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(57) Abstract: The invention provides methods for producing hydrogen using a carbon nitride (CN_x) photocatalyst or a carbon dot (CD) photocatalyst. The method may include exposing a photocatalyst to visible and/or ultraviolet light in the presence of an organic substrate, such as a biomass or an organic component having a molecular weight of 200 or more, and a co-catalyst that is a hydrogen evolution catalyst. The method may include exposing a photocatalyst within untreated water to visible and/or ultraviolet light in the presence of a co-catalyst that is a hydrogen evolution catalyst.

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PHOTOCATALYST AND PHOTOCATALYTIC METHODS FOR
PRODUCING HYDROGEN

Abstract

- 5 The present case claims the benefit and priority of GB 1808905.2 filed on 31 May 2018, the contents of which are hereby incorporated by reference in their entirety.

Field of the Invention

- 10 The present invention provides photocatalysts and the use of those photocatalysts in photocatalytic methods for degrading an organic substrate, such as a biomass, or a species, such as pollutant, in untreated water. Also provided is the use of the photocatalysts in photocatalytic methods for generating hydrogen, and methods for preparing those photocatalysts.

15

Background

- Solar-driven hydrogen production with semiconductor particles is a sustainable strategy to generate clean and renewable energy carriers. Research in this area typically focuses on
20 coupling hydrogen production to the oxidation of water into oxygen, which is the kinetically demanding half-reaction in the water splitting process. In addition, overall water splitting generates a hydrogen and oxygen gas mixture in a single-pot photoreactor, which is a potentially explosive combination, and requires costly separation of the components.

- 25 An emerging strategy is to replace the water oxidation reaction by the direct reformation of unprocessed biomass such as lignocellulosic waste, which does not compete with food production (see Kuehnel *et al.*). Here, the biomass is oxidized instead of water and enables sustainable hydrogen production driven by solar light in the presence of a photocatalyst.

- 30 Such a process has the potential to provide large scale, affordable and clean hydrogen generation. Photocatalytic reforming of biomass is thermodynamically more favourable (thus potentially enabling higher hydrogen generation rates than classical water splitting), and prevents the formation of potentially unwanted oxygen. Lignocellulosic biomass is the most abundant form of biomass and its photoreformation has been previously achieved using
35 CdS/CdOx and Pt/TiO₂ photocatalysts. However, these photocatalysts are problematic as they can be toxic (for example, owing to the presence of Cd), expensive (for example, owing to the use of Pt), inefficient and/or require harsh experimental conditions (*e.g.*, strongly alkaline solutions). Furthermore, the reported photocatalysts suffer from a combination of limited visible-light absorption, low surface area and poor interfacial interactions, as well as
40 photoinstability, which limit their potential for real-world applications.

Most currently studied solar-driven catalytic systems, do not only rely on non-scalable photocatalysts, but also only operate in organic solvents, purified water and the presence of unsustainable sacrificial reagents (see Martindale *et al. J. Am. Chem. Soc.* **2015**; Hutton *et al. J. Am. Chem. Soc.* **2016**; Hutton *et al. Chem. Soc. Rev.* **2017**; Martindale *et al. Angew. Chemie Int. Ed.* **2017**, 56, 6459). This bottleneck is critical for the future development as it prevents the implementation of an economic process

Photoreformation of lignocellulose with low cost and non-toxic photocatalysts in a benign environment has not yet been reported and is at the focus of this invention disclosure.

Some of the present inventors have previously described the use of photocatalysts in the degradation of organic substrates, including biomass and organic polymers.

For example Wakerley *et al.* describe the use of a CdS quantum dot-based photocatalyst that has activity to generate hydrogen from biomass under incident simulated solar-light (see also PCT/EP2017/080371).

The photocatalyst has an oxygenated surface, and this is generated by treatment of the CdS semiconductor material under highly alkaline conditions, such as pH 10 or more, and preferably pH 14 or more. The exemplified photocatalyst also makes use of Cd, and there is a desire to avoid the use of this toxic species, where possible.

There is a need for alternative photocatalysts that work under environmentally benign conditions, at ambient temperature, and do not require the use of toxic metal species.

Summary of the Invention

The present inventors have identified a particular class of catalysts that have useful properties when exposed to visible and/or UV light, such as sunlight or simulated visible light, in combination with a co-catalyst. These photocatalysts may be reliably and efficiently used in photocatalytic methods for degrading organic substrates, such as biomass, and photocatalytic methods for producing hydrogen. The catalysts are carbonaceous, and therefore of low cost and low toxicity, and are additionally well suited to large scale applications.

The catalyst is therefore a photocatalyst. The photocatalyst of the invention is a carbon-containing catalyst, where the carbon may be present in a graphitic and/or amorphous phase. For example, the photocatalyst may be a carbon nitride (CN_x) photocatalyst or a carbon dot (CD) photocatalyst.

The photocatalyst may be a carbon- and nitrogen-containing catalyst, such as a carbon nitride (CN_x) photocatalyst or a nitrogen-doped carbon dot (CD) photocatalyst.

In a preferred embodiment, the photocatalyst is a NCNCN_x photocatalyst, and more preferably such a photocatalyst having a high surface area, such as obtainable from sonication, such as ultrasonication, of a bulk sample of NCNCN_x . The photocatalyst may have a surface area that is at least $60 \text{ m}^2 \text{ g}^{-1}$.

In a further preferred embodiment, the photocatalyst is a carbon dot photocatalyst, and more preferably such a photocatalyst is obtained or obtainable from a biomass, for example by calcination of the biomass. The biomass may be a readily available and an abundant natural or processed resource. Alternatively, the carbon dot photocatalyst is obtained or obtainable from readily available and low cost organic molecular precursors.

The photocatalysts of the invention have excellent photocatalytic activity in methods for degrading (or reform) biomass, such as those biomasses having a high cellulose content, and this degradation may be accomplished at ambient temperatures and pressures using natural light or simulated natural light, such as solar-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 photocatalysts are also capable of catalysing the degradation of lignin, which is also a component of many biomasses, and which is difficult to process on an industrial scale. Further, the photocatalyst may also be used to degrade semi-refined biomass, for example the photocatalyst may be used to degrade other biomass components, such as cellulose and xylan, which have been extracted from a biomass.

The photocatalysts of the invention may be used in a photocatalytic method for the generation of hydrogen, for example from biomass. Thus, the photocatalysts are therefore capable of producing a useful fuel from abundant raw and waste biomass.

