Cambridge, UK. Cardboard was obtained from a Sigma Aldrich box, newspaper from an issue of the Cambridge News, bagasse from a Duni bagasse plate and paper from Office Depot. Waste cellulose and biomass sources were cut roughly into pieces < 0.25 cm long before use. All other reagents were obtained from commercial sources at the highest available purity.

Equipment

UV-Visible spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz Avance spectrometer at room temperature. Transmission electron microscopy (TEM) images were collected using a FEI Philips Tecnai 20 microscope, with 200 kV accelerating voltage. XPS analysis was carried out at the Cambridge Microelectronics centre on a Thermo Scientific ESCALAB Xi+ XPS Microprobe in an ultrahigh vacuum chamber. Freeze drying was carried out in a VirTis SP Scientific freeze dryer. Powder X-ray diffraction measurements were carried out on an X'Pert PRO by PANalytical BV instrument. Photoluminescence measurements were carried

out on an Edinburgh Instruments FS5 spectrofluorometer. pH was measured on a Mettler Toledo pH meter and probe, with the exception of the pH of solutions containing $[\text{KOH}] > 1$ M, which was estimated based on the assumption $[\text{OH}^-] \approx [\text{KOH}]$.

5 Characterisation of CdS|CdO_x

CdS|CdO_x was synthesised from ligand-free CdS quantum dots with a diameter of 5 nm, as confirmed by transmission electron microscopy (TEM, Fig. 2a,b). The ligand-free CdS is passivated by weakly-bound tetrafluoroborate anions and *N,N*-dimethylformamide (DMF), presenting an accessible surface that can be modified for improved catalytic activity. Addition of the quantum dots to basic solution caused CdO_x to instantaneously form on the particle surface through OH⁻ binding to Cd surface sites.

This was confirmed using X-ray photoelectron spectroscopy (XPS) of CdS QDs after suspension in various concentrations of KOH. The expected Cd 3d_{5/2} and 3d_{3/2} binding energies for emissions in CdS are 405 and 412 eV, respectively, which was observed in the photoemission spectrum of QDs isolated from a pH neutral solution (Fig. 2c, see Fig. 6 for S and O spectra). After isolation from 0.1 M KOH the Cd emissions tail towards lower binding energies and after isolation from 10 M KOH the peaks shift 1 eV lower to 404 and 411 eV. The lowered binding energy is consistent with CdO/Cd(OH)₂ environments on the CdS at high pH.

Raman measurements provided *in situ* evidence for the formation of surface-bound CdO_x. Under 514 nm laser excitation, highly resolved off-resonant Raman spectra of ligand-free CdS QDs in 0, 0.1 and 10 M KOH aqueous solutions were obtained (Fig. 2d). In agreement with literature, vibrational bands at 305 cm⁻¹ and 605 cm⁻¹ were observed that can be assigned to scattering and double-scattering on the longitudinal optical phonon of CdS (LO and 2LO), respectively. As the KOH concentration is increased, a broadening of the LO peak on the low frequency side is observed that cannot be accounted for by the KOH (Figs. 2e and 7). Spectral deconvolution by band-fitting analysis revealed contributions from two bands located at 260 cm⁻¹ and 292 cm⁻¹. These bands can be attributed to CdO by comparison to a reference spectrum of CdO (bulk) and literature values. The positions of these bands are slightly lower than those reported for bulk CdO (265-268 cm⁻¹ and 298-305 cm⁻¹). Although the formation of Cd(OH)₂ was not visible in the Raman spectra (see Fig. 7 for reference spectrum), this does not confirm that the surface consists solely of CdO, as the dynamic nature of the QD modification would introduce numerous Cd-O functionalities.

TEM images of CdS|CdO_x after isolation from 10 M KOH show that the surface change occurs with a concomitant decrease in average particle size by 0.6 nm (Fig. 2f,g).

Formation of CdO_x in highly basic solution was corroborated by zeta potential analysis of the QDs (Fig. 2h), which shows a rapid increase in negative surface charge above pH 12. This shift is similar to that observed on ZnS/Zn(OH)₂ surfaces, and is indicative of Cd-O⁻ forming on the particle surface.

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The decrease in size is a result of the removal of a few layers of CdS to generate a CdO_x passivation. This does not affect the bulk properties of the particle as the X-ray diffraction pattern (Fig. 8) displays only marginal changes after dissolution in 10 M KOH.

10 The UV-visible spectrum after dissolution in 10 M KOH also retains the visible-light absorption consistent with CdS QDs, although the spectrum is broadened and slightly red-shifted relative to the spectrum in DMF (λ_{\max} = 450 nm in DMF and 470 nm in 10 M KOH, Fig. 9).

15 This red-shift is attributed to a lower QD dispersibility in the aqueous solvent, which leads to a degree of particle aggregation, as seen previously for ligand-free CdS QDs. Considering the presented data it is proposed that CdO_x exists as a monolayer or at most as a few layers on the CdS surface at high concentrations of KOH. This is evidenced by the spectroscopic confirmation of CdO_x (Fig. 2c,d and e), combined with the still-present bulk properties of CdS
20 (Figures 8 and 9) and lack of a larger, visible CdO_x shell in the TEM image (Fig. 2f).

The influence of the CdO_x surface passivation on the CdS QD photoluminescence is presented in Fig. 2i. As OH⁻ is added a stronger near band-gap emission is visible at 480 to 490 nm, which is most pronounced in 10 M KOH. A comparison between the emission and
25 absorption spectra in 10 M KOH is presented in Fig. 9b. The increasing intensity of the emission is attributed to the formation of CdO_x, which blocks CdS defect sites that promote radiationless charge-carrier recombination. The near band gap energy of the emission also indicates that CdO_x may provide shallow trap-states (below 0.1 eV in depth) above the valence band and below the conduction band that increase the lifetime of charge separation.
30 These effects lead to more efficient light-harvesting capacity, and thereby photocatalytic activity, of the QD and may also enhance particle stability through prevention of S[•] radical formation that is responsible for CdS degradation.

Photoreforming (Degradation) of Cellulose

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To test the efficacy of the CdS|CdO_x photocatalyst for lignocellulose reforming, we initially focused on the oxidation of its major component, cellulose. We used the most crystalline and unreactive form, referred to as 'α-cellulose', as its conversion is most crucial if complete lignocellulose reformation is to be achieved. Photocatalysis was carried out with CdS QDs
40 (1 nmol) and α-cellulose suspended in a deaerated aqueous solution (2 mL) kept at 25°C, which was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²).

The cellulose exists as a suspension due to its low solubility and optimisation revealed that a loading of 50 mg mL⁻¹ led to the highest photocatalytic activity (Table 1). Large volumes of H₂ could be produced provided strongly alkaline conditions were employed (Fig. 3a) with the activity rapidly increasing towards pH 15 (10 M KOH). This concurs with the *in situ* formation of CdO_x on the QD surface (Fig. 2) and a similar pH dependence was observed when photoreforming other substrates (Table 2), as seen in other CdS-based systems. H₂ evolution by the photocatalyst originates mostly from reduction of aqueous protons, as photocatalysis in D₂O produced D₂ and HD in a 4:1 ratio (Fig. 10). Formation of the latter originates from H/D exchange with cellulose OH groups. No H₂ evolution was observed without QDs or light (see Table 1).

In addition to promoting the formation of CdO_x, the high concentration of KOH provides the added benefit of solubilising a portion of the suspended cellulose, as seen for NaOH-water systems. Dissolved cellulose chains were confirmed to be the major substrate through use of a 10 M KOH solution that had been stirred in the presence of α-cellulose for 24 hours and subsequently centrifuged to remove the suspended, insoluble cellulose. The supernatant was then added to a vial containing ligand-free CdS QDs and irradiated (Fig. 11, Table 3). Here, photocatalytic H₂ evolution (AM 1.5G, 100 mW cm⁻²) from CdS|CdO_x QDs (0.5 μM) was studied under an anaerobic atmosphere at 25°C with 50 mg mL⁻¹ suspended α-cellulose in 1 mL aqueous 10 M KOH (top line) and 1 mL of a suspension-free α-cellulose solution in 10 M KOH (bottom line). The suspension-free solution was prepared by irradiating 50 mg mL⁻¹ α-cellulose for 24 hours at 25°C in anaerobic conditions (shaded region) and subsequently centrifuging the solution to remove the solid material.

The H₂ evolution rate from this solution was initially faster relative to the rate observed when using suspended cellulose, as more dissolved substrate was available. Without the suspended cellulose present however, the activity dropped over time as the solubilised substrate depleted. The photoreforming reaction therefore occurs through continuous dissolution of the suspended cellulose by the basic solution followed by its fast oxidation by the CdS|CdO_x photocatalyst. The presence of the dissolved polysaccharides is confirmed in Fig. 3c (discussed below) and was also evidenced by an increase in solution viscosity after several days of photocatalysis.

Long-term photocatalytic H₂ evolution activity from cellulose is illustrated in Fig. 3b. After 6 days there was no evidence of photocorrosion and nearly 600 mmol_{H₂} g_{CdS}⁻¹ had been produced in the headspace of a closed photoreactor, equating to a turnover number of 100,000 with respect to the QD. The activity of CdS|CdO_x is over an order of magnitude higher than the aforementioned TiO₂ systems, even without the use of prohibitively expensive noble metal co-catalysts or the need for UV light to operate. No evolution of CO was observed during catalysis (gas chromatograph CO detection limit = 35 ppm), resulting in inhibitor-free H₂ in the photoreactor headspace.

All CO₂ generated was sequestered by the basic solution as CO₃²⁻ (see Fig. 3c), removing any potential environmental impact of the oxidation reaction. CdS|CdO_x without cellulose present (Fig. 3b, black line) shows 10% of the photocatalytic H₂ evolution activity for the first 24 h irradiation and then ceases (4% after 6 days), which originates from oxidation of residual DMF from the stock solution or sulfide displaced from the quantum dots.

The narrower bandgap of CdS also allows the system to function effectively under visible light and 50% of the catalytic activity was maintained by CdS|CdO_x when UV-light ($\lambda < 400$ nm) was filtered from the solar spectrum (Table 1). The drop in activity is due to the decrease in the number of photons available to the CdS, demonstrating that UV-light is not needed to facilitate the photoreforming reaction. Cellulose photoreforming may therefore be undertaken with visible light only, an essential development if this process is to be undertaken in realistic operating conditions.

An external quantum yield of 1.2 ± 0.4 % was achieved when irradiating with 430 nm monochromatic light (Table 4), which is comparable to reported efficiencies of Pt/TiO₂ for the much simpler glucose reforming reaction under UV light. The yield was substantially higher when photoreforming MeOH (17.7 ± 1.5 %, Table 5), indicating that the efficiency is reduced by the slow oxidation rate of the polysaccharide chains, as well as light-scattering by the cellulose suspension.

The products of α -cellulose oxidation were identified by ¹³C-NMR spectroscopy using uniformly ¹³C-labelled cellulose in 10 M NaOD in D₂O (Fig. 3c). Photocatalysis was carried out with 10 mg of ¹³C α -cellulose in NaOD for 3 days, after which the reaction solution was filtered of insoluble cellulose and analysed. A control experiment wherein ¹³C-cellulose was irradiated without CdS|CdO_x produced signals between $\delta = 55$ -110 ppm (see Fig. 3c, black line, i), corresponding to C-environments in the anhydroglucose repeating unit. This confirms that the basic conditions are able to partially dissolve the α -cellulose, providing solvated cellulose chains as a substrate for photocatalysis.

After irradiation in the presence of CdS|CdO_x the polymeric cellulose resonances ($\delta = 55$ to 110 ppm, i) are reduced in intensity, indicating that the photocatalyst is able to break down the large cellulose chains. This leads to a broad polymeric carboxylic acid resonance ($\delta = 182$ ppm, ii), from oxidised polysaccharide end groups.

Decomposition of the cellulose by CdS|CdO_x forms smaller saccharides, however sharp monosaccharide peaks are not present in the spectrum. This suggests that if smaller saccharides do form they are rapidly consumed by the photocatalyst. The fast affinity of the photocatalyst for smaller saccharide oxidation was confirmed by photoreforming 0.1 M glucose, which produced H₂ at a rate of $10.0 \text{ mmolH}_2 \text{ g}_{\text{CdS}}^{-1} \text{ h}^{-1}$ (Table 2); 130% higher than with α -cellulose ($4.4 \text{ mmolH}_2 \text{ g}_{\text{CdS}}^{-1} \text{ h}^{-1}$).

At an α -cellulose loading of 50 mg mL^{-1} the potential anhydroglucose concentration (0.3 M) is three times higher than glucose. Dehydration of monosaccharides produces furfural species, such as 5-hydroxymethyl furfural (HMF), as intermediates in the oxidation of cellulose by Pt/TiO₂ systems. HMF resonances are not visible in the ¹³C spectrum after photocatalysis, as confirmed by reference to an authentic sample (Fig. b). This illustrates that either HMF is not formed as an intermediate in photocatalysis or that upon its formation it is rapidly decomposed. The latter is unlikely as photoreforming HMF by the photocatalyst proceeded at a relatively slow rate of $4.7 \text{ mmol H}_2 \text{ g}_{\text{CdS}}^{-1} \text{ h}^{-1}$ (Table 2).

Instead, formate was identified as the major intermediate during catalysis ($\delta = 171 \text{ ppm}$, iii), which is a common product of biomass oxidation by thermally-driven metal oxide catalysts. The accumulation of formate was assigned to its slow oxidation by CdS|CdO_x, as its photoreformation generated H₂ at an even slower rate of $1.3 \text{ mmol H}_2 \text{ g}_{\text{CdS}}^{-1} \text{ h}^{-1}$ (Table 2). A combination of decarboxylation of carboxylic acids and formate oxidation then produces CO₂, which was solubilised as carbonate (CO₃²⁻) at the employed pH ($\delta = 169 \text{ ppm}$, d) (Fig. 3c). These assignments were corroborated by reference to authentic samples and ¹H NMR spectroscopy (Fig. 12).

¹³C-NMR spectroscopy was also undertaken of insoluble cellulose that had been irradiated for 12 hours in $10 \text{ M NaOD/D}_2\text{O}$ both with and without CdS|CdO_x. The suspended cellulose was collected after photocatalysis *via* centrifugation and dissolved in molten ZnCl₂ before measuring a spectrum (Fig. 12e). Both spectra showed the expected cellulose resonances, as well as numerous sp² C-environments. When CdS|CdO_x is present there are a number of extra peaks that can be assigned to the heterogeneous oxidation of the cellulose. This indicates that there is both homogeneous and heterogeneous oxidation of the cellulose chains during photocatalysis, however due to the mass-transport limitations of the heterogeneous reaction, oxidation of the dissolved cellulose will provide the major contribution to the H₂ evolution activity.

Proton reduction occurs on CdS through Cd⁰ sites formed by electron accumulation on the photocatalyst surface, however this leads to slow rates of H₂ evolution. Transition metal co-catalysts are typically added to semiconductor systems to accelerate the proton reduction activity, but showed a limited effect in the present system. Addition of Ni(BF₄)₂ lowered the H₂ generated and K₂PtCl₄ halted activity completely over 24 h of photocatalysis (see Table 6). The addition of Co(BF₄)₂ increased the H₂ produced by 12%, but only after several days of photocatalysis (Fig. 13).

XPS analysis of Co(BF₄)₂ in 10 M KOH showed emissions consistent with Co(OH)₂/CoOOH (Fig. 14), which is believed to be the co-catalyst in this case. When replacing cellulose with more easily oxidised glucose the addition of Co ions had a larger influence on the photoactivity, increasing the H₂ generated by over 100% (see Table 2). This indicates that the cellulose oxidation reaction limits the rate of photocatalytic H₂ generation on CdS|CdO_x.

This was further confirmed through studies of the kinetic isotope effect in a solution of H₂O/NaOH vs. D₂O/NaOD. When the rate of reaction is dictated by breaking/making a H-containing bond the activity drops substantially upon changing to deuterated substrates, due to the lower vibrational frequency of the D-containing bond. In the deuterated solvent, the rate of photocatalysis was lowered by only 25% (k_H/k_D of 1.35 ± 0.16) (Table 7), indicating that the formation/cleavage of an O–H bond is not rate-limiting. The limiting oxidation rate is reflected in the conversion yield of cellulose to H₂, which reached a maximum of 9.7% after 6 days (Table 8, this data was corrected by background activity and assumes a theoretical maximum of 12 equivalents of H₂ formed per anhydroglucose monomer).