The photocatalysts of the invention are active under solar-light, including simulated solar-light, and may be used for sustained periods, for example for more than two days, such as more than 12 days, without appreciable loss in activity. The photocatalysts are therefore have long term photocatalytic activity and stability.

The rate of substrate degradation, such as biomass degradation, is remarkably high, and the photocatalyst of the invention has a significant advantage in that no substrate chemical processing is required in order to obtain the hydrogen product. In particular, the photocatalyst is able to catalyse biomass reformation without the need for pre-treatment under highly basic conditions.

The photocatalysts of the invention are for use together with a co-catalyst for the generation of hydrogen. The co-catalyst is a hydrogen evolution catalyst, such as those well known in

the art, including NiP-, Pt- and Mo-based co-catalysts. Preferably, the co-catalyst is a noble metal-free co-catalyst, such as NiP.

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 and a co-catalyst that is a hydrogen evolution catalyst. 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 an organic substrate and a co-catalyst that is a hydrogen evolution catalyst. The method may also comprise the step of collecting the hydrogen. Carbon monoxide may be optionally produced in this method.

In the methods of the invention, the photocatalyst and the organic substrate may be provided as an aqueous mixture, together with a co-catalyst that is a hydrogen evolution catalyst. Advantageously, the photocatalyst may be used within a broad pH range, and the aqueous mixture may have a pH in the range pH 2 to 15, such as a pH in the range pH 2 to 9. For example, the aqueous mixture may be basic, acidic or substantially neutral.

In a further embodiment, the aqueous mixture may contain untreated water. Thus, water for the aqueous mixture may be obtained, without treatment, from a river, lake, canal, or a sea, or from industrial waste water, such as sewage water. The photocatalysts of the invention therefore allow the production of clean hydrogen under real-world conditions, without the need for purified drinking water or laboratory quality water.

Organic pollutants and chloride anions, which inherently exist in these untreated media, serve as sacrificial electron donors, promote high activity and thereby enable simultaneously substantial fuel generation and water purification. As noted previously, current solar-driven catalysis systems only operate in organic solvents, purified water and in the presence of unsustainable sacrificial reagents. The present photocatalysts may address these limitations in the art.

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 a monosaccharide, 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, xylan and lignin.

5 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.

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

15 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.

20 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 group.

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

25 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 may require pre-treatment, such as with aqueous base, prior to the photocatalytic reaction.

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

35 The organic substrate may be a component that is a pollutant in an untreated water source. For example, the organic substrate may be selected from chloromethylphenol, pentachlorophenol, benzaldehyde, trichlorophenol, nitroaniline, dichlorophenol, dimethyl phenol, atrazine, dinitrophenol and naphthylamine. These components may be found in sea water. The component may additionally or alternatively be selected from atrazine, desmetryn, dicamba, chloromehtylphenoxyacetic acid, mecoprop, prometryn, propazine, 40 simazine, terbutryn, and trietazine. The component may also be an inorganic component, such as chloride. These components may be found in river water, also including canal and lake water (or "fresh water" in contrast to sea water).

The incident light in the photocatalytic reaction 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.

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.

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 light, including natural light, such as solar light.

Also provided by the present invention are methods of preparing the photocatalysts.

In one aspect there is provided a method of preparing $^{NCN}CN_x$, the method comprising the step of forming a bulk sample of $^{NCN}CN_x$ and subsequently treating the bulk $^{NCN}CN_x$ thereby to increase the surface area of the $^{NCN}CN_x$.

The bulk $^{NCN}CN_x$ may be sonicated, such as ultrasonicated, to increase its surface area. The bulk $^{NCN}CN_x$ may be obtained or obtainable from $^{H2N}CN_x$.

In one aspect there is provided a method of preparing a carbon dot, the method comprising the step of calcining an organic substrate. 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 method may provide a product that is a plurality of carbon dots.

This method of the invention provides a complete and self-contained approach to dealing with organic substrate waste and hydrogen production: the organic substrate may be the source for the photocatalyst as well as a source - an electron donor - in the hydrogen production method. In these systems the biomass may be sourced locally together with local untreated water, to provide a substantial proportion of the chemical input for the method from the immediate environment, thereby minimising transport costs for the user.

The invention also provides photocatalysts obtained or obtainable from the methods of preparation described above.

These and other aspects and embodiments of the invention are described in further detail herein.

5 **Summary of the Figures**

Figure 1 is a schematic representation of a photocatalytic system according to an embodiment of the invention for photoreforming lignocellulose to H₂ based on carbon nitride and carbon nanodot photocatalysts. In alternative methods of the invention, the
 10 lignocellulose may be replaced with a component, such as a pollutant, present within untreated water.

Figure 2 shows the characterisation data for bulk and sonicated ^{NCN}CN_x, where (a) is the UV-vis absorption spectra for bulk and sonicated ^{NCN}CN_x at 0.0125 mg mL⁻¹; (b) is the photoluminescence emission spectra for bulk and sonicated ^{NCN}CN_x at 0.67 mg mL⁻¹, where
 15 $\lambda_{\text{ex}} = 360 \text{ nm}$, 25°C; (c) is the N₂ adsorption–desorption isotherms for ultrasonicated and bulk ^{NCN}CN_x from which BET surface areas were calculated; (d) is the XRD patterns for bulk and sonicated ^{NCN}CN_x; (e) is the IR spectra for bulk and sonicated ^{NCN}CN_x; (f) is are TEM images for a sample of bulk (top) and sonicated (bottom) ^{NCN}CN_x. The measurement bars in (f) are
 20 20 nm; and (g) are SEM images for a sample of bulk (top) and sonicated (bottom) ^{NCN}CN_x. The measurement bars in (g) are 250 nm.

Figure 3 shows the characterising data for CDs synthesised from purified and waste biomass, where (a) are the HR-XPS C 1s and N 1s spectra of α -cellulose (top) and
 25 *G. Nivalis*-derived CDs (bottom). The black traces show the ‘as recorded’ spectra and the colored plots (red, blue and green) are the deconvoluted bands for each element; (b) HR-TEM images of α -cellulose (top) and *G. Nivalis*-derived CDs (bottom). The white lines denote the (100) intralayer spacings; (c) Raman spectra of the CDs derived from purified and waste biomass. The intensity was normalized with respect to the G band for all samples
 30 to allow the easy determination of the I_D/I_G ratio; and (d) UV/vis spectra of CDs recorded in water (0.1 mg mL⁻¹) at 25°C.

Figure 4 shows the recorded photocatalytic H₂ evolution using CDs from purified and waste biomass, in purified water in the presence of EDTA (3 mL, 0.1 M, pH 6) and 50 nmol of NiP, where (a) shows the absolute quantities of H₂ produced (in μmol) from α -cellulose, xylan and
 35 lignin-derived photoabsorbers after 6 h (solid bars) and 24 hrs of irradiation (empty bars); (b) specific activities of α -cellulose CDs, xylan and lignin light-harvesters after 24 h of irradiation; and (c) quantities of H₂ produced (in μmol) from waste biomass photoabsorbers after 24 h of irradiation. For comparison, the hydrogen yield of α -cellulose CDs is shown (red close
 40 symbols) under the same conditions. The numbers on the right indicate the RFA of α -cellulose CDs for each biomass sample. All experiments were carried out upon simulated

solar light irradiation (100 mW cm^{-2} , AM1.5G) for 24 h, under N_2 atmosphere with 2% CH_4 as internal GC standard, at 25°C .

Figure 5 shows the photocatalytic performances of CDs from purified and waste biomass in untreated sea, river and sewage water, where (a) shows photo- H_2 production with α -cellulose CDs in river, sea, sewage and pure water, in the absence (filled symbols) and presence (open symbols) of EDTA (0.1 M, pH 6, 3 mL); (b) shows solar- H_2 generation of α -cellulose CDs in KPi (0.1 M, pH 6, 3 mL), in the absence of EDTA, but instead in the existence of organic pollutants (200 μmol) and chloride ions (3.2 wt %), found in river (open symbols) and sea water (filled symbols). The results in the absence of any electron donor (ED) are also provided for comparison; and (c) and (d) show the photo- H_2 production in sea and river water, respectively, using CDs from α -cellulose and waste biomass, in the presence of EDTA (0.1 M, pH 6, 3 mL). All experiments were carried out under full solar light irradiation (AM 1.5 G, 100 mW cm^{-2}), for 24 h, in the presence of NiP (50 nmol), under N_2 atmosphere containing 2% CH_4 , at 25°C .

Figure 6 shows solar-light driven H_2 evolution using α -cellulose CDs at quantities between 0.03 and 2.8 mg. All photocatalytic experiments were carried out at 50 nmol NiP and in aqueous EDTA solutions (0.1 M, pH 6, 3 mL), under full solar spectrum irradiation (AM 1.5 G, 100 mW cm^{-2}), at 25°C .

Figure 7 shows the results of control photocatalytic experiments in the absence of α -cellulose CDs, NiP and EDTA, carried out under full solar spectrum irradiation (AM 1.5 G, 100 mW cm^{-2}), at 25°C .

Figure 8 shows solar-induced H_2 production using CDs from cotton. Namely, cotton from different sources, such as cotton wool, pads and cotton T-shirt, were employed as precursors for this purpose. The photocatalytic systems were carried out in aqueous EDTA solutions (0.1 M, pH 6, 3 mL), for 24 h, under full solar spectrum irradiation (AM 1.5 G, 100 mW cm^{-2}), in the presence of 50 nmol NiP.

Figure 9 shows (a) light-driven H_2 evolution (24 h) using α -cellulose CDs as photoabsorbers in untreated river, sea and sewage water, in the absence of NiP and in the presence of EDTA (0.1 M, 3 mL, pH 6); (b) the chemical structures of organic water pollutants, which exist in sea (Gulf of Mexico) and river water (River Cam, UK), based on reports of the US Department of Interior (Torres *et al.*) and the British environmental agency (Huber *et al.*), respectively; (c) photo- H_2 production (24 h) using α -cellulose CDs, in KPi (0.1 M, pH 6, 3 mL), in the absence of EDTA, but instead in the presence of the organic pollutants (200 μmol), prometryn (PT), terbutryn (TT), benzaldehyde (BA) and atrazine (AZ), as well as chloride ions (3.2 wt %), which all exist in sea and river water; and (d) photo- H_2 production (24 h) using CDs from α -cellulose and crude biomass, in purified and untreated river and sea water, in the presence of EDTA (0.1 M, 3 mL, pH 6). Biomass waste samples; Cotton Wool,

G. Nivalis (G. N.), Olive leaves (Ol. leav.), *G. Elliptica* (G. E.), *T. Baccata* (T. B.) and *Elaeagnus X. ebbingei* (E. X. E). All experiments were carried out upon full solar light irradiation (AM 1.5 G, 100 mW cm⁻²) and under N₂ atmosphere (containing 2% CH₄), at 25°C.

Figure 10 shows the H₂ production using activated (10 min ultra-sonicated) ^{NCN}CN_x (5 mg) with NiP (50 nmol) and polymer substrates (100 mg) in KPi solution (0.1 M, pH 4.5, 3 mL) under 1 sun irradiation for 24 hours (100 mW cm⁻², AM1.5G, 25°C, where PET: polyethylene terephthalate; PUR: polyurethane; and PS: polystyrene.

Detailed Description of the Invention

The present inventors have found that a particular class of photocatalysts may be used to degrade organic substrates under incident light, such as under incident solar light, so as to provide hydrogen and optionally other products, including carbon monoxide.

Generally, a photocatalyst of the invention is a carbon-containing catalyst, and more specifically the photocatalyst contains carbon in a graphitic and/or amorphous phase. The photocatalysts typically have a predominant carbon sp² character. For example, the photocatalyst may be a carbon nitride (CN_x) photocatalyst or a carbon dot (CD) photocatalyst.

Meyer *et al.* have previously described the use of carbon nitride as photocatalysts, including Melon-type amino terminated carbon nitride (^{H2N}CN_x), Urea-CN_x and ^{NCN}CN_x. Here, the photocatalysts were used together with an oxidant to catalyse the sulfonylation reaction between a sulfinate and an alkene. There is no disclosure of suggestion that a carbon nitride photocatalyst could or should be used to degrade a biomass.

Kasap *et al.* have previously described the use of the carbon nitride photocatalyst ^{NCN}CN_x. Here, the photocatalyst was used together with NiP to generate hydrogen from 4-methyl benzaldehyde (4-MBA). There is no disclosure of suggestion that ^{NCN}CN_x could or should be used to degrade a biomass.

Lau *et al.* (*Angew. Chemie Int. Ed.* **2016**) describes the use of carbon nitride for time-delayed hydrogen generation. Here, the carbon nitride catalyses the reaction of 4-methyl benzaldehyde (4-MBA). There is no disclosure of suggestion that ^{NCN}CN_x could or should be used to degrade a biomass.