The yield is not yet comparable with the conversion attained by thermochemical reforming processes, due to the inaccessibility of the undissolved cellulose, however this disadvantage is offset by the high purity of the H₂ produced and significantly reduced energy input of the presented system. It is likely that much higher conversions will be realised as study of the system matures.

Photoreforming of Lignocellulose

Study into the reformation of the other lignocellulose components, lignin and hemicellulose, is presented in Fig. 4a (Table 9). Hemicellulose, in this case xylan from beech wood, could be reformed at similar rates to α -cellulose, as expected from its similar chemical composition. A lowered loading of hemicellulose at 25 mg mL⁻¹ was used to reflect the levels of hemicellulose present in lignocellulose. The heightened specific H₂ evolution performance is due to the higher solubility of hemicellulose, which presents more accessible oxidation sites for the particulate CdS|CdO_x photocatalyst.

Lignin is strongly light-absorbing and consequently its light-driven oxidation to form H₂ has rarely been reported. UV visible spectroscopy of lignin shows a broad absorption peaking at 300 nm with a shoulder at 350 nm that tails into visible wavelengths of light; the region over which wide-band gap semiconductors absorb most strongly. The smaller band gap of CdS|CdO_x absorbs wavelengths above 420 nm, where there is little competition for light between the photocatalyst and substrate (Fig. 15), allowing photocatalysis to occur effectively.

At lignin loadings of 0.25 mg mL⁻¹, CdS|CdO_x was able to evolve H₂ at an unprecedented rate of 0.44 mmol_{H₂} g_{cat}⁻¹ h⁻¹ (Fig. 4a). The decomposition of lignin during photocatalysis was followed by UV-visible spectroscopy over 5 days of irradiation, which showed a decrease in the peak at 300 nm and growth of the shoulder at 350 nm (Fig. 16a). This change is a result of oxidation of phenols within lignin to quinone functionality. This also occurred without

CdS|CdO_x present, due to UV-light absorption and self-oxidation by lignin, but 3.7 times slower with no evolved H₂ (Fig. 16b/c).

5 Solar-driven H₂ evolution from unprocessed lignocellulose stands as a long-sought objective for progress in the field of biomass conversion. Fig. 4b (Table 10) summarises the rate of H₂ evolution from suspensions of raw biomass available in areas local to Cambridge, UK and lignocellulosic waste. Each source was added to the reaction mixture after a rough cutting procedure to attain pieces < 0.25 cm long, and the H₂ produced by CdS|CdO_x was measured after 24 hours of solar irradiation. Rates of up to 9 mmol g_{CdS}⁻¹ h⁻¹ were observed using wood from a tree branch, whereas the other natural lignocellulose sources (bagasse, 10 sawdust and grass) exhibited lower activity.

Waste paper, cardboard and newspaper were also reformed to H₂, despite the highly crystalline cellulose present in their structure. The rate at which H₂ is evolved from each 15 substrate is remarkably high, competing with the activity of purified monosaccharide reforming systems (typically 1 to 9 mmol H₂ g_{CdS}⁻¹ h⁻¹) and reaches values two orders of magnitude higher than previous reports of photocatalytic lignocellulose reforming. The high activity is assigned to the employed conditions that benefit both the photocatalyst and the substrate; the alkaline conditions provides an *in situ* pre-treatment of the lignocellulose, 20 dissolving hemicellulose, lignin, cellulose and other saccharides into the solution, which are then accessible for oxidation by CdS|CdO_x. This provides a one-pot system that is responsive to highly unprocessed substrates, thereby allowing facile H₂ generation from the most ubiquitous lignocellulose in a given area.

25 *Mechanism of Lignocellulose Reforming on CdS|CdO_x*

Photocatalytic lignocellulose oxidation is often believed to occur through the formation of hydroxyl radicals (•OH), which subsequently oxidise the substrate. This possibility was explored using the •OH-scavenger benzene-1,4-dicarboxylic acid (terephthalic acid, TPA). 30 TPA reacts with •OH to form 2-hydroxyterephthalic acid (TPA-OH), which can be characterised by its fluorescence at 430 nm when excited with 315 nm light. CdS QDs irradiated for 18 hours in the presence of TPA showed low levels of TPA-OH formation below pH 14 (Fig. 17a), typically amounting to < 2 μmol •OH when compared to a TPA-OH reference (assuming the reaction yield of •OH and TPA to be 35%, Fig. 17b). Above pH 14, 35 when CdS|CdO_x is formed, no TPA-OH was detected and therefore it is unlikely that •OH plays a role in the presented system.

The function of the probe above and below pH 14 was confirmed through controlled generation of •OH by H₂O₂ photolysis (see Fig. 18). Here, photoluminescence emission 40 spectra (bandwidth 2 nm) were recorded at an excitation wavelength of 315 nm (bandwidth 2 nm) for a 10 mM terephthalic acid solution (2 mL) before and after exposure to •OH through the photolysis of 0.5 mM H₂O₂ with 1 mM KOH (pH 5.2), 0.1 M KOH (pH 12.9) and 5

M KOH (pH 14.7). Photolysis was induced during each measurement by the excitation beam. A 100% photolysis yield would generate a maximum of 2 μmol of $\bullet\text{OH}$, but the actual yield will be much lower than this value. A peak from 2-hydroxyterephthalic at 430 nm arises after addition of H_2O_2 in all cases. This does not differ significantly from the background of terephthalic acid (410 nm) as only minimal amounts of the 2-hydroxyterephthalic is present, but the peak is clearly distinguishable. These controls confirm that even minimal $\bullet\text{OH}$ formation is detectable by the probe

Instead it is proposed that the CdO_x coverage promotes effective binding between the photocatalyst and the substrate, which would contain numerous alkoxide groups at the employed pH. This interaction may be similar to TiO_2 , which forms Ti-O-R bonds during photocatalysis, facilitating effective hole transfer and a weakening of the C-C bonds in the bound substrate, leading to efficient oxidation to CO_2 .

Lignocellulosic substrates may bind to the CdS|CdO_x surface through analogous Cd-O-R bonds, as evidenced by the formation of the decarboxylation product, CO_3^{2-} . Such binding is not normally possible on CdS QDs as available Cd-binding sites are passivated by surface ligands or sulfide. It is speculated that dissolved lignocellulose chains bind to the CdS|CdO_x surface, possibly through multiple alkoxide groups, allowing the photocatalyst to undertake fast oxidation of alcohols to aldehydes. At this point, C-C bond cleavage can generate formate, or the aldehyde can be further oxidised to a carboxylic acid, which is decarboxylated to CO_3^{2-} . The fast realisation of these reactions is further assisted by the efficient charge separation in the photocatalyst, as a result of the CdO_x surface modification, and the basic pH, which rapidly facilitates deprotonation steps necessary during oxidation.

This reaction almost completely occurs in the homogeneous phase using solubilised lignocellulosic biomass, although a small amount of photoreforming on the surface of insoluble substrates may occur based on ^{13}C -NMR evidence (Fig. 12e). A strong interaction between the CdO_x surface and insoluble cellulose is also apparent in TEM images after reforming, which show the particles embedded in a cellulose matrix (Fig. 19).

Photocatalytic generation of H_2

Photocatalysis was carried out in a Pyrex glass photoreactor thermostated at 25°C . Solar irradiation was emulated by a solar light simulator (Newport Oriel, 100 mW cm^{-2}) equipped with an air mass 1.5 global filter (AM 1.5G) and a water filter (10 cm path length) to remove IR radiation. In a typical experiment, ligand-free CdS QDs in DMF (1 nmol) were transferred to a photoreactor and the DMF was removed *in vacuo* while stirring. Upon removal of the solvent, the substrate and 2 mL of 10 M KOH were added. Co-catalyst solutions were made through dissolution of the metal salt in 10 M KOH and were added to the reaction solution when required. The photoreactor was sealed with a rubber septum and purged with N_2 (containing 2% CH_4 for gas chromatographic analysis) for 10 min, after which the vial was

irradiated whilst stirring at 600 rpm. The accumulation of H₂ was quantified through periodic headspace gas analysis (50 µL) by gas chromatography.

Synthesis of Oleic Acid Capped CdS Quantum Dots (CdS-OA)

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CdS-OA were synthesised following a modified literature procedure. A mixture of CdO (0.64 g) and oleic acid (OA, 29 mL) in octadecene (89 mL) were heated under an Ar atmosphere to 280°C. Separately, a solution of sulfur (0.08 g) in octadecene (20 mL) was prepared. Half of the sulfur solution was then added rapidly to the Cd-containing solution and the other half was added continuously over the course of 2 minutes. The vessel was then immediately cooled to 220°C with N₂ gas and rapidly cooled in a water bath. The solution was diluted with 1:1 hexane:methanol (100 mL) and the particles were precipitated using excess acetone (c.a. 300 mL). Isolation of the particles was achieved by centrifugation at 5000 rpm for 3 min, after which they were re-dispersed in hexane. Two further washing steps were carried out by dispersion in hexane and precipitation with acetone, before finally dispersing in hexane.

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Ligand-free CdS Quantum Dots (CdS-BF₄)

A solution of CdS-OA in hexane (3 mL) was reduced to dryness and re-dispersed in a mixture of anhydrous CHCl₃ (15 mL) and anhydrous *N,N*-dimethylformamide (DMF, 1.9 mL) under a N₂ atmosphere. Et₃OBF₄ (1.0 M in dichloromethane, 9 mL) was added and the reaction solution was stirred for 1 hour. Me₃OBF₄ (1.0 M in acetonitrile) was added slowly until the particles precipitated (around 3 mL). The precipitate was collected by centrifugation (6,000 rpm, 3 min), and re-dispersed in a minimum of DMF. The quantum dot concentration and particle size was determined by UV-visible spectroscopy based on the position and size of the absorption maximum around 440-450 nm in DMF.

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Gas Analysis

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Gas chromatography (GC) was carried out on an Agilent 7890A gas chromatograph with a thermal conductivity detector. H₂/D₂ were analysed using a HP-5 molecular sieve column (0.32 mm diameter) and N₂ carrier gas with a flow rate of approximately 3 mL min⁻¹. CO and CO₂ were analysed using a HP-PLOT/Q column (0.53 mm diameter) attached to a HP-5 column (0.32 mm diameter) with a He carrier gas at an approximate flow rate of 2 mL min⁻¹. The GC oven temperature was kept at 45°C in both cases. Methane (2% CH₄ in N₂) was used as internal standard after calibration with different mixtures of known amounts of H₂/D₂/CO/CO₂/N₂/CH₄.

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Mass spectrometry was carried out on a Hiden Analytical HPR-20 benchtop gas analysis system with custom-designed 8-way microflow capillary inlet to a HAL 101 RC electron impact quadrupolar mass spectrometer with a Faraday detector. The sample inlet was

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connected to the reactor headspace and the composition of gases with mass/charge ratios between 1 and 10 was analysed.

External Quantum Yield (EQY) Determination

5 CdS-BF₄ (1 nmol) in DMF was added to a quartz cuvette (1 cm path length) and evacuated to dryness while stirring. Cellulose (100 mg) and 10 M KOH (2 mL) were added and the cuvette was sealed with a rubber septum. The solution was purged with N₂ containing
10 2% CH₄ for 10 min in the dark. Each sample was irradiated by a Xe lamp (LOT LSH302) equipped with a monochromator (LOT MSH300) that was used to focus a single wavelength of 430 nm (accurate to a full width at half maximum of 5 nm). The light intensity was adjusted to 796 mW cm⁻², which was measured using a power meter (ILT 1400, International Light Technologies). The cuvette was irradiated across an area of 0.28 cm². The evolved headspace gas was analysed by gas chromatography and the EQY (%) was
15 calculated according to equation (3).

$$EQY = 100 \times \frac{2 \times n_{H_2} \times N_A \times h \times c}{t_{irr} \times \lambda \times I \times A} \quad (3)$$

Where n_{H_2} is the amount of H₂ generated (mol), N_A is Avogadro's constant (mol⁻¹), h is Planck's constant (J s), c is the speed of light (m s⁻¹), t_{irr} is the irradiation time (s), λ is the
20 wavelength (m), I is the light intensity (W m⁻²) and A is the irradiated area of exposed to the light beam (m²).

Raman Analysis

25 Raman spectra were recorded using a confocal Raman spectrometer LabRam (Horiba Jobin Yvon) equipped with a liquid nitrogen cooled Symphony CCD detector (Horiba Jobin Yvon). A 514.73 nm line of an Ar ion laser (Coherent Innova 300c) was used as excitation wavelength. CdS-BF₄ QDs in water (10 μM), KOH (100 mM) and KOH (10 M) were measured in a rotating quartz cuvette. The accumulation time of the Raman spectra was 60
30 seconds. The laser power was set to 2.5 mW. The laser light was focused into the solution using a 20 × objective (Nikon, 20 × NA 0.5). Cd(OH)₂ was obtained by slowly adding 1.5 mL 1 M NaOH into 10 mL of a 0.1 M CdSO₄ solution. The white precipitate was centrifuged and washed with Millipore water ($\rho > 18.2$ MΩ cm) three times.

35 Band fitting of the Raman spectra was employed to evaluate the band structures with low intensities arising at high KOH concentrations around the LO band at 305 cm⁻¹. For this, the spectra were first cut in the region from 225 cm⁻¹ to 475 cm⁻¹. Then, the spectra of ligand-free CdS in water were fitted. As the LO band dominates the spectra, this band was fitted

first using a Lorentzian band profile. The frequency is directly derived from the local maximum in the measured spectrum (i.e. 305 cm^{-1}). The band width was adjusted until the experimental band is properly accounted affording a width of 13 cm^{-1} , which is comparable to values reported in the literature. Small bands with frequencies around the LO frequency had to be included to enhance the match of generated and experimental spectrum (see Figure 7b, green dashed lines). These bands do not necessary reflect real bands but may be a result of artefacts due to difficulties in baseline subtraction. The baseline at lower frequencies was dominated by a very strong polynomic increase of intensity towards the Rayleigh line, which made it difficult to properly estimate the baseline. As a result, the band width can be slightly inhomogeneous, which then requires inclusion of smaller bands around the middle frequency to achieve a match with convergence criteria of the fit. Importantly, the intensities of these bands are typically very low compared to the actual band. In this case, the integral intensities are smaller than 5 % and can therefore be neglected.

The spectra of ligand-free CdS in 10 M KOH were evaluated next using the bands already derived from the water spectra. To reconstruct the spectra properly, more bands needed to be included, particularly on the low frequency side of the LO band. To account for the additional spectral contribution, the local intensity maxima were searched for and, at each frequency maxima, an additional Lorentz band was included with a pre-defined width of 20 cm^{-1} . Subsequently, the widths of these bands and their intensities were iteratively altered until the best convergence between overall fit and experimental spectrum was achieved (see Figure 7c). This set of bands was then used to fit the 0.1 M KOH spectra by allowing only the relative intensities of the bands to change. The fit allowed a very good reconstruction of the spectra (see Figure 7d).

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Zeta Potential Analysis

A range of aqueous solutions with different pH values were made through addition of various amounts of KOH or HCl to deionised water. The ionic strength of each solution was kept constant at 0.5 M through addition of KCl. CdS-BF₄ (2 nmol) in DMF was injected into a vial and dried. An aliquot of a given solution (1 mL) was added to the vial, the solution was sonicated for 20 min and the pH was recorded. Zeta potential was measured in a disposable folded capillary cell on a Malvern Zetasizer Nano Z zeta potential analyser.

X-Ray Photoelectron Spectroscopy

CdS-BF₄ (10 nmol) in DMF was injected into a vial and the solvent was removed. An aqueous solution (2 mL) containing various [KOH] was added and the solution was stirred for 5 min. The particles were isolated from solution through centrifugation (10,000 rpm, 10 min), the supernatant was removed carefully and the resultant yellow precipitate was transferred onto a gold-coated silicon substrate and dried. *N.B.*, the dried sample is very

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hygroscopic, and as much supernatant as possible must be removed for the sample to dry effectively.

¹³C-NMR Spectroscopy of Cellulose

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Prior to use, ¹³C-cellulose (50 mg) was stirred for 20 min in 0.1 M NaOH (10 mL) at 80°C in air. The solid was collected by filtration, washed with water (500 mL) and freeze dried, producing a fine white powder. A photoreactor was charged with CdS-BF₄ in DMF (1 nmol) and dried. ¹³C-cellulose (10 mg) and 10 M NaOD in D₂O (1 mL) were added, the solution
10 purged with N₂ (cont. 2% CH₄) and was irradiated for 3 days. Subsequently, the reaction mixture was filtered through a hydrophilic syringe filter and a ¹³C-NMR spectrum was taken of the resultant solution.