Long *et al.* have previously described the use of carbon nitride photocatalysts, and in particular mesoporous graphitic carbon nitride (mpg-CN). Here, the photocatalyst acts to selectively oxidise aromatic alcohols in water under visible light. Long *et al.* do not suggest

the use of carbon nitride photocatalysts for the use in degrading biomass, or for the use in generating hydrogen from biomass.

Lau *et al.* (*Nat. Commun.* **2016**) have previously described the design and optimisation of carbon nitride photocatalysts. Lau *et al.* do not suggest the use of the photocatalyst to degrade biomass.

Martindale *et al.* have previously described the use of carbon dots photocatalysts together with the hydrogen evolution catalyst NiP for the generation of hydrogen using EDTA as a sacrificial donor. There is no suggestion that EDTA could or should be replaced with a biomass, and there is no suggestion that the hydrogen evolution reaction could be performed in untreated water, with pollutants used as sacrificial donors.

Guo *et al.* have previously described the use of carbon dots in seawater. However, the carbon dots act as a draw solute in a forward osmosis method for seawater desalination. There is no suggestion that the carbon dots could be used to generate hydrogen from components, such as pollutants, within untreated seawater.

CN 107961808 describes the preparation of a carbon nitride photocatalyst, and the use of the photocatalyst to generate hydrogen from water. There is no suggestion anywhere that the catalyst should be used to degrade an organic substrate. There is also no suggestion that the photocatalyst could be used to degrade pollutants within waste water. There is also no reference to the use of the carbon nitride photocatalyst together with a hydrogen evolution catalyst, which is a requirement of the methods of the present case.

CN 107413378 describes the preparation of a carbon nitride photocatalyst. This catalyst is for use in generating hydrogen from water. There is no mention of the catalyst for use together with a hydrogen evolution catalyst, and there is no mention of any organic substrate, such as a polysaccharide, or a pollutant from waste water.

CN 107297217 describes the preparation of a platinum-based carbon nitride catalyst. This catalyst is for use in the generation of hydrogen from water. This water is not said to be waste water, and the action of the catalyst is on water as a substrate not any pollutant. The worked examples show the use of the carbon nitride catalyst together with water and sacrificial triethanolamine to generate hydrogen. There is no mention of organic substrates (other than the triethanolamine), and there is no mention of a co-catalyst for generation of hydrogen.

CN 107008484 describes a metal sulfide-modified carbon-nitride photocatalyst. This photocatalyst is used to generate hydrogen from water. There is no reference to any biomass materials and there is no reference to the treatment of waste water and its

pollutants. There is no disclosure in this Chinese application of the use of two separate catalysts species in the reaction mixture.

- 5 CN 106902803 describes the modification of carbon dots with KNbO_3 to give a composite photocatalyst. The photocatalyst has use in the degradation of organic pollutants, whilst also producing hydrogen. However, there is no reference to the use of the photocatalyst to degrade a biomass materials, such as paper, or large organic molecules such as polysaccharides.
- 10 CN 107837817 describes a composite material that is a combination of carbon dots, carbon nitride and titanium dioxide. This material is said to be useful for the photocatalytic generation of hydrogen from water. The carbon dots are prepared from the soot of a burning candle. There is no suggestion that these dots could be prepared from saccharides.
- 15 The worked examples refers to the use of water to generate hydrogen, in the presence of the electron donor triethanolamine. There is no suggestion that waste water could be used, and there is no reference to any biomass or any polymeric organic material, such as a polysaccharide.
- 20 CN 106902857 refers to the use of a carbon nitride photocatalyst to degrade organic pollutants, and it also refers to the use of the photocatalyst to generate hydrogen. However, it does not suggest the two together.
- 25 In a worked example, the organic dye Rhodamine B is degraded in the presence of a photocatalyst. There is no description of the degradation products, and the example only looks at the loss of absorbance at a single wavelengths as indicative of a degradation event. There is no suggestion that hydrogen is generated.
- 30 In a second worked example, the carbon nitride photocatalyst is used in water together with ascorbic acid and chloroplatinic acid to generate hydrogen. There is no reference to anything that that is a biomass.
- 35 The carbon nitride photocatalyst itself is called an expanded carbon nitride, which apparently has an increased surface area. There is no reference to ultrasonication as a method to treat bulk carbon nitride.
- 40 CN 107552083 describes a carbon nitride photocatalyst combined with FeP. The photocatalytic activity is only briefly described: the photocatalyst is for use in producing hydrogen from water. There is no mention of any other substrate.
- The use of carbonaceous-based catalysts for the degradation of biomass, and the use of carbonaceous-based catalysts for the generation of hydrogen from untreated water, is believed to be non-obvious in view of the disclosures within the prior art.

Photocatalyst

The photocatalyst of the invention is a material, which may be in the form of a particle, which
5 may be at least partially aggregated with other photocatalyst particles. The photocatalyst is
a carbonaceous photocatalyst such as a carbon nitride or a carbon dot. The use of a
carbonaceous photocatalyst to degrade biomass has not previously been reported in the
literature.

10 The photocatalyst for use in the present invention may be a carbon nitride catalyst, and in
particular a $^{NCN}CN_x$ catalyst.

Although $^{NCN}CN_x$ catalysts are known, their use to degrade organic substrates such as
 α -cellulose and biomass components such as paper, sawdust, and wood, has not previously
15 been described.

Thus, in one embodiment, the methods of the invention use a known $^{NCN}CN_x$ catalyst to
generate hydrogen from a biomass.

20 The inventors have also developed new $^{NCN}CN_x$ catalysts having greater activity than those
 $^{NCN}CN_x$ catalysts reported to date. In particular, these catalysts have a greater surface area
than those known in the art. This increase in surface area is achieved by treating $^{NCN}CN_x$ to
reduce the size of agglomerates within a bulk sample, for example by sonicating, such as
ultrasonication, the bulk.

25 In one embodiment, the surface area of the carbon nitride catalyst is at least 60, at least 70,
at least 80, at least 90 or at least 95 $m^2 g^{-1}$. The surface area of the carbon nitride catalyst
may be about 97 $m^2 g^{-1}$.

30 For reference, a bulk $^{NCN}CN_x$ catalyst produced by methods known in the art has a surface
area of 59.5 $m^2 g^{-1}$. The carbon nitride catalyst produced in the present case has a surface
area of 97.4 $m^2 g^{-1}$.

The surface area may be determined by BET measurement, such as described herein.
35

The photocatalyst for use in the invention may be a carbon dot, which is optionally doped,
such as nitrogen, sulfur, or phosphorous doped, such as nitrogen doped.