To attain a spectrum of the insoluble cellulose, a photoreactor was charged with
15 ¹³C-cellulose (10 mg) and 10 M NaOD in D₂O (1.0 mL), either with or without CdS-BF₄ QDs (1 nmol). The resultant solution was purged with N₂ and irradiated, as described above, for 12 hours.

The reaction mixture was centrifuged (15 min, 12,000 rpm) and the solid residue was
20 washed with water and freeze-dried to give a pale yellow powder. The yellow powder was added to an NMR tube containing ZnCl₂ (1.00 g), LiCl (200 mg) and D₂O (360 μL). The mixture was degassed by three freeze-pump-thaw cycles, sealed and heated to 100°C overnight. The resulting brown melt was cooled to room temperature before a ¹³C NMR spectrum was taken.

25

¹H-NMR Spectroscopy of Cellulose

A photoreactor was charged with CdS-BF₄ (2 nmol) and dried. α-cellulose (100 mg) and
30 10 M NaOD in D₂O (2 mL) were added, the solution purged with N₂ (cont. 2% CH₄) and irradiated for 3 days. Subsequently, the reaction mixture was filtered through a hydrophilic syringe filter and a ¹H-NMR spectrum was taken of the resultant solution.

Transmission Electron Microscopy

CdS|CdO_x particles were prepared for TEM by adding CdS-BF₄ (1.5 nmol) to a vial and
35 drying *in vacuo*. Aqueous KOH (0.2 mL, 10 M) was added and the resultant solution was sonicated for 5 min. The suspension was centrifuged at 10,000 rpm for 5 min and the supernatant was removed. The particles were re-suspended in diethyl ether (around 1 mL) and 10 μL of the suspension was loaded onto a Cu TEM (TAAB) grid and dried.

40

Treatment of Data

All analytical measurements were performed in triplicate and are given as the unweighted mean \pm standard deviation (σ). The standard deviation of a measured value was calculated using equation (4).

$$\sigma = \sqrt{\frac{\sum(x-\bar{x})^2}{n-1}} \quad (4)$$

Where n is the number of repeated measurements, x is the value of a single measurement and \bar{x} is the unweighted mean of the measurements. σ was increased to 5% of \bar{x} in the event that the calculated σ was below this threshold.

10

The specific activity ($\text{mol}_{\text{H}_2} \text{g}_{\text{CdS}}^{-1}$) was calculated by equation (5) from the molar weight of the quantum dot (QD).

$$\textit{Activity} = \frac{n_{\text{H}_2}}{4/3\pi r_{\text{CdS}}^3 N_a \rho_{\text{CdS}} n_{\text{QD}}} \quad (5)$$

Where n_{H_2} is the H_2 produced (mol), r_{CdS} is the radius of the QD (cm), ρ_{CdS} is the density of CdS (4.84 g cm^{-3}), N_a is Avogadro's number (mol^{-1}) and n_{QD} is the number of moles of QD (mol).

15

Tables

Table 1

Details	CdS diam. nm	[KOH] M	α -cellulose loading mg/mL	Co-Cat.	[Co-Cat.] mM	Time h	H ₂ μ mol	$\pm \sigma$. μ mol
<i>pH optimisation</i>	4.77	-	50.00	-	-	18	0.02	0.01
		1.00					0.15	0.06
		2.50					0.86	0.14
		5.00					2.23	0.81
		10.00					22.51	1.13
<i>Cellulose loading optimisation</i>	5.19	10.00	100.00	-	-	18	17.90	1.03
			50.00				19.02	1.32
			37.50				17.82	3.37
			25.00				13.58	0.75
			10.00				9.39	0.85
			5.00				7.03	0.35
			2.50				5.27	0.26
0.00	1.53	0.14						
Long-term cellulose oxidation	4.77	10.00	50.00	-	-	0	0.00	0.00
						24	26.36	1.80
						48	48.30	3.48
						72	64.41	3.22
						96	75.94	3.80
						125	87.48	4.37
144	93.03	4.65						

Details	CdS diam. nm	[KOH] M	α -cellulose loading mg/mL	Co-Cat.	[Co-Cat.] mM	Time h	H ₂ μ mol	$\pm \sigma$. μ mol
Long-term cellulose oxidation	4.77	10.00	-	-	-	0	0.00	0.00
						24	2.74	0.37
						48	3.27	0.32
						72	3.41	0.28
						96	3.49	0.27
	125	3.56	0.26					
	144	3.73	0.27					
	0	0.00	0.00					
	24	31.73	2.12					
	48	50.49	3.70					
72	69.89	3.49						
96	83.77	4.19						
125	97.69	4.88						
144	104.43	5.22						
Visible-light experiment ($\lambda > 400$ nm)	5.30	10.00	50.00	Co(BF ₄) ₂ ·6H ₂ O	0.34	24	13.34	1.31
						24	0.00	0.00
Control – No QDs	-	10.00	50.00	-	-	24	0.00	0.00
Control – No light	5.29	10.00	50.00	-	-	24	0.00	0.00

Table 2

Details	CdS diam. nm	[KOH] M	α -cellulose loading mg/mL	Co-Cat.	[Co-Cat.] mM	Time h	H ₂ μ mol	$\pm \sigma$ μ mol	Activity mmolH ₂ g _{cds} ⁻¹ h ⁻¹	$\pm \sigma$ mmolH ₂ g _{cds} ⁻¹ h ⁻¹	
											CdS diam. nm
Glucose reforming	5.30	10.00	-	Co(BF ₄) ₂ ·6H ₂ O	0.34	0	0.00	0.00	0.00	0.00	0.00
						2	36.71	2.32	81.33	5.15	
						4	50.30	2.51	55.42	2.77	
						22	111.73	9.69	22.50	1.95	
						0	0.00	0.00	0.00	0.00	
	5.30	10.00	-	-	-	2	5.79	0.78	12.84	1.72	
						4	10.28	0.96	11.38	1.07	
						22	50.04	2.50	10.08	0.50	
						24	25.77	3.84	4.77	0.71	
						10	111.41	23.12	18.34	6.34	
HMF	5.29	10	-	-	-	24	25.77	3.84	4.77	0.71	
						10	111.41	23.12	18.34	6.34	
MeOH	5.19	1	Co(BF ₄) ₂ ·6H ₂ O	0.25	24	20.64	3.26	3.39	0.99		
						1	20.64	3.26	3.39	0.99	

Substrate	CdS diam. nm	[KOH] M	Co-Cat.	[Co-Cat.] mM	Time h	H ₂ μmol	± σ μmol	Activity mmolH ₂ gcds ⁻¹ h ⁻¹	± σ mmolH ₂ gcds ⁻¹ h ⁻¹
Formate	5.19	10	-	-	24	6.37	0.37	1.25	0.07
		1				1.18	0.23	0.23	0.05
		0.1				0.33	0.05	0.06	0.01

Table 1 illustrates photocatalytic H₂ evolution from cellulose reforming. 0.5 μM CdS quantum dots were irradiated at 25°C with simulated solar light (AM 1.5G, 100 mW cm⁻²). Solution volume was 2 mL in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL. Samples in the 'no light' control were wrapped with foil and stirred at room temperature. Photocatalysis solutions for glucose reforming contained 0.1 M glucose.

Table 2 illustrates photocatalytic H₂ evolution from various organic substrates. 0.5 μM CdS quantum dots were irradiated at 25°C with simulated solar light (AM 1.5G, 100 mW cm⁻²). Solution volume was 2 mL in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL. The substrate concentration was 0.1 M.

Table 3

Details	CdS diam. nm	[KOH] M	α-Cellulose Loading mg mL ⁻¹	Time h	H ₂ μmol	± σ. μmol
Suspended cellulose	5.19	10.00	50	0	0.00	0.00
				3	0.47	0.07
				6	1.99	0.25
				24	13.15	0.94
				48	25.44	1.27
				72	35.73	1.79
				96	44.73	2.24
				120	52.21	2.61
Suspension-free cellulose	5.19	10.00	-	0	0.00	0.00
				3	1.19	0.18
				6	2.85	0.39
				24	12.18	1.28
				48	22.21	2.12
				72	30.43	2.73
				96	36.42	3.19
				120	41.95	3.02

Table 3 illustrates photocatalytic H₂ evolution from suspended cellulose and suspension-free cellulose. 0.5 μM CdS quantum dots were irradiated at 25°C with simulated solar light (AM 1.5G, 100 mW cm⁻²). Solution volume was 1 mL in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL. The suspension-free cellulose solution was prepared by combining 50 mg mL⁻¹ of α-cellulose in 10 M KOH and irradiating with simulated solar light (AM 1.5G, 100 mW cm⁻²) without photocatalyst for 24 hours at 25°C. The solution was centrifuged (5,000 rpm, 10 minutes) and the supernatant was used for photocatalysis as described previously.

Table 4

Time h	H ₂ since previous time point μmol	EQY %
48	0.18	0.3
72	0.34	1.0
96.4	0.32	0.9
120	0.31	0.9
144	0.63	1.8
162	0.43	1.6
Average EQY		1.2 \pm 0.4

5 Table 4 illustrates the external quantum yield measurements from photocatalytic cellulose reforming. CdS|CdO_x quantum dots (5.29 nm, 0.5 μM) were irradiated with monochromatic light (430 nm, full-width at half maximum: 5 nm, intensity: $796 \pm 15 \text{ mW cm}^{-2}$) with KOH (2 mL, 10 M) and 50 mg mL⁻¹ α -cellulose at room temperature in a sealed photoreactor under anaerobic conditions with an internal volume of 3.83 mL. Each sample was irradiated over an area of 0.28 cm². The 48 hour time point is not included in the average.

10

Table 5

Time h	H ₂ since previous time point μmol	EQY %
3.1	0.33	7.9
4.1	0.20	15.4
24.1	4.70	17.7
48.1	6.13	19.2
72	5.91	18.6
96.2	5.55	17.3
Average EQY		17.7 \pm 1.5

15 Table 5 illustrates the external quantum yield measurements from photoreforming MeOH. CdS|CdO_x quantum dots (5.19 nm, 0.5 μM) were irradiated with monochromatic light (430 nm, full-width at half maximum: 5 nm, intensity: $725 \pm 15 \text{ mW cm}^{-2}$) with 2 mL KOH (10 M) and 0.1 M MeOH at room temperature in a sealed photoreactor under anaerobic conditions with an internal volume of 3.83 mL. The sample was irradiated over an area of 0.28 cm². The 1 hour time point is not included in average.

20

Table 6

Details	Co-Catalyst	[Co-Catalyst] mM	Time h	H ₂ μmol	± σ. μmol
<i>Metal loading</i>	Co(BF ₄) ₂ ·6H ₂ O	0.51	18	22.08	1.99
	K ₂ PtCl ₄	0.50	18	0.01	0.01
	Ni(BF ₄) ₂ ·6H ₂ O	0.50	18	11.80	1.23
<i>Cobalt Loading Study</i>	-	-	0	0.00	0.00
			1	0.34	0.05
			2	1.43	0.07
			3	2.63	0.13
			18	22.51	1.13
	Co(BF ₄) ₂ ·6H ₂ O	0.17	0	0.00	0.00
			1	1.61	0.12
			2	3.04	0.43
			3	4.27	0.45
			18	21.00	1.50
		0.34	0	0.00	0.00
			1	1.91	0.32
			2	3.60	0.45
			3	5.02	0.25
			18	23.20	1.64
		0.51	0	0.00	0.00
			1	1.44	0.28
			2	3.07	0.40
			3	4.52	0.48
			18	22.08	1.99
		0.68	0	0.00	0.00
	1		1.38	0.22	
	2		3.25	0.16	
	3		4.98	0.25	
	18		25.02	1.25	
	1.02	0	0.00	0.00	
		1	0.39	0.31	
		2	2.45	0.51	
		3	4.18	0.30	
		18	23.11	2.13	
	1.37	0	0.00	0.00	
		1	0.07	0.02	
2		1.36	0.29		
3		3.08	0.57		
18		20.52	1.07		

Table 6 illustrates photocatalytic H₂ evolution from cellulose reforming in the presence of varying co-catalysts. CdS|CdO_x (0.5 μM, 4.77 nm) was irradiated at 25°C with simulated solar light (AM 1.5G, 100 mW cm⁻²) in KOH (10 M, 2 mL) with 50 mg mL⁻¹ α-cellulose under an anaerobic atmosphere in a sealed photoreactor with an internal volume of 7.91 mL.

5

Table 7

Base/solvent	[Base] M	H ₂ μmol	± σ μmol	kH/kD	kH/kD error
NaOH/H ₂ O	9.75	12.02	1.51	1.36	0.16
NaOD/D ₂ O	9.75	8.95	0.86		

Table 7 illustrates kinetic isotope studies of photocatalytic cellulose reforming. CdS|CdO_x (0.5 μM, 4.96 nm) and 50 mg mL⁻¹ α-cellulose irradiated at 25°C with simulated solar light (AM 1.5G, 100 mW cm⁻²) for 24 hours. Solvent volume was 2 mL in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL.

10

Table 8

15

Experiment Number	α-Cellulose mg	Anhydroglucose monomers μmol	H ₂ μmol	background corrected H ₂ μmol	Conversion %
1	1.18	7.28	18.42	8.04	9.21
	0.00	-	10.38		
2	0.81	5.00	16.24	5.84	9.73
	0.00	-	10.40		
3	1.65	10.18	19.07	7.72	6.32
	0.00	-	11.35		

Table 8 illustrates percentage conversion of photocatalytic cellulose reforming. CdS|CdO_x (2 μM, 5.29 nm) was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C in 1 mL KOH (10 M) over 6 days with 0.34 mM Co(BF₄)₂ in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL. Moles of anhydroglucose were calculated by dividing the weight of added α-cellulose by the molar mass of an anhydroglucose repeating unit (162.14 g mol⁻¹) assuming weight contribution from polysaccharide end groups is negligible. Background correction was achieved by subtracting the H₂ produced in the equivalent experiment without α-cellulose. Conversion was calculated assuming a theoretical maximum of 12 equivalents of H₂ form per anhydroglucose repeating unit.

20

25

Table 9

Details	Substrate	Substrate loading mg/mL	H ₂ μ mol	$\pm \sigma$ μ mol	Activity m molH ₂ gCdS ⁻¹ h ⁻¹	$\pm \sigma$ mmolH ₂ gCdS ⁻¹ h ⁻¹
<i>Lignocellulose component reforming</i>	α -cellulose	50.00	23.71	1.36	4.38	0.25
	hemicellulose	25.00	21.39	3.27	3.95	0.60
	lignin	2.00	2.60	0.40	0.48	0.07
	lignin	0.25	4.91	1.94	0.91	0.36
	None	-	2.54	0.13	0.47	0.02

Table 9 illustrates photocatalytic H₂ evolution from reforming the components of lignocellulose. CdS|CdO_x (0.5 μ M, 5.30 nm) was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C in KOH (10 M, 2 mL) over 24 h with 0.34 mM Co(BF₄)₂ in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL.

Table 10

Details	Substrate	Substrate loading mg mL ⁻¹	H ₂ μ mol	$\pm \sigma$ μ mol	Activity mmolH ₂ gCdS ⁻¹ h ⁻¹	$\pm \sigma$ mmolH ₂ gCdS ⁻¹ h ⁻¹
<i>Raw lignocellulose reforming</i>	Paper	50.00	12.37	1.92	2.28	0.35
	Cardboard	50.00	9.04	2.78	1.67	0.51
	Newspaper	50.00	5.81	0.29	1.07	0.05
	Bagasse	50.00	5.95	2.49	1.10	0.46
	Wooden branch	50.00	51.47	2.57	9.50	0.48
	Grass	50.00	11.80	6.58	2.18	1.21
	Sawdust	50.00	9.51	4.09	1.76	0.76
	None	-	2.54	0.13	0.47	0.02

Table 10 illustrates photocatalytic H₂ evolution from raw lignocellulosic biomass reforming. CdS|CdO_x (0.5 μ M, 5.30 nm) was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C over 24 hours in KOH (10 M, 2 mL) with Co(BF₄)₂ (0.34 mM) in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL. Raw biomass substrates were cut roughly into pieces < 0.25 cm long before photocatalysis.

Additional Experimental and Results

In addition to the oxidation of organic substrates such as biomass, the photocatalyst of the invention is capable of degrading and/or generating hydrogen from common organic polymers, including those used as commercial plastics in consumer products.

The photocatalyst of the invention was used together with the following organic substrates: poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), poly(vinyl pyrrolidone) (PVP), and poly(ethylene glycol) (PEG).