A carbon dot may also be referred to as a carbon quantum dot (CQD). Carbon dots are
40 described by some of the present inventors in Martindale et al. (*Angew. Chem. Int. Ed.* **2017**)
and Guo *et al.*

A carbon dot may be a particle having a largest dimension of at most 10 nm, such as at most 5 nm, such as at most 3 nm. The size of a quantum dot may be determined by, for example, analysis of TEM imagery of a collection of carbon dots.

- 5 A carbon dot is obtained or is obtainable by calcination (pyrolysis) of an organic substrate, such as a described herein.

Although carbon dot photocatalysts are known, their use to degrade organic substrates such as α -cellulose has not previously been described. Furthermore, although the preparation of
10 carbon dots is well known from small organic starting materials, such as amino acids, the use of biomass materials, such as α -cellulose, for the preparations of carbon dots has not previously been described.

Aqueous Mixture

15 The photocatalyst is provided in an aqueous mixture together with an organic substrate and a co-catalyst.

The photocatalyst may be used within a broad pH range, and the aqueous mixture may have
20 a pH in the range pH 2 to 15, such as pH 2 to 9. For example, the aqueous mixture may be basic, acidic or substantially neutral.

In one embodiment, the aqueous mixture may be acidic, such as a pH in the range pH 2-6, such as a pH in the range pH 3-5. In one embodiment, the aqueous mixture has a pH of
25 about pH 4.5.

In one embodiment, the aqueous mixture may have a pH that is pH 9 or less, such as pH 8 or less.

In one embodiment, the aqueous mixture may have a pH that is around pH 7.
30

The aqueous mixture may be provided with a buffer to maintain a stable pH during the photocatalytic reaction. The buffer may be a phosphate buffer, such as potassium phosphate buffer (KPi buffer), and such are readily available from commercial sources.

35 The aqueous mixture may contain additional co-solvents, however such are not typically required in the methods of the present case, which may advantageously avoid the need to use any co-solvent.

The inventors have found that the photocatalysts of the invention tolerate the presence of
40 many different components within the aqueous mixture, making them suitable for use in a variety of situations, particularly where the water for the aqueous mixture is untreated water.

The aqueous mixture may contain water that is treated, for example such that the water is suitable for drinking or suitable for use in laboratory.

However, the aqueous mixture may alternatively or additionally contain water that is untreated, for example the water may be obtained from a river, lake, canal, or a sea, or from industrial waste water, such as sewage water. The photocatalysts of the invention can be used under real-world conditions, without the need for purified drinking water or laboratory quality water for the degradation of an organic substrate and the production of hydrogen.

The aqueous mixture, where it contains untreated water, typically contains one or more organic components, optionally together with inorganic components, which are pollutants within the untreated water. These organic components may be used as sacrificial electron donors in the photocatalytic reaction.

Co-Catalyst

The photocatalysts of the invention are used together with a co-catalyst, which is a hydrogen evolution catalyst.

Preferably, the co-catalyst is water soluble.

The co-catalyst may be provided as a separate component within the aqueous mixture. Thus, the photocatalyst and the co-catalyst are not provided together, for example, they are not provided together in a composite. The co-catalyst may also not be physically adsorbed onto the photocatalyst.

The co-catalyst is not a photocatalyst of the invention.

As is apparent from the description of hydrogen generation herein, together with the worked examples, the co-catalyst is provided as a hydrogen evolution catalyst for the generation of hydrogen (for example, as illustrated in Figure 1). Here, the photocatalyst is not used directly to generate hydrogen. Rather, irradiation of the photocatalyst results in the formation of a photoexcited state, in which the holes are quenched by the substrate or pollutant, and the photoexcited electrons are effectively transferred from the photocatalyst to the hydrogen evolution catalyst, resulting in hydrogen formation at the hydrogen evolution catalyst (see Kasap *et al.*).

The use of co-catalysts together with a photocatalyst for the generation of hydrogen is well known in the art. For example, co-catalysts are described for use by Kasap *et al.*, Lau *et al.* (*Angew. Chemie Int. Ed.* **2016**), and Martindale *et al.* (*Angew. Chemie Int. Ed.* **2017**).

The co-catalyst may be selected from a Ni-, Pt- or Mo-containing hydrogen evolution catalyst.

- 5 In one embodiment, the co-catalyst is a Ni catalyst, such as NiP (molecular Ni bis(diphosphine), also written as **NiP**). The present inventors have previously disclosed a Ni co-catalyst for use as a hydrogen generation catalyst. See, for example, Kasap *et al.*

In one embodiment, the co-catalyst is a Pt catalyst, such as H_2PtCl_6 .

- 10 In one embodiment, the co-catalyst is a Mo catalyst, such as a MoS_2 -based catalyst, such as $\text{H}_8\text{N}_2\text{MoS}_4$.

Use of the Photocatalyst

- 15 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 reformation or reforming, and more specifically as photoreformation or photoreforming.

- 20 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 may be provided in an aqueous mixture, and preferably a substantially neutral aqueous mixture.

- 25 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 monoxide from the organic substrate.

- 30 The methods of the invention also provide for the generation of hydrogen and/or a product such as carbon monoxide, 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.

- 35 The photocatalyst and the organic substrate may both be provided in an aqueous mixture.

The aqueous mixture may have a pH in the range 2 to 15

- 40 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.
The aqueous mixture may have a pH in the range 8 to 12, such as 9 to 10.

The aqueous mixture may be an acidic mixture, such as a mixture having a pH of 6 or less, such as 5 or less.

The aqueous mixture may have a pH in the range 2 to 6, such as 4 to 5.

- 5 The aqueous mixture may be substantially neutral.

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.

10

In the methods for generating carbon monoxide the source of carbon is the organic substrate.

- 15 The photocatalyst is active ("excited") under incident light in the visible and/or ultraviolet range, and preferably the photocatalyst is used under incident light, including incident light having a visible light component, such as solar 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.

- 20 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, AM1.5G and AM0.

- 25 The incident light may be monochromatic.

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

- 30 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.

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.

- 35 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.

- 40 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 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.

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.

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. The mixture may be 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. Generally, however, the methods of the invention do not require the substrate to pre-heat, and the photocatalytic reaction is performed at ambient temperature.

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.

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.

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, such as described in further detail below.

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 monoxide. 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.

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 at any location 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.

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.

The ability to generate hydrogen from any organic substrate, including wood and cardboard as well as refined cellulose, xylan 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.