5 In a typical experiment, CdS-BF₄ (1 nmol) was added to a pyrex photoreactor and dried. The desired polymer (from 20-200 mg) was weighed into the photoreactor and aqueous KOH (2 mL, 10 M) was added. Optionally, Co(BF₄)₂·6H₂O (0.25 mM) was added to the solution as a co-catalyst. The mixture was purged with N₂ (containing 2% CH₄) for 10 minutes prior to photocatalysis, and the solution was irradiated as described previously. Thus, a sample
10 mixture was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere for 24 hours.

PVP was purchased from Sigma-Aldrich, having a M_w of 55,000. PEG was purchased from Sigma-Aldrich, having a M_w of 1,500. PET and PLA were purchased from Goodfellow Cambridge Ltd.

15

The photocatalyst works adequately without the need for a co-catalyst (see Figure 20), however activity can be enhanced upon addition of Co(BF₄)₂ catalyst (Figure 21).

20 An increase in photocatalyst activity should also be achievable with other transition metal co-catalysts, such as Ni and Pt.

An increase in photocatalyst activity was seen when an organic polymer or an organic biomass was pre-heated in aqueous base prior to irradiation (Figure 22). In this experiment, the PVP or α-cellulose substrate (100 mg of each, α-cellulose as used in the experiments
25 described above) was suspended in aqueous KOH (1 mL, 10 M) and heated to 100°C for 1 h whilst stirring. After cooling to room temperature, the resultant suspension was transferred to a pyrex photoreactor, containing dried CdS-BF₄ (1 nmol) and KOH (1 mL, 10 M). Optionally, Co(BF₄)₂·6H₂O (0.25 mM) may be added to the solution as a co-catalyst. Each mixture was purged with N₂ (containing 2% CH₄) for 10 minutes prior to photocatalysis,
30 and the solution was irradiated as described previously. Thus, a sample mixture was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere for 24 hours. The amount of hydrogen evolved is shown in Figure 22.

Further Experimental and Results

35

As noted in the experimental section above, the photocatalyst of the invention may be used to degrade and generate hydrogen from common organic polymers. For example, the inventors have shown that poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), poly(vinyl pyrrolidone) (PVP), and poly(ethylene glycol) (PEG) are suitable substrates for the
40 photocatalyst. In further work, the photocatalyst of the invention is shown to be capable of degrading and/or generating hydrogen from other polymer types, including polyurethane (PUR), polyethylene glycol (PEG) and low-density polyethylene (LDPE). The photocatalyst

may also be used to generate hydrogen from a polymer substrate pre-treated with base prior to the photocatalytic reaction.

Substrates for Use

5

It is now established that the photocatalysts of the invention may be used for photocatalytic reforming of a broad range of natural and synthetic organic polymers. It has been found that some organic polymers are poor substrates for the photocatalyst, but the hydrogen production rate may be enhanced or initiated after pre-treatment of the polymer with base, such as NaOH, prior to the photocatalytic reaction. The pre-treatment of a polymer is described in further detail in the section below.

10

In a series of reactions, different organic polymers were treated with a photocatalyst, and the hydrogen evolution over time was monitored. In a typical experiment a polymer substrate (100 mg) was treated with CdS|CdO_x (0.5 μM) in 10 M NaOH. The mixture was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C for 4 h under an anaerobic atmosphere.

15

Photoreforming of each of the polymers was also studied after pre-treatment of the polymer with base. Here, each polymer (100 mg) was mixed with 10 M NaOH (2 mL), and stirred for 24 h. at 40°C. The mixture was centrifuged, and the precipitate removed. The supernatant was then added to CdS|CdO_x (0.5 μM), and the mixture was irradiated as before (thus, simulated solar light (AM 1.5G, 100 mW cm⁻² at 25°C for 4 h, under an anaerobic atmosphere).

20

The polymers tested included α-cellulose, PLA (polylactic acid), PET (polyethylene terephthalate), PUR (polyurethane), PVP (polyvinylpyrrolidone), PEG (polyethylene glycol), LDPE (low-density polyethylene), PVC (polyvinyl chloride), PMMA (poly(methyl methacrylate)), PS (polystyrene), PC (polycarbonate), chitin, chitosan, casein and BSA (bovine serum albumin).

25

Polycarbonate (pellets, M_w 45,000), polyethylene glycol (M_w 1,500), polymethyl methacrylate (M_w 350,000), polypropylene (amorphous), polystyrene (pellets, M_w 35,000), and poly(vinylpyrrolidone) (powder, M_w 55,000) were purchased from Sigma-Aldrich and used without further purification.

30

Low density polyethylene (powder, 300 μm), polyethylene terephthalate (powder, 300 μm), polylactic acid (pellets, 3 mm), polyurethane (foam, 10 × 100 × 100 mm³, density 0.08 g cm⁻³), and unplasticised polyvinyl chloride (powder, 250 μm) were obtained from Goodfellow Cambridge Ltd.

35

40

Poly(lactic acid) and polyurethane were ground in a coffee grinder to provide powders with particles having diameters of approximately 900 and 1,400 μm , respectively.

5 NaOD (40 wt% in D_2O), and NaOH were purchased from Fischer Scientific. D_2O (99.96 atom% D) was obtained from Euriso-Top. The plastic water bottle was purchased from M&S Cambridge Rail Simply Food, Station Rd, Cambridge CB1 2JW, drained of water, dried and then ground using a coffee grinder into pieces $\leq 1 \text{ cm}^2$.

10 Figures 23 and 24 show the amount of hydrogen evolved from a range of polymers with and without pre-treatment of that polymer with base. The amount of hydrogen collected is the amount collected after 4 hours of irradiation.

15 The results show that many polymers may be degraded under the photocatalytic reaction conditions, and frequently the pre-treatment of the polymer substrate with base enhances hydrogen evolution. In some cases, hydrogen evolution is not observed when a polymer substrate is irradiated in the presence of the photocatalyst (for example, for the polymers PVC, PS and PC). However, hydrogen evolution is seen when these polymer substrates are pre-treated with base.

20 A summary of the results is set out below for each polymer tested.

25 Poly(lactic acid) (PLA). Very high hydrogen production was observed, and the hydrogen evolution was not greatly affected by a pre-treatment. The polymer is believed to degrade to lactic acid when it is added to the basic photocatalyst-containing mixture. It is also believed that pyruvic acid is formed during photoreforming.

30 Poly(ethylene terephthalate) (PET). Moderate hydrogen production was observed, and the hydrogen production rate was increased greatly (by around five times) when the substrate was pre-treated with base. The inventors were also able to repeat the work using a PET sample taken from a consumer product water bottle.

35 During the reaction it was observed that terephthalic acid was produced, and this precipitated from the reaction mixture as its disodium salt (disodium terephthalate) and could be recovered. Other products of the reaction were likely to include ethylene glycol, glycolic acid, acetic acid, formic acid and ethanol.

40 Polyurethane (PUR). Low hydrogen production was observed, and the production rate was increased greatly (by around six times) when the substrate was pre-treated with base. The products of the photoreformation reaction likely included diaminotoluene, formic acid, acetic acid, lactic acid and pyruvic acid.

Polyvinylpyrrolidone (PVP). Low hydrogen production was observed, and the production was increased greatly (by greater than ten times) when the substrate was pre-treated with base.

- 5 Polyethylene glycol (PEG). Low hydrogen production was observed, and the production was increased greatly (by around three times) when the substrate was pre-treated with base.

Low density polyethylene (LDPE). A very low hydrogen production was observed, both with and without pre-treatment of the polymer substrate.

10

Poly(methyl methacrylate) (PMMA), Polystyrene (PS) and Polycarbonate (PC). No hydrogen production was observed without pre-treatment of the polymer substrate. With pre-treatment a very low hydrogen production was observed.

- 15 The results for the polymers described above are shown in Figure 23, and are set out in Table 11 below.

Table 11

Substrate	Substrate loading mg mL ⁻¹	H ₂ μmol	± σ μmol	Activity mmol _{H₂} g _{CdS} ⁻¹ h ⁻¹	± σ mmol _{H₂} g _{CdS} ⁻¹ h ⁻¹
Without Pre-Treatment					
PLA	50.00	79.6	3.80	93.4	4.67
PET	25.00	3.27	0.830	0.850	0.279
PUR	25.00	0.665	0.230	2.57	0.460
PVP	50.00	0.097	0.005	0.850	0.279
PEG	50.00	0.195	0.009	0.118	0.006
LDPE	50.00	0.666	0.033	0.237	0.012
PVC	50.00	0	0	0.0801	0.004
PMMA	50.00	0	0	0	0
PS	50.00	0	0	0	0
PC	50.00	0	0	0	0
With Pre-Treatment					
PLA	50.00	49.5	12.6	58.9	15.2
PET	25.00	11.9	1.95	12.4	2.04
PUR	25.00	2.65	0.400	3.22	0.126
PVP	50.00	3.37	0.168	4.13	0.206
PEG	50.00	0.584	0.029	0.754	0.038
LDPE	50.00	0.179	0.009	0.264	0.013
PVC	50.00	0.170	0.008	0.253	0.013
PMMA	50.00	0.142	0.007	0.218	0.011
PS	50.00	0.118	0.006	0.177	0.009
PC	50.00	0.109	0.005	0.146	0.007

Chitin, chitosan, casein and bovine serum albumin (BSA). Low hydrogen production was observed. The casein and BSA polymers were not pre-treated. The results are shown in Figure 24, and are set out in Table 12 below. In further experiments, chitin and chitosan were pre-treated, and the results are shown in Figure 25.

Table 12

Substrate	Substrate loading mg mL ⁻¹	H ₂ μmol	± σ μmol	Activity mmol _{H2} g _{CdS} ⁻¹ h ⁻¹	± σ mmol _{H2} g _{CdS} ⁻¹ h ⁻¹
Chitin	50.00	0.181	0.009	0.264	0.013
Chitosan	50.00	0.046	0.002	0.102	0.005
Casein	50.00	3.94	0.197	5.52	0.276
BSA	50.00	0.553	0.027	0.867	0.043

10

Analysis of Substrate and Substrate Degradation Products

The reaction of the polymer substrates under the photodegradation methods of the present invention was studied by ¹H NMR spectroscopy. In a series of experiments the degradation of PLA, PET and PU was investigated.

Similar to the photoreforming experiments describe above, a polymer substrate (50 mg) was treated with CdS|CdO_x (0.5 μM) in 10 M NaOD in D₂O (2 mL). The mixture was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C for 24 h under an anaerobic atmosphere.

Samples of each polymer were taken before and after photoreforming, filtered and analysed by ¹H NMR spectroscopy using a Bruker 400 MHz Avance spectrometer at room temperature. The spectra are shown in Figure 26.

25

Pre-Treatment of Organic Substrate

The inventors have found that hydrogen production, such as the hydrogen production rate, in the photocatalytic treatment of an organic substrate may be enhanced when that organic substrate is pre-treated with base. It has also been found that this pre-treatment prevents contamination of the solid photoreforming leftovers with Cd.

The improvement in hydrogen production rate is shown in Figures 23 and 25 and Table 11 for a range of organic substrates.

35

The conditions for the pre-treatment were studied in order to identify an optimal set of conditions. In each pre-treatment a PET substrate (at 25 mg/mL) was treated with 10 M NaOH for a set time. After this time undissolved substrate was optionally removed by centrifugation, and the supernatant was used in a photoreforming reaction.

5

The supernatant (2 mL) was added to CdS|CdO_x (0.5 μM), and the mixture was irradiated with simulated solar light (AM 1.5G, 100 mW cm⁻² at 25°C for 4 h) in a sealed photoreactor under an anaerobic atmosphere with an internal volume of 7.91 mL.

10 The conditions investigated for the pre-treatment are set out below:

A: 24 h stir at 40°C, centrifuge

B: 24 h rest at room temperature, centrifuge

C: 24 h stir at 80°C, centrifuge

15 D: 24 h stir at 40°C, no centrifuge

E: 48 h stir at 40°C, centrifuge

F: 24 h stir at room temperature, centrifuge

None: no pre-treatment

20 The amount of hydrogen evolved after 4 hours in the subsequent photoreforming reaction was recorded. The results are shown in Figure 27. The results show that condition A provided the highest rate of hydrogen evolution, and these conditions were used in the experiments described above for the range of organic substrates.

25

Base for Use

In the experimental preparation of the photocatalyst described previously, CdS|CdO_x was formed in a highly basic aqueous solution of KOH. It has now been shown that aqueous NaOH can be used in place of aqueous KOH to lower the cost of photoreforming without affecting the performance of the CdS|CdO_x photocatalyst.

30

Thus, the CdS|CdO_x photocatalyst was prepared as described previously except that 10 M KOH was replaced with 10 M NaOH. The resulting photocatalyst was used to treat α-cellulose and PET. Thus, α-cellulose (100 mg) and PET (100 mg) were exposed to CdS|CdO_x (0.5 μM) in the presence of 10 M NaOH or KOH (10 mL) under simulated solar light (AM 1.5G, 100 mW cm⁻²) at 25°C under an anaerobic atmosphere. The evolution of hydrogen from the photoreforming reaction was monitored, and the amount of hydrogen collected after 4 hours of irradiation was measured. The results are shown in Figure 28.

40

References

All documents mentioned in this specification are incorporated herein by reference in their entirety.

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Claims

1. A method of producing hydrogen, the method comprising the step of exposing a photocatalyst to visible and/or ultraviolet light in the presence of an organic substrate, wherein the photocatalyst has a semiconductor core having an oxide- and/or hydroxide-functionalised surface, thereby to generate hydrogen from the organic substrate, and the hydrogen is optionally collected.
2. A method for degrading an organic substrate, the method comprising the step of exposing a photocatalyst to visible and/or ultraviolet light in the presence of the organic substrate, wherein the photocatalyst has a semiconductor core having an oxide- and/or hydroxide-functionalised surface.
3. The method of claim 2, where the degradation of the organic substrate produces hydrogen, and the hydrogen is optionally collected.
4. The method of any one of the preceding claims, wherein the photocatalyst semiconductor core comprises a semiconductor selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, CuI GaS, $Cd_{(1-x)}Zn_{(x)}S_{(1-y)}Se_{(y)}$, $CuGa_3S_5$, $ZnO_{(1-x)}S_{(x)}$, FeS_2 , SiC, CuO, SnS_2 , SnSe and carbon nanoparticles, such as CdS, wherein each x is between 0 and 1, and each y is between 0 and 1, and the semiconductor core has an oxide- and/or hydroxide-functionalised surface.
5. The method of claim 4, wherein the photocatalyst semiconductor core consists essentially of a semiconductor material selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, CuI GaS, $Cd_{(1-x)}Zn_{(x)}S_{(1-y)}Se_{(y)}$, $CuGa_3S_5$, $ZnO_{(1-x)}S_{(x)}$, FeS_2 , SiC, CuO, SnS_2 , SnSe and carbon nanoparticles, such as CdS, and the semiconductor core has an oxide- and/or hydroxide-functionalised surface.
6. The method of claim 4 or claim 5, wherein the photocatalyst semiconductor core is $Cd_{(1-x)}Zn_{(x)}S_{(1-y)}Se_{(y)}$.
7. The method of claim 6, wherein the photocatalyst semiconductor core is CdS having oxide- and/or hydroxide-functionality at its surface ($CdS|CdO_x$).
8. The method of any one of the preceding claims, wherein the photocatalyst is a particle having a diameter in the range 1 to 100 nm, such as in the range 1 to 10 nm.
9. The method of any one of the preceding claims, wherein the photocatalyst is exposed to visible light in the presence of the organic substrate, such as light having a wavelength in the range 400 to 700 nm.