It is possible that other degradation products are also produced, such as carbon monoxide. The production of degradation products therefore provides an additional or alternative pathway for creating value from the organic substrate.

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 hydrogen directly from any source of unprocessed lignocellulose.

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 hydroxymethyl groups within their core structures.

- 5 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.

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
10 photocatalyst is shown to be useful in degrading cellulose, hemi-cellulose, xylan 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
15 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.

20

It is noted that many of the reported uses of carbon dots and carbon nitride photocatalyst are with small organic substrates, and many documents use the photocatalysts not for degradation but to catalyse organic bond-forming reactions.

- 25 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 thermal,
30 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 cellulose, such as α-cellulose.

35

The organic substrate may be or comprise a polypeptide.

A mixture of different organic substrates, such as those described above, may be present.

- 40 In the worked examples of the present case, the organic substrate is a complex biomass 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 wood or a biomass that is plant matter.

- 5 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.

10

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
15 of the substrate or simply to ensure that the organic substrate can be handled and distributed within a processing facility.

20

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.

25

The present inventors have also found that the photocatalysts of the invention have broad application in degrading, or reforming, organic substrates that are organic polymers, and preferably the degradation reaction yields hydrogen.

30

The inventors found that the photocatalysts could be used to degrade organic polymers such as polysaccharides, including cellulose, hemicellulose, and lignin. The photocatalyst is also found to have use in the degradation of other organic polymers, and may be used to generate hydrogen from those organic polymers. For example, PET, PUR and PS may be used as feedstocks to generate hydrogen, as shown in the worked examples of the present case.

35

The organic polymers described here may be used in the same way as the organic substrates described above.

40

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. An organic polymer may contain both carbon-carbon and carbon-oxygen bonds within the backbone.

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 and polyethylene terephthalates. Carbon-oxygen and carbon-nitrogen bonds are present in polyurethanes.

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 group of the monomer.

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 mixture.

The organic polymer may therefore comprise functionality, either in the backbone chain or the side chain, which is hydrolysable, for example under basic or acidic conditions. For example, the organic polymer may contain ester, amide, ether, carbonate, and/or urethane (carbamate) functionality.

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).

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.

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.

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

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).

5

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.

10

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.

15

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

The polyethylene may be an acrylate polymer, for example a poly(methyl acrylate).

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

20

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.

25

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

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

30

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

35

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.

40

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

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
5 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.

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
10 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.

The organic polymer may also be mechanically treated, for example by cutting, grinding and
15 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.

20 *Water Treatment*

The photocatalysts of the invention may be used in untreated water to generate hydrogen. Here, the method of generating hydrogen may use the photocatalyst together with a
25 co-catalyst and a sacrificial electron donor, which donor is typically a component, such as an organic or inorganic pollutant, within the untreated water.

The hydrogen generation method has the advantage of providing useful fuel, in the form of hydrogen, whilst also degrading pollutants within the untreated water, thereby to at least
30 partially purify the untreated water.

The sacrificial electron donor is a compound, which may be an organic compound or an ionic species, within the water that is capable of quenching holes, by the donation of electrons, that are photochemically generated in the photocatalyst.

35 Examples of sacrificial electron donor compounds that are found in river water include one or more compounds selected from atrazine, desmetryn, dicamba, chloromehtylphenoxyacetic acid, mecoprop, prometryn, propazine, simazine, terbutryn, and trietazine. These components may also be found in untreated water from lakes and canals.

40 Examples of sacrificial electron donor compounds that are found in sea water include one or more compounds selected from chloromethylphenol, pentachlorophenol, benzaldehyde,

trichlorophenol, nitroanaline, dichlorophenol, dimethyl phenol, atrazine, dinitrophenol and naphthylamine.

5 A sacrificial electron donor compound may be selected from the group consisting of from atrazine, prometryn, terbutryn and benzaldehyde.

The untreated water may contain chloride, as an example of an ionic sacrificial electron donor.

10 Untreated water may contain one or more components identified in sea water and river water as noted by the US Department of Interior (Torres *et al.*) and the British environmental agency (Huber *et al.*).

15 The untreated water may be supplemented by the addition of material that is capable of acting as a sacrificial electron donor. For example, an organic substrate, such as those substrates described above, including biomass, may be added to the untreated water.

20 Where an untreated water is used together with a biomass, it is preferable that the untreated water and the biomass are taken from the same locality, for example within 5 km from each other, such as 1 km from each other. Here, the methods for generating hydrogen and optionally also purifying the untreated water, do not require large movement of materials, and hydrogen may be generated close to the source of the water and the biomass. This provides a great efficiency to these methods.

25 In a preferred embodiment, the photocatalyst for use here is a carbon dot photocatalyst. Such a photocatalyst may itself be generated from an organic substrate, such as a biomass. This same organic substrate may be used as a sacrificial electron donor in the methods for generating hydrogen from untreated water. Thus, many of the components for use in the method may be sourced locally, and typically at minimum cost also, and may be prepared
30 from local components. This provides a further efficiency to the system.

Methods of Preparation

35 The present case provides methods for preparing a photocatalyst, including methods for preparing a carbon nitride photocatalyst and a carbon dot photocatalyst.

The preparation of carbon dot photocatalysts from simple organic starting material is well known in the art. For example, Martindale *et al.* (*Angew. Chemie Int. Ed.* **2017**) describe the preparation of amorphous carbon dots (a-CD) by calcination of citric acid at 180°C for 40 h.
40 Martindale *et al.* also describe the preparation of graphitic nitrogen-doped carbon dots (g-N-CD) by calcination of aspartic acid at 320°C. Graphitic undoped carbon dots were

prepared by calcination of citric acid at 180°C for 40 h, then further heating at 320°C for 100 h.

The present inventors have now found that more complex organic substrates may be used to generate carbon dots. In particular, the present inventors have shown that biomass waste may be used as a starting material for preparing carbon dots having photocatalytic activity. By way of example, the inventors have shown that carbon dots may be prepared from cotton, including cotton products, *G. Nivalis*, *G. Elliptica*, *T. Baccata*, *Elaeagnus X ebbingei* and olive leaves.

The present inventors have also found that biomass components isolated, such as at least partially purified, from plants may also be used as starting materials for preparing carbon dots having photocatalytic activity. By way of example, the inventors have shown that carbon dots may be prepared from α -cellulose, xylan and lignin.

The invention provides a method of preparing a carbon dot, the method comprising the step of calcining an organic substrate.