10. The method of any one of the preceding claims, wherein the photocatalyst and the organic substrate are provided in an aqueous mixture.
- 5 11. The method of claim 10, wherein the photocatalyst and the organic substrate are provided in an aqueous mixture having a pH of 10 or more, such as pH 11 or more, such as pH 12 or more.
12. The method of claim 11, wherein the aqueous mixture is an aqueous NaOH or an aqueous KOH mixture.
- 10 13. The method of claim 10 or claim 11, wherein the method produces carbon dioxide, and the carbon dioxide is retained in the aqueous mixture as carbonate.
14. The method of any one of the preceding claims, wherein the organic substrate
15 contains a component having a molecular weight of 50 or more, such as 500 or more.
15. The method of any one of the preceding claims, wherein the organic substrate may be or comprise a polyol.
- 20 16. The method of any one of the preceding claims, wherein the organic substrate is a biomass.
17. The method of any one of the preceding claims, wherein the organic substrate is cellulose or a cellulose-containing material.
- 25 18. The method of any one of claims 1 to 14, wherein the organic substrate is selected from the group consisting of wood, paper, cardboard, bagasse, grass and sawdust.
19. The method of any one of claims 1 to 14, wherein the organic substrate is selected
30 from the group consisting of general waste, plastics, packing materials, waste food, aliphatic polyols, algae, sugars, starches, biomass, sewage and/or domestic waste.
20. The method according to any one of claims 1 to 14, wherein the organic substrate is an organic polymer.
- 35 21. The method according to claim 20, wherein the organic polymer is selected from the group consisting of polyester, substituted polyethylene, polyether, polycarbonate, and polyurethane, optionally together with polysaccharide, polypeptide and lignin.
- 40 22. The method according to claim 21, wherein the organic polymer is selected from the group consisting of poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), poly(vinyl pyrrolidone) (PVP), and poly(ethylene glycol) (PEG), and optionally alternatively or

additionally selected from PUR (polyurethane), LDPE (low-density polyethylene), PVC (polyvinyl chloride), PMMA (poly(methyl methacrylate)), PS (polystyrene), PC (polycarbonate), chitin, chitosan, casein and BSA (bovine serum albumin).

- 5 23. The method of any one of the preceding claims, wherein the organic substrate is at least partially degraded prior to the exposure of the photocatalyst to visible and/or ultraviolet light.
24. The method of any one of the preceding claims, wherein the organic substrate is pre-
10 treated with base prior to the exposure of the photocatalyst to visible and/or ultraviolet light.
25. The method of claim 24, wherein the base is an aqueous inorganic base, such as aqueous NaOH or aqueous KOH.
- 15 26. The method of claim 24 or claim 25 wherein the pre-treatment comprises heating the organic substrate in the presence of the base.
27. The method of any one of claims 23 to 26, further comprising the step of removing solid materials produced in the pre-treatment, such as by centrifugation.
- 20 28. A photocatalyst having a semiconductor core having an oxide- and/or hydroxide-functionalised surface, which is obtained or obtainable by oxygenation of a surface of a semiconductor selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, CuI GaS, $Cd_{(1-x)}Zn_{(x)}S_{(1-y)}Se_{(y)}$, $CuGa_3S_5$, $ZnO_{(1-x)}S_{(x)}$, FeS_2 , SiC, CuO, SnS₂, SnSe and carbon nanoparticles, such as CdS, wherein each x is between 0 and 1, and each y is between 0 and 1, thereby to provide a photocatalyst having an oxide- and/or
25 hydroxide-functionalised surface.
29. The photocatalyst of claim 28, wherein the photocatalyst is obtained or obtainable by
30 oxygenation of a surface of CdS.
30. The photocatalyst of claim 28 or claim 29, wherein the photocatalyst is provided in a basic aqueous mixture having a pH of 10 or more, such as a pH of 11 or more, such as a pH of 12 or more.
- 35 31. The photocatalyst of any one of claims 28 to which is provided in an aqueous NaOH or an aqueous KOH mixture.
32. A method of preparing a photocatalyst, the method comprising the step of
40 oxygenating the surface of a semiconductor selected from the group consisting of CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, CuI GaS, $Cd_{(1-x)}Zn_{(x)}S_{(1-y)}Se_{(y)}$, $CuGa_3S_5$, $ZnO_{(1-x)}S_{(x)}$, FeS_2 , SiC, CuO, SnS₂, SnSe and carbon nanoparticles, such as CdS, wherein

each x is between 0 and 1, and each y is between 0 and 1, thereby to provide a photocatalyst having an oxide- and/or hydroxide-functionalised surface.

5 33. The method of claim 32, the method comprising the step of oxygenating the surface of CdS, thereby to yield a CdS|CdO_x photocatalyst.

10 34. The method of claim 32 or claim 33, wherein the method comprises treating the semiconductor with aqueous base having a pH of 10 or more, such as a pH of 11 or more, such as a pH of 12 or more.