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

The organic substrate may be lignin, cellulose or hemicellulose.

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

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

The calcining step is a heating step and the temperature and duration of the heating step may be selected for optimal production of the carbon dot.

The minimum heating temperature may be at least 200°C, at least 250°C, at least 300°C or at least 350°C.

The maximum heating temperature may be at most 400°C, at most 450°C or at most 500°C. The heating temperature may be in a range selected from the minimum and maximum temperature given above. For example, the heating temperature may be in the range 250 to 450°C. If necessary the temperature can be varied within this range, for example with an initial lower heating temperature followed by a subsequent higher heating temperature.

The heating may be performed for a total of at least 12 hours, at least 24 hours, at least 2 days, at least 3 days or at least 4 days.

The heating may be performed for a total at most 5 days, at most 6 days, at most 7 days or at most 1 week.

The worked examples in the present case demonstrate that the products formed from the calcination reactions have excellent activity as photocatalysts, and these photocatalysts may be used to generate hydrogen from a range of organic substrates provided in purified and untreated water, including α -cellulose, EDTA (as an exemplary sacrificial electron donor), and pollutants in sea water and river water, such as atrazine, terbutyrn, benzaldehyde and prometryn. Other species, such as chloride, which is ionic and inorganic, may also act as sacrificial electron donors.

The preparation of carbon nitride catalysts is well known in the art, and the $^{NCN}CN_x$ has previously been reported for use as a photocatalyst, for example in sulfonylation reactions (see Meyer *et al.*).

The inventors have found that $^{NCN}CN_x$ may be used as a photocatalyst in the degradation of organic substrates, as described herein. The inventors have also found that the activity of the carbon nitride photocatalyst may be enhanced when the surface area of a catalyst sample is increased.

The preparation of $^{NCN}CN_x$ from $^{H2N}CN_x$ as described to date, provides a bulk sample of material where product particles are provided as aggregates (as shown in the TEM images of Figure 2(f) in the present case). The inventors have found that by disrupting the aggregates, such as by sonication, including ultrasonication, to reduce the aggregate size, increases the surface area of a sample, as judged by BET analysis. This increase in surface area is shown to increase the photocatalytic activity of the material.

The invention therefore provides a method of preparing $^{NCN}CN_x$, the method comprising the step of forming a bulk sample of $^{NCN}CN_x$ and subsequently treating the bulk $^{NCN}CN_x$ thereby to increase the surface area of the $^{NCN}CN_x$.

The bulk $^{NCN}CN_x$ may be sonicated to increase its surface area.

The bulk $^{NCN}CN_x$ may be obtained or obtainable from $^{H2N}CN_x$.

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.

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

“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.

5

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.

10 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

15 Materials

The pure biomass components, α -cellulose, xylan and lignin, as well as natural sea water (from Gulf of Mexico) and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), were purchased from Sigma-Aldrich and used without any further purification. Cotton wool
20 was purchased from Stores, Department of Chemistry, University of Cambridge, UK, whereas cotton pads from Waitrose, UK and cotton T-shirt from an open market in Trumpington, UK. The crude plant biomass samples, *Galanthus Nivalis* (*G. Nivalis*), *Garrya Elliptica* (*G. Elliptica*), *Taxus Baccata* (*T. Baccata*) and *ElaeagnusX ebbingei*, were collected from St John's College garden, University of Cambridge, UK, whereas the olive leaves from
25 D. S. Achilleos house garden, Trachoni, Cyprus. The untreated river water was obtained from the River Cam (Midsummer Common, September 2017), Cambridge, UK and used without any purification.

Buffer solutions were prepared using analytical grade reagents and titrated to the desired pH
30 with a pH meter (Mettler Toledo; SevenEasy).

Quantification of Photocatalyst Products

The amount of H₂ accumulation was quantified via periodic headspace gas injections (20 μ L)
35 to gas chromatography (GC), Agilent 7890A equipped with a 5 Å molecular sieve column. The temperature of the GC oven was maintained at 45°C and N₂ was used as the carrier gas, with a flow rate of 3 mL min⁻¹.

The amounts of alcohol (4-MBA) and aldehyde (4-methylbenzyl aldehyde, 4-MBA_d) were
40 quantified by nuclear magnetic resonance (¹H-NMR) spectroscopy (Bruker DPX 400 spectrometer). Thus, the reaction suspension was extracted with CH₂Cl₂ (2 × 3 mL), and combined extracts were concentrated *in vacuo*. The residue was then characterised by ¹H

NMR spectroscopy on a Bruker DPX 400 spectrometer at 298 K. Comparison of the methyl peak integrals of 4-MBA and 4-MBA_d, as well as the distinctive aldehyde (COH) peak, allowed for the determination of a quantitative ratio of the starting material to product.

5 *Treatment of Analytical Data*

All measurements were performed as triplicates and the data is reported as mean value $\pm$ standard deviation (σ).

10 ^{NCN}CN_x

Synthesis of CN_x and NiP

^{H₂}NCN_x was prepared by heating melamine at 550°C for 4 h under air. The yellow solid
15 obtained was then thoroughly ground using a pestle and mortar prior the surface functionalisation of the material. ^{NCN}CN_x was prepared from grounded ^{H₂}NCN_x upon reaction with KSCN (mass ratio 1:2) at 400°C for 1 h, and then at 500°C for 30 min under Ar. After cooling to room temperature, the resulting solid was excessively washed with water to remove the residual KSCN and then dried *in vacuo* to yield ^{NCN}CN_x.

20 To prepare a higher surface area ^{NCN}CN, the material was suspended in solvent (KPi, water, iPrOH and MeOH; at 1 or 5 mg/mL), followed by ultrasonication for 1, 10, or 30 min, using a Sonic Dismembrator (Model 120, Fischer Scientific).

25 NiP was synthesised following a reported procedure: see Gross *et al.*

Analysis and Characterisation of CN_x

^{NCN}CN_x was characterised before and after ultrasonication by UV-visible (UV-vis) absorption
30 and photoluminescence (PL) spectroscopy, Brunauer–Emmett–Teller (BET) surface area analysis, X-ray diffraction (XRD), Scanning (SEM) and Transmission Electron Microscopy (TEM), Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), to reveal the effect of the ultrasonication on the structural and optical properties of the bulk material, and thus its photocatalytic
35 performance.

Ultraviolet-visible (UV-Vis) absorption spectra were collected by a 50 Varian Cary UV-vis spectrophotometer in the wavelength range between 200 and 800 nm (in water) using quartz
cuvettes with 1 cm pathlength. Photoluminescence emission spectra of bulk and
40 ultrasonicated ^{NCN}CN_x were recorded on a FS5 spectrofluorometer (Edinburgh Instruments) equipped with an integrating sphere.