35. The method of claim 34, wherein the aqueous base is aqueous NaOH or aqueous KOH.

Fig. 1

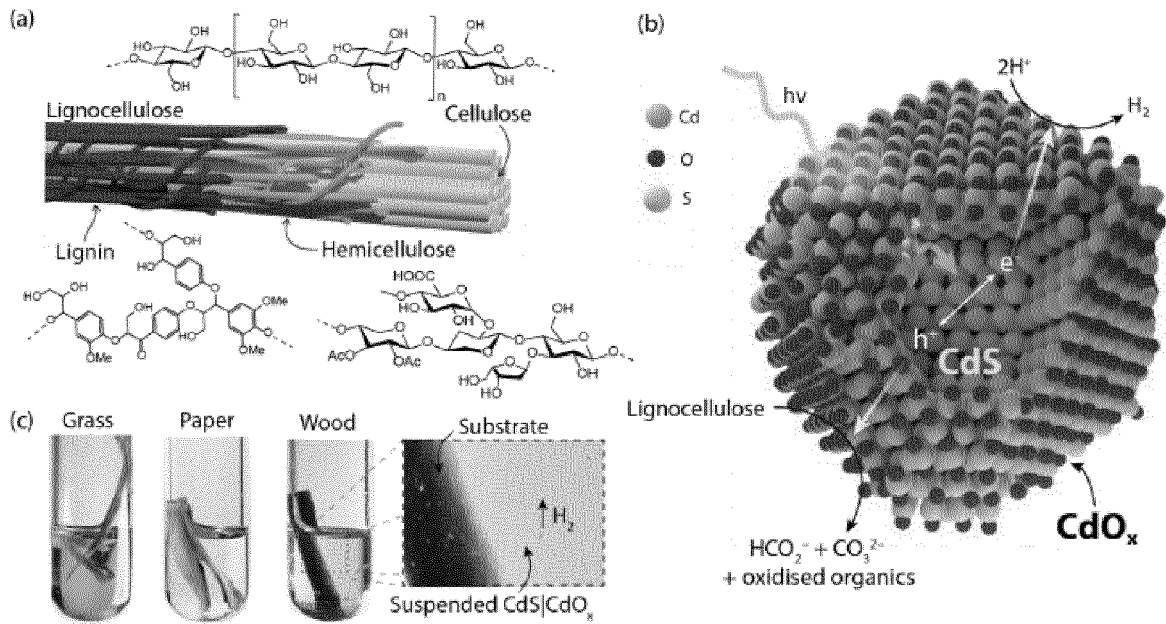


Fig. 2

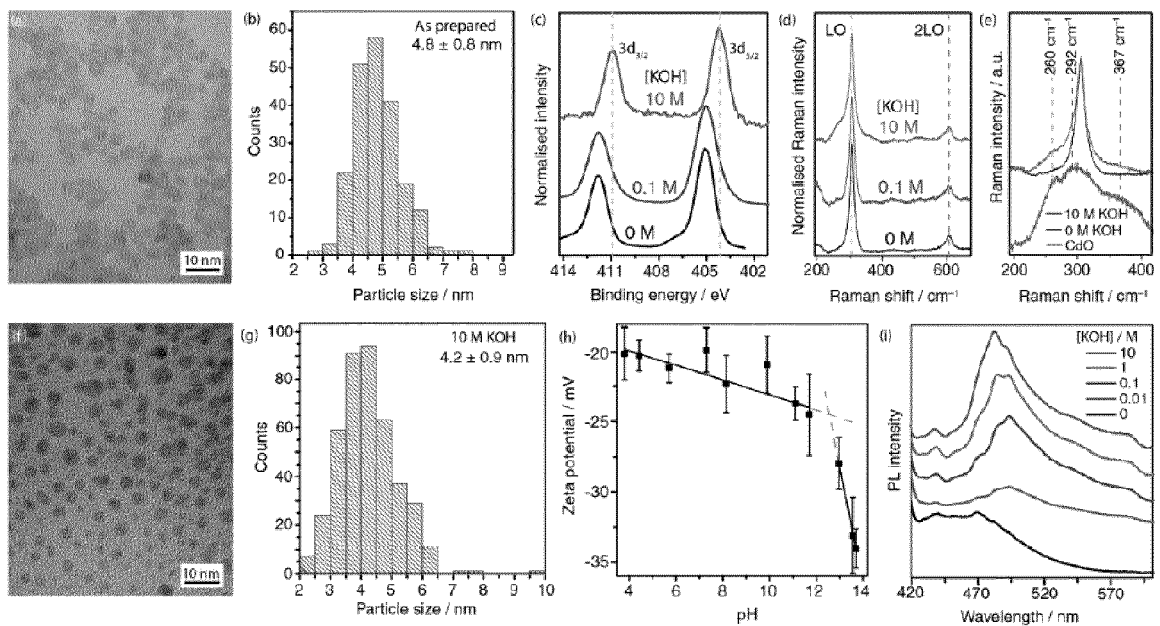


Fig. 3

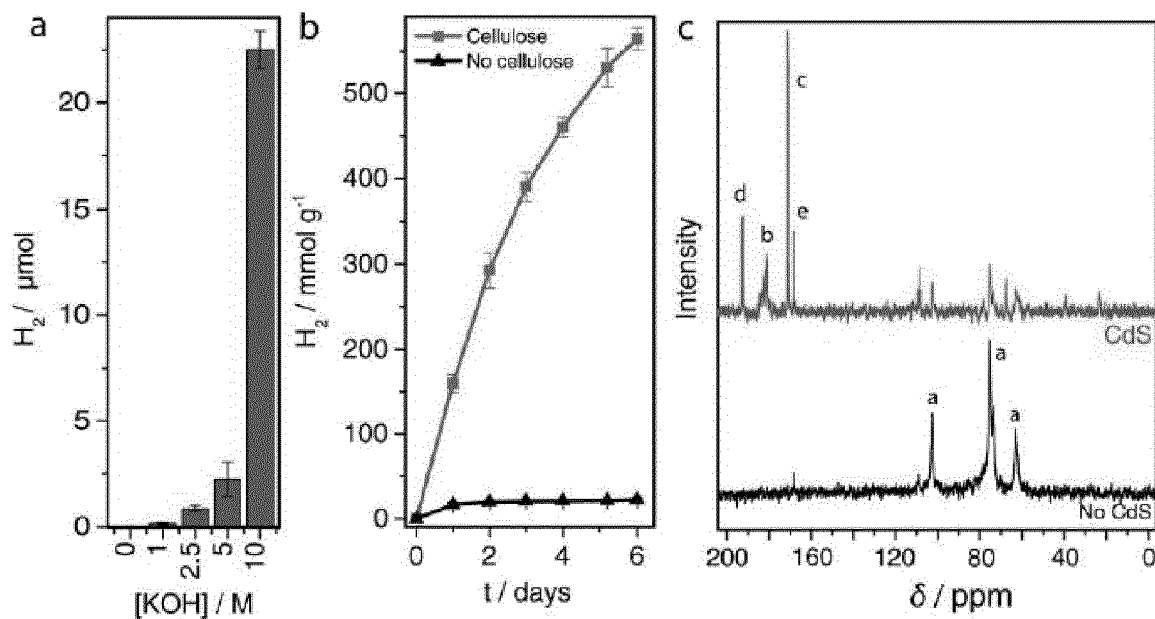


Fig. 4

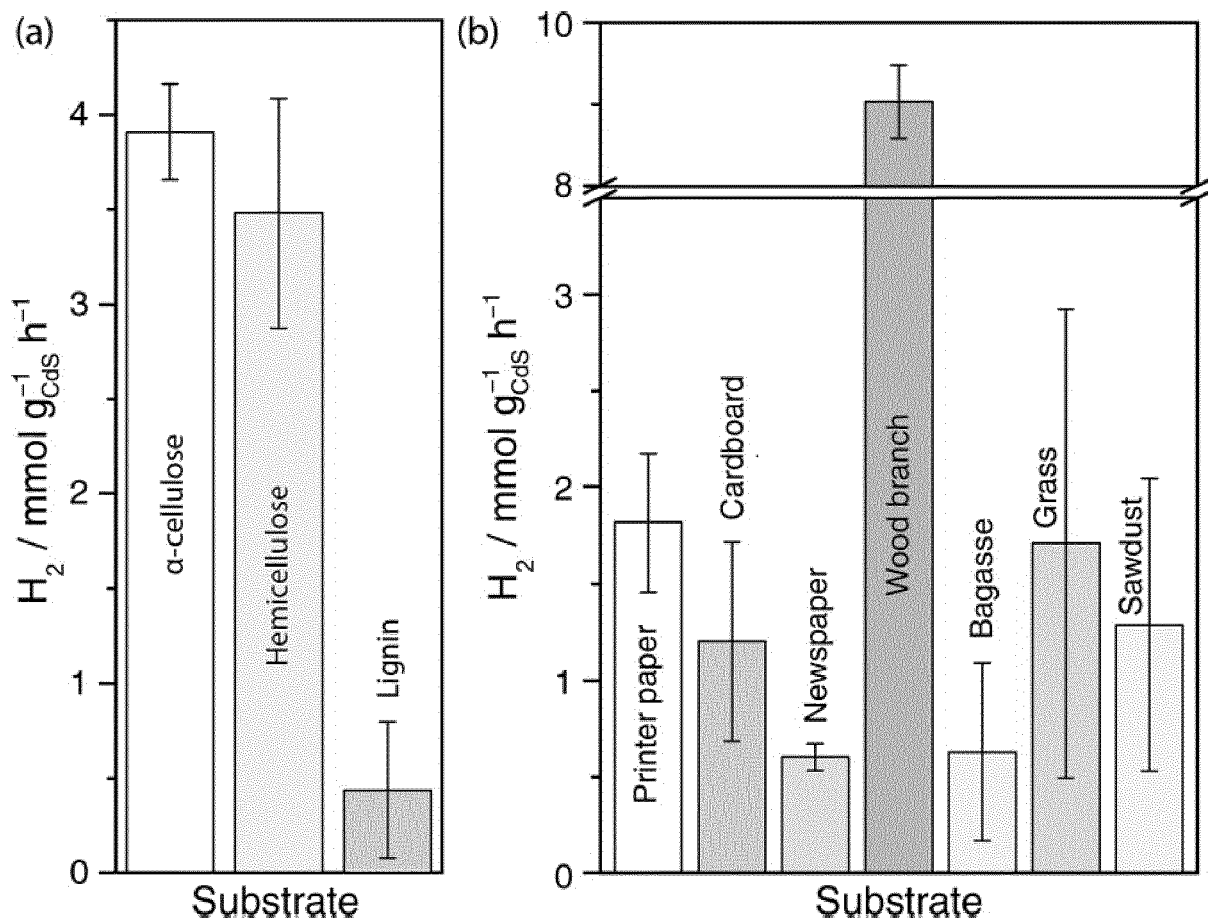


Fig. 5

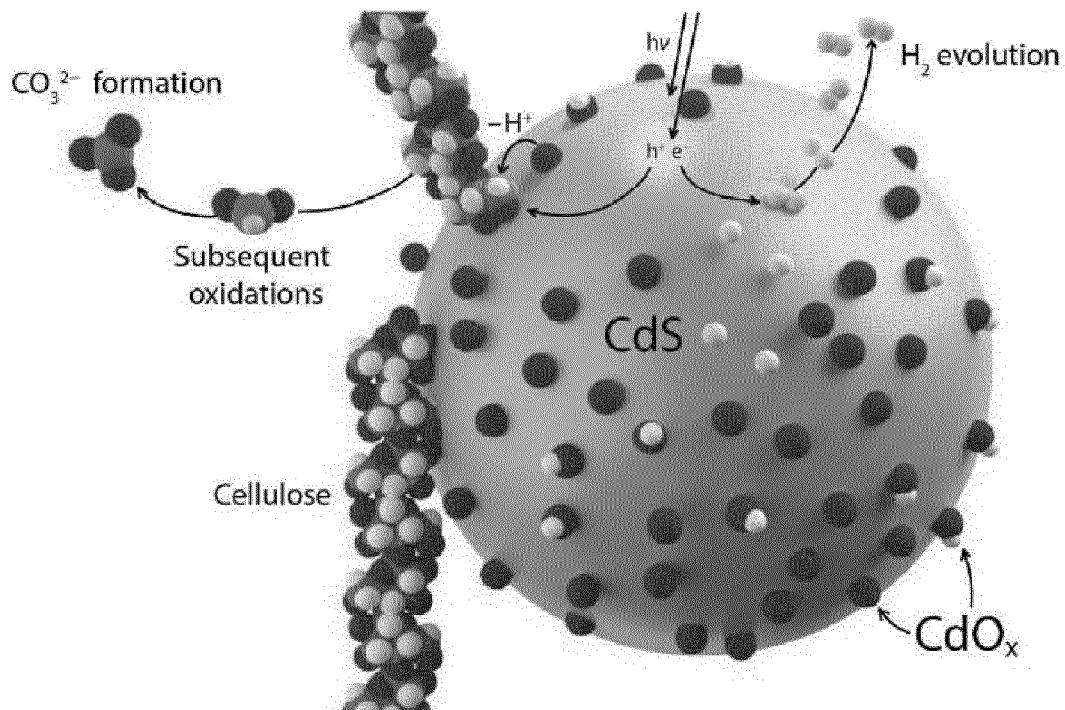


Fig. 6

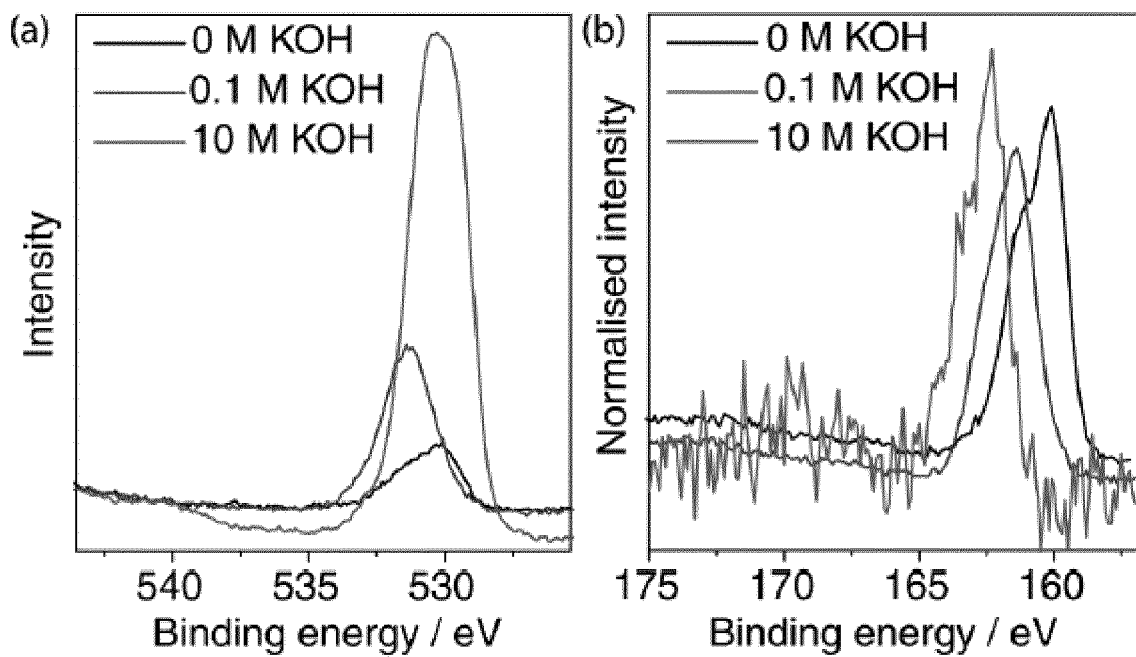


Fig. 7

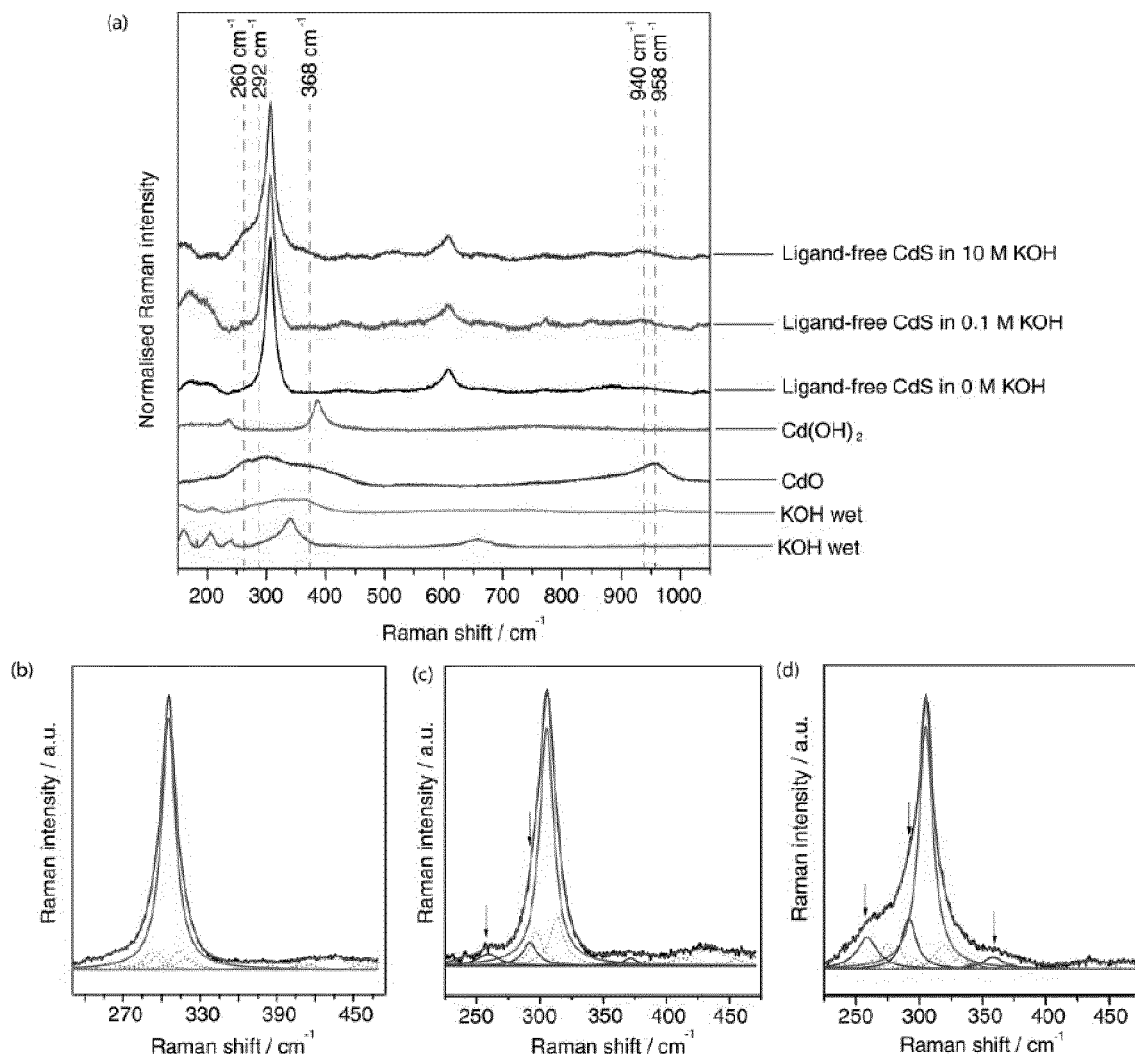


Fig. 8

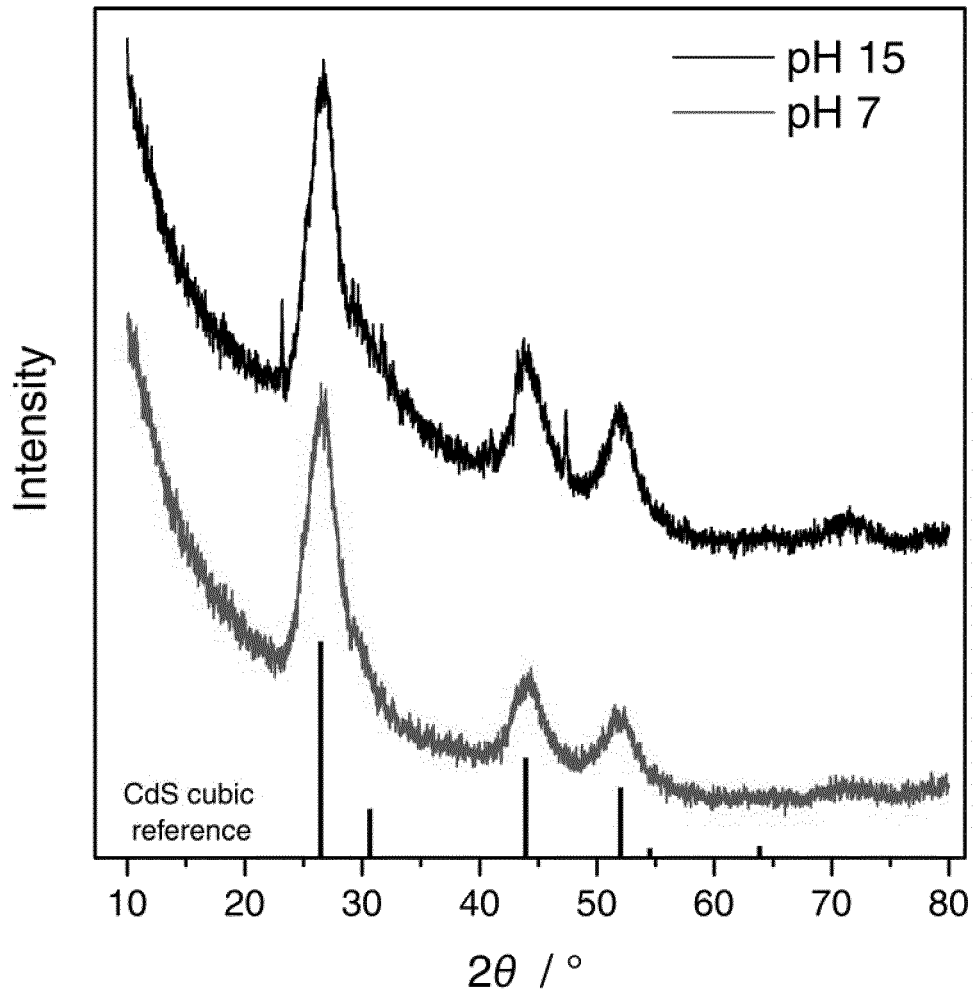


Fig. 9

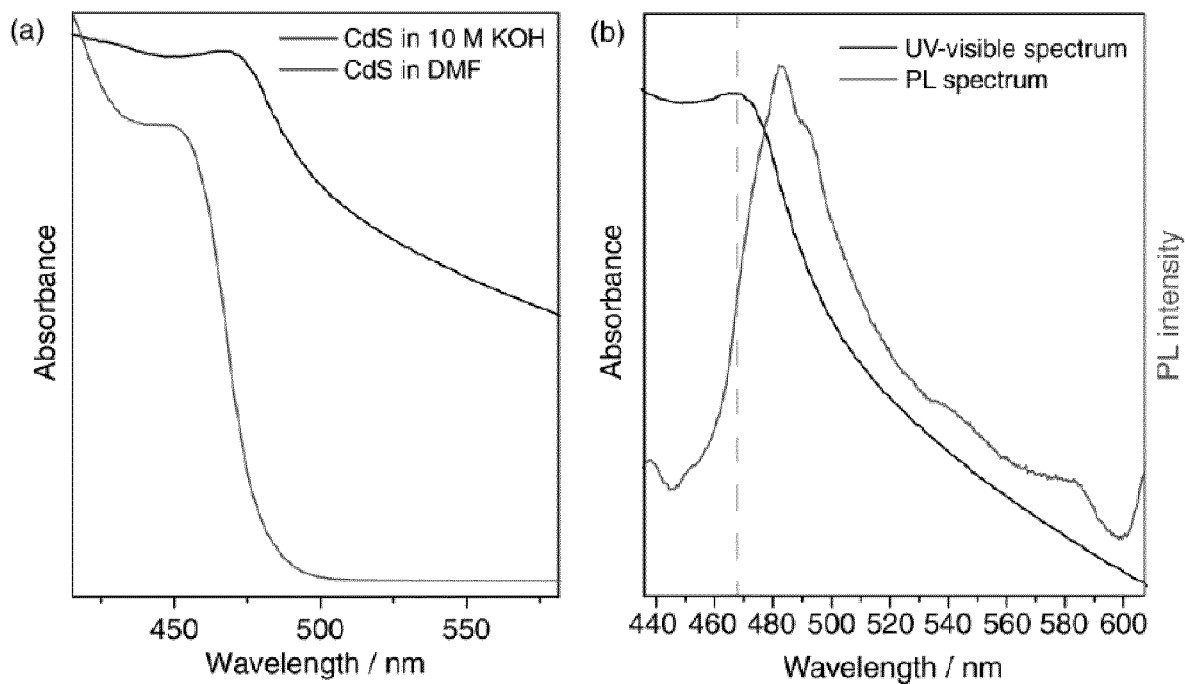


Fig. 10

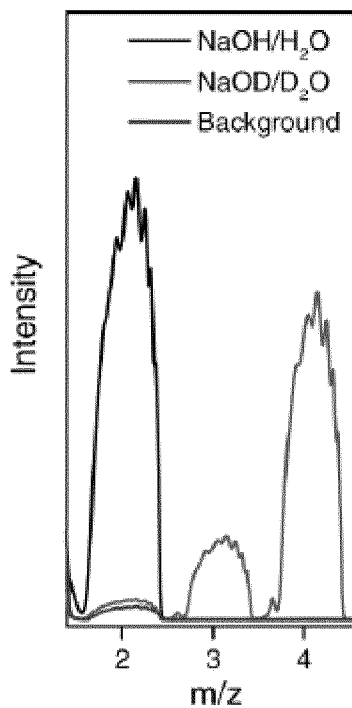


Fig. 11

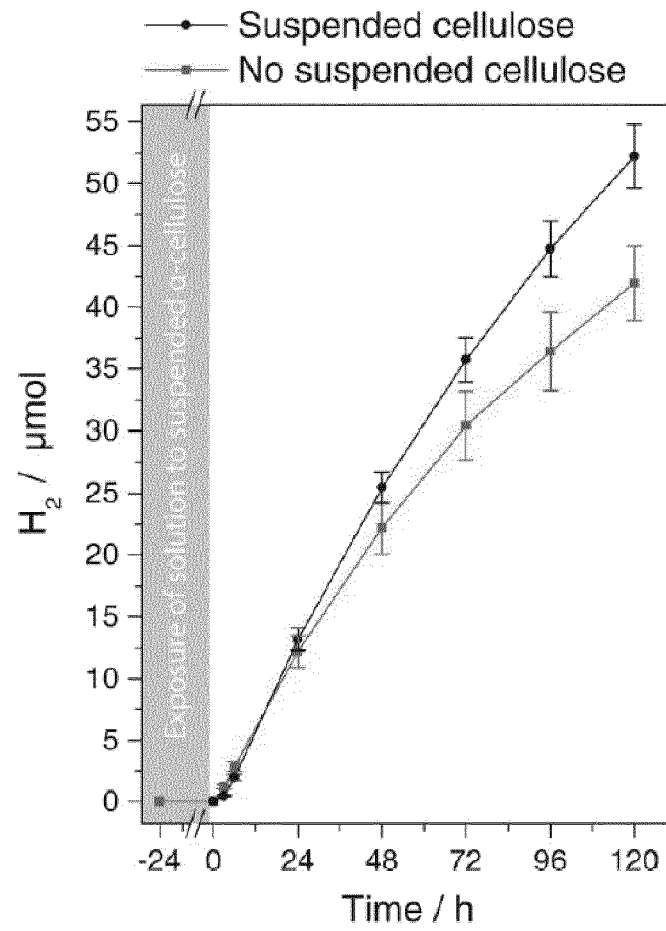


Fig. 12

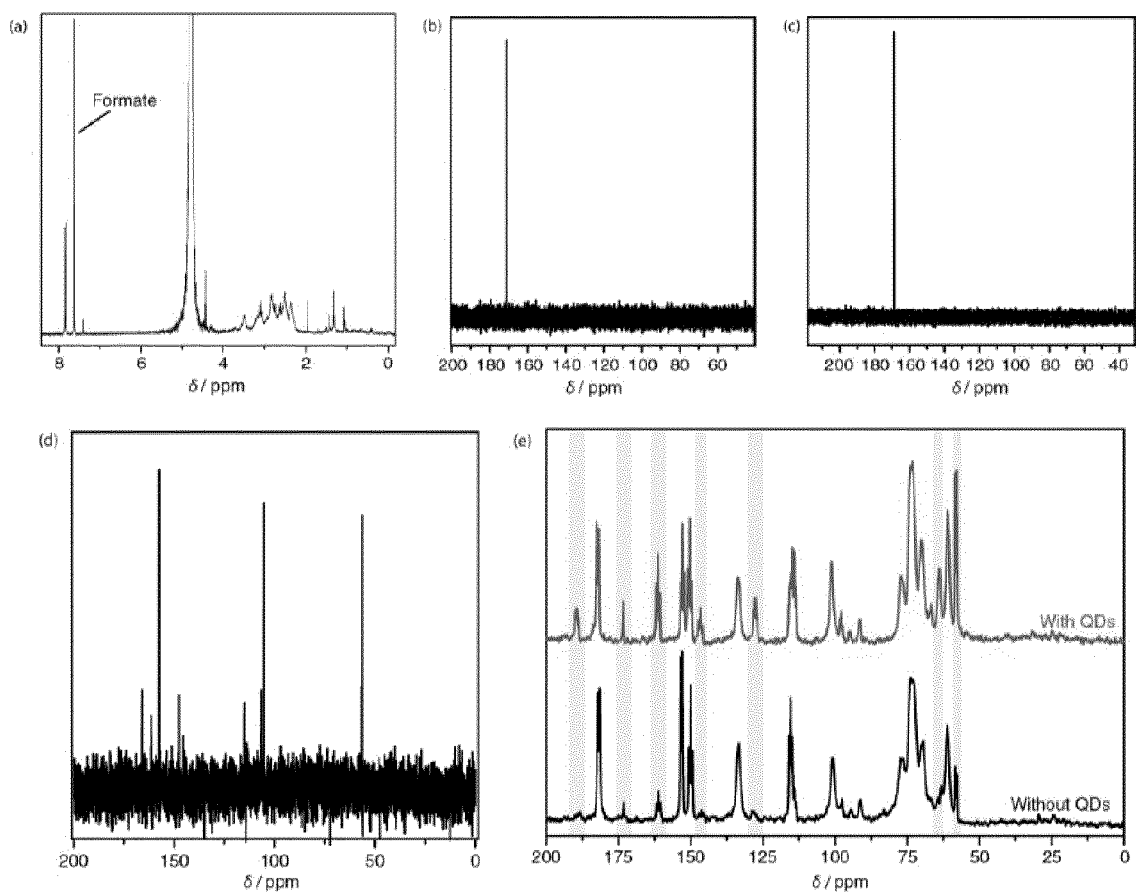


Fig. 13

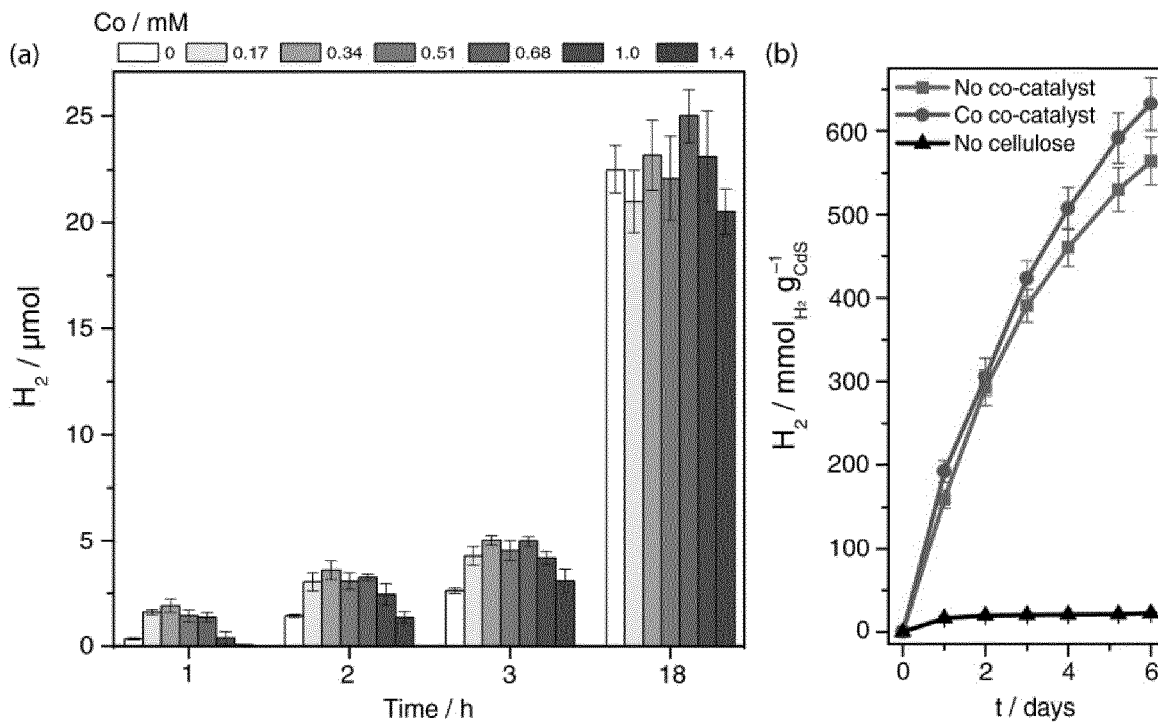


Fig. 14

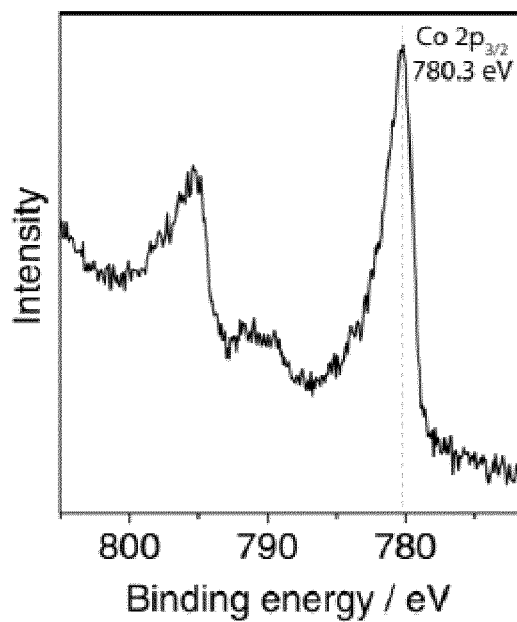


Fig. 15

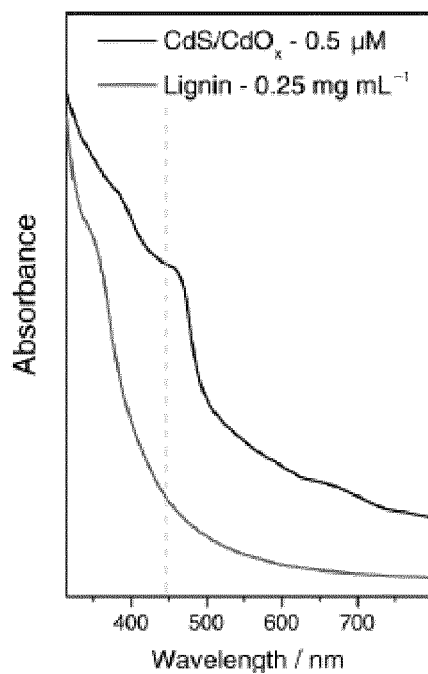


Fig. 16

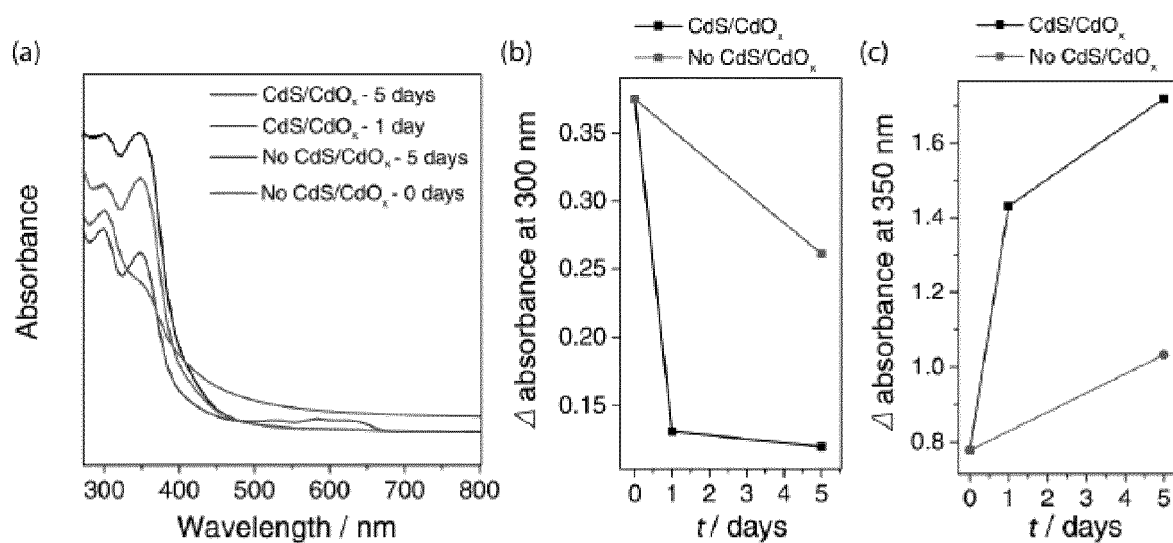


Fig. 17

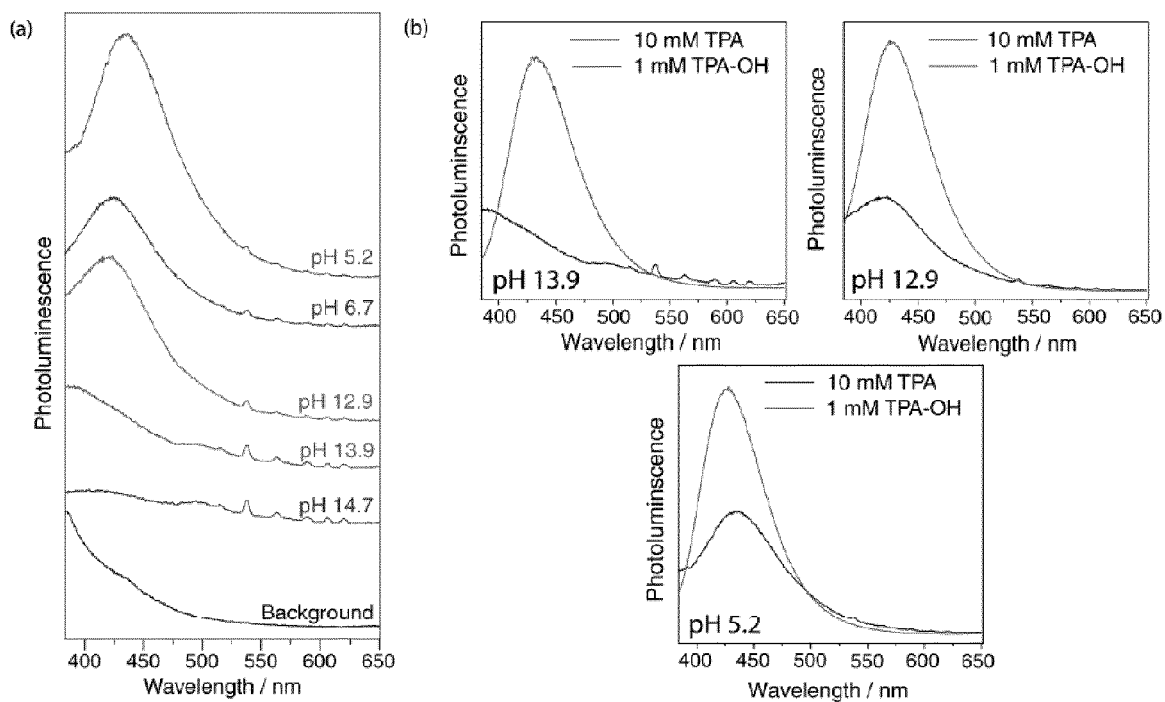


Fig. 18

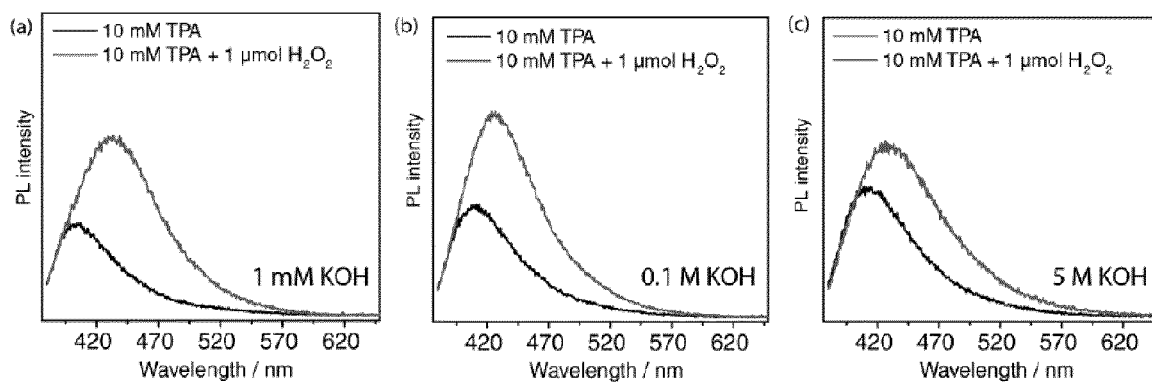


Fig. 19

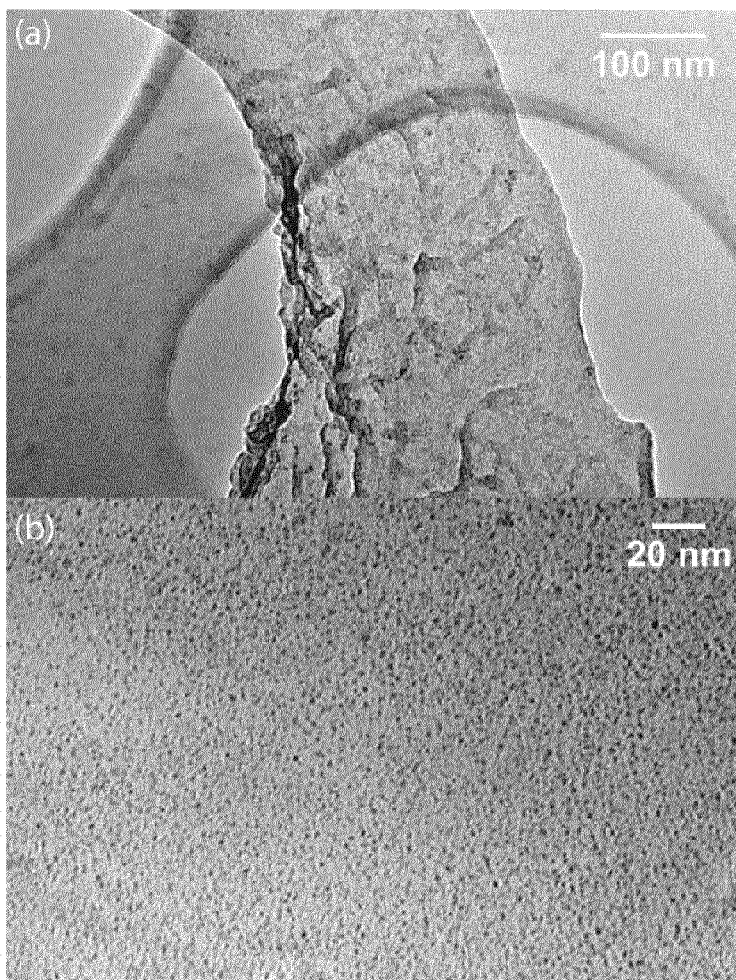


Fig. 20

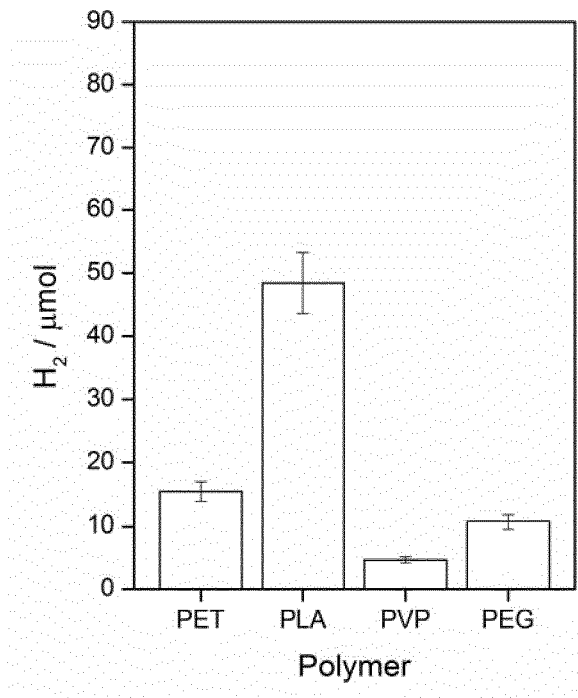


Fig. 21

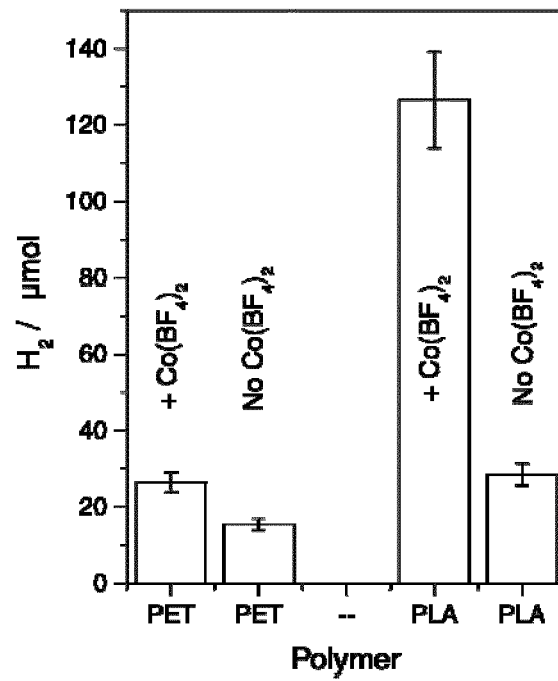


Fig. 22

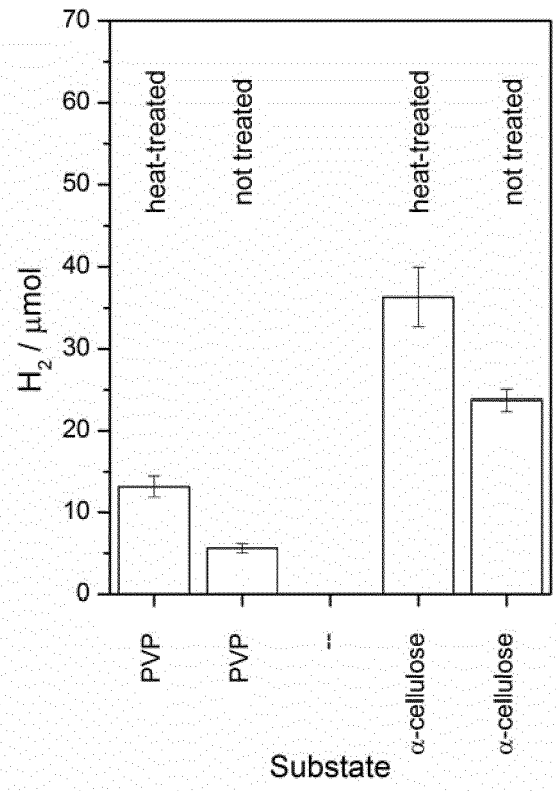


Fig. 23

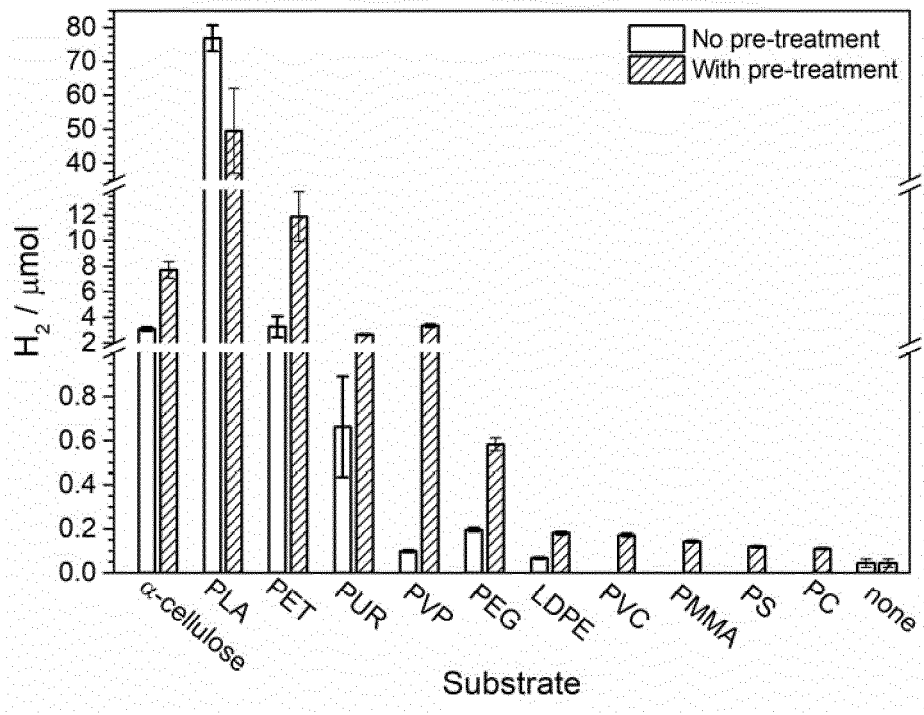


Fig. 24

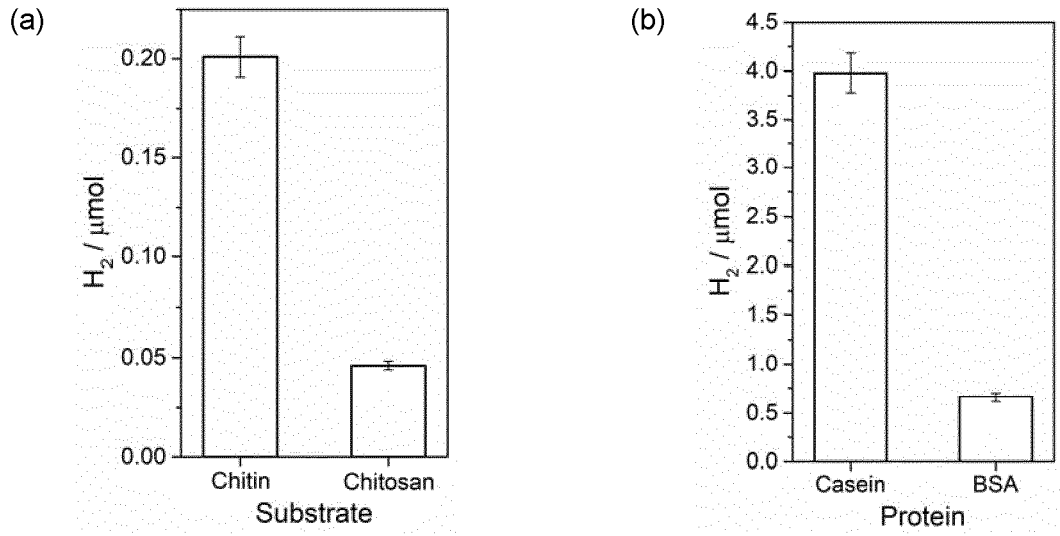


Fig. 25

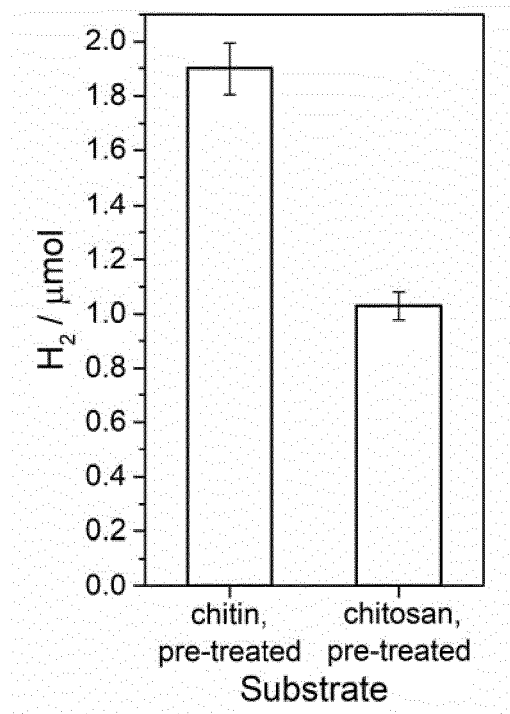
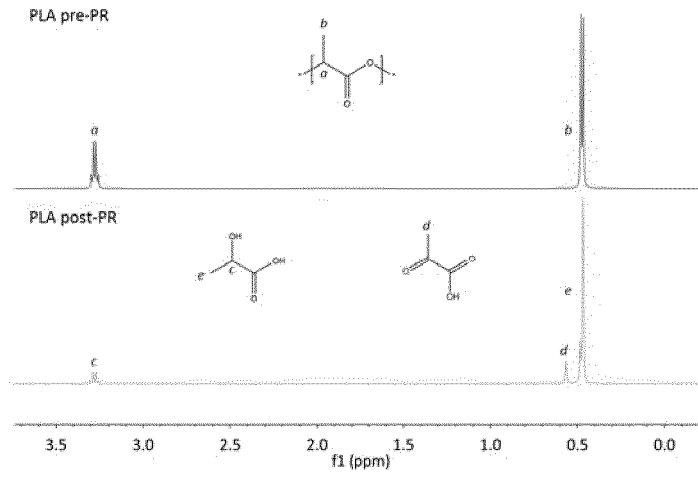
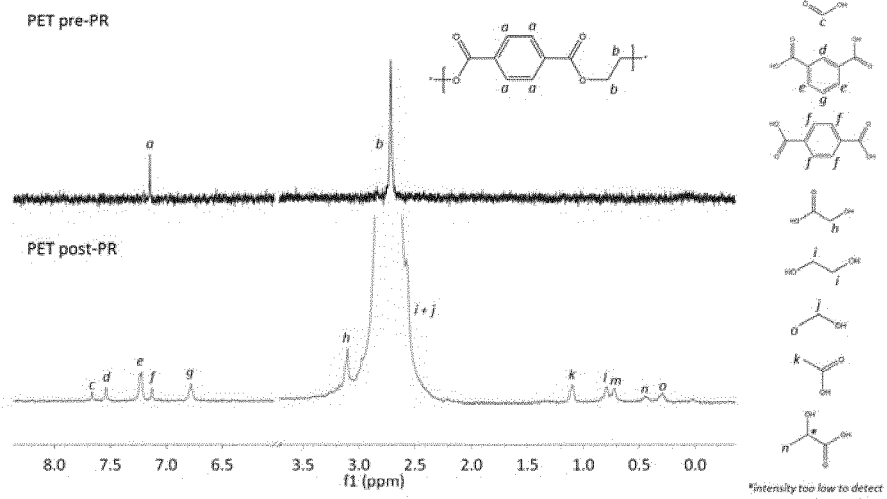


Fig. 26

(a)



(b)



(c)

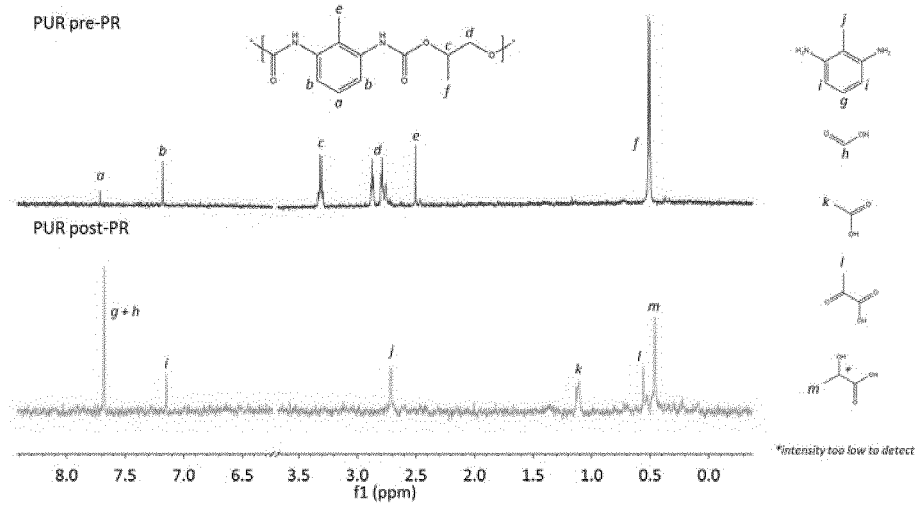


Fig. 27

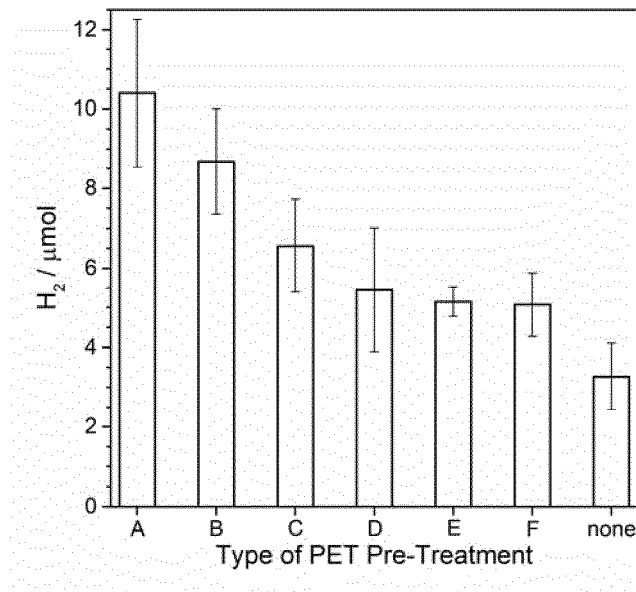
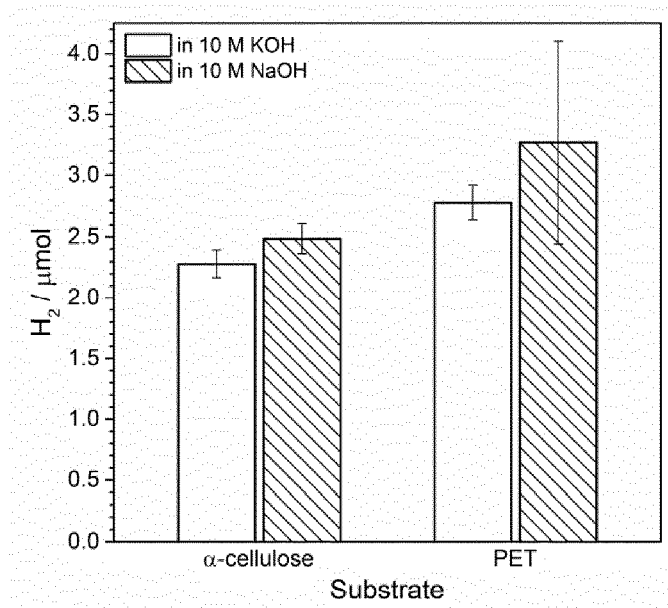


Fig. 28



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/080371

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01J37/02 B01J35/00 B01J23/06 B01J37/34 B01J37/04
 C01B3/26
 ADD.
 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)
 B01J C01B

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)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/224105 A1 (WU LIZHU [CN] ET AL) 29 August 2013 (2013-08-29) paragraph [0001] paragraph [0005] paragraph [0007] paragraph [0009] - paragraph [0020] paragraph [0022] - paragraph [0027] paragraph [0035] paragraph [0037] - paragraph [0040] paragraph [0054] - paragraph [0060] paragraph [0088] - paragraph [0094] paragraph [0122] - paragraph [0123] paragraph [0146] - paragraph [0147] examples 12, 94-108 figures 1-6, 14-21 claims 1, 3, 4, 6-11, 13-15, 17, 19-22 ----- -/--	1-35

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

* Special categories of cited documents :

"A" 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 24 January 2018	Date of mailing of the international search report 05/02/2018
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kyriopoulos, Alik
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/080371

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PHILIP KALISMAN ET AL: "Perfect Photon-to-Hydrogen Conversion Efficiency", NANO LETTERS, vol. 16, no. 3, 9 March 2016 (2016-03-09), pages 1776-1781, XP055443527, ISSN: 1530-6984, DOI: 10.1021/acs.nanolett.5b04813 abstract page 1777, left-hand column, paragraph first - page 1778, left-hand column, paragraph second page 1778, right-hand column, paragraph first - page 1779, right-hand column, paragraph first page 1779, right-hand column, last paragraph - page 1780, left-hand column, paragraph first figures 1, 2, 4, 5 -----</p>	1-35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/080371

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013224105	A1	29-08-2013	EP 2636641 A1 11-09-2013
			JP 5890842 B2 22-03-2016
			JP 2014500788 A 16-01-2014
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