Brunauer-Emmett-Teller (BET) analysis was carried out with a 3Flex Surface Characterisation Analyzer (Micromeritics) at -196°C, using N₂ as the absorbing gas. Prior to measurements, the samples were outgassed under vacuum for 6 h at 150°C. The specific surface areas were calculated by fitting the data to the Brunauer-Emmett-Teller (BET) isotherm.

The X-ray diffraction (XRD) patterns were recorded with a BV X'Pert PRO diffractometer (PANalytical). The Scanning and Transmission Electron Microscopy (SEM and TEM, respectively) images, were recorded with MIRA3 FEG-SEM (TESCAN) and Tecnaï G2 80-200kV transmission electron (FEI) microscopes, respectively. Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) spectra were recorded on a Nicolet iS50 FTIR spectrometer (ThermoScientific) and analysed using the Omnic software.

The external quantum efficiency (EQE) of a ^{NCN}CN_x-NiP photosystems was measured using a solar light simulator (LOT LSN 254) equipped with a monochromator (LOT MSH 300) to irradiate the samples at a wavelength of $\lambda = 360 \pm 10$ nm, at a light intensity (*I*) of $I = 4.05 \text{ mW cm}^{-2}$. EQE was calculated using the following equation:

$$\text{EQE (\%)} = \frac{2 \cdot n_{\text{H}_2} \cdot N_A \cdot h \cdot c}{t_{\text{irr}} \cdot \lambda \cdot I \cdot A} \cdot 100$$

where n_{H_2} is the moles of photogenerated H₂, N_A the Avogadro's constant, h the Planck constant, c the speed of light, t_{irr} the time of irradiation, and A the cross-sectional area of irradiation (0.28 cm^2).

Brunauer-Emmett-Teller (BET) measurements showed a 60% increase in the surface area of ^{NCN}CN_x after ultrasonication ($97.4 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$), compared to bulk ($59.5 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$) (Figure 2(c)), in accordance with the literature (Meyer *et al.*). The BET values were obtained from the recorded absorption data by fitting to the UPAC Type IV isotherm.

The increase in surface area is due to the presence of smaller aggregate sizes in the sample after ultrasonication, compared to the bulk ^{NCN}CN_x, as indicated by TEM images (see Figure 2(f)), which also show negligible changes in particle size and morphology (only a small fraction of rod-like particles was observed), in accordance with SEM images (Figure 2(g)).

This also explains the almost identical X-ray diffraction (XRD) patterns of the two materials, and the preservation of the characteristic inter-layer ($28^\circ 2\theta$) and intra-layer ($7.9^\circ 2\theta$) periodicities of bulk ^{NCN}CN_x after ultrasonication (see Figure 2(d)) (Lau *et al.*).

Optical characterisation of the bulk and ultrasonicated ^{NCN}CN_x by UV-vis spectroscopy, at the same concentration ($0.0125 \text{ mg mL}^{-1}$), revealed mainly UV absorption attributed to the π - π^* transitions of the heptazine units (Zhuo *et al.*), which tails into the vis region for both

materials. However, after ultrasonication, although the spectroscopic features of the two materials remain identical (Figure 2(a)), there is a dramatic increase in the UV absorption of the ultrasonicated sample by about 9 times (Figure 2(a)). This is due to the increased surface area of the material and the smaller aggregate sizes (that minimize light scattering), which both maximize light absorption (Wu *et al.*).

PL studies ($\lambda_{\text{ex}} = 360 \text{ nm}$) revealed increased emission intensity and no significant shift in the emission peak position ($\lambda = 438 \text{ nm}$, corresponding to a band gap of approximately 2.8 eV) for the ultrasonicated $^{\text{NCN}}\text{CN}_x$, which implies no change in the band levels, but instead a higher number of delocalised C=N π - π^* transitions and photoexcited states (Figure 2(b)). The increased intensity, according to literature, also signifies smaller aggregates size and higher dispersity of the ultrasonicated sample, in agreement with the observed change in BET surface area (Shiravand *et al.*).

The external quantum efficiency (EQE) of the $^{\text{NCN}}\text{CN}_x$ -NiP photosystems was determined, and the EQE of the ultrasonicated and bulk systems are respectively $22.2\% \pm 1.1\%$ and $13.2\% \pm 1.2\%$. The former is approximately 68% higher than latter, which is highly consistent with the increase of BET surface area. The EQE of both the bulk and ultrasonicated $^{\text{NCN}}\text{CN}_x$ -NiP systems are much higher than the previously reported $^{\text{H}^2\text{N}}\text{CN}_x$ -NiP and RuP-NiP systems (Caputo *et al.*; Gross *et al.*).

Moreover, the material preserves its surface functionalities (Figure 2(e)) after ultrasonication. More specifically, both the bulk and ultrasonicated $^{\text{NCN}}\text{CN}_x$ samples show similar features in their FTIR spectra; a broad peak at about 3300 cm^{-1} assigned to N-H stretching, a pair of sharp peaks at 2175 cm^{-1} and 2144 cm^{-1} which signify the preservation of the C $\equiv$ N groups after ultrasonication, the bands at 1639 cm^{-1} and 1557 cm^{-1} which are attributed to secondary amine -C-N bending, whereas the signal at 807 cm^{-1} is due to the heptazine core vibration (Kasap *et al.*; Lau *et al. Nat. Commun.* **2016**).

Finally, XPS measurements (spectra not shown) show no significant changes between the high-resolution C 1s spectra of bulk and ultrasonicated samples, indicating that ultrasonication does not change the chemical properties of $^{\text{NCN}}\text{CN}_x$, which is consistent with FTIR characterization. The two C 1s environments at 288.01 eV and 287.02 eV are assigned to $\text{sp}^2 \text{ C}$ in the heptazine units and terminal N-C $\equiv$ N groups respectively (Miller *et al.*), and the peak at 284.4 eV is typical of adventitious carbon contamination (Algara-Siller *et al.*).

Overall, there is no evidence that ultrasonication induced any significant structural or chemical change to the bulk $^{\text{NCN}}\text{CN}_x$. As such, the enhancement in photocatalytic activity of the ultrasonicated $^{\text{NCN}}\text{CN}_x$ is mainly attributed to the increased surface area due to aggregate breakage in the bulk $^{\text{NCN}}\text{CN}_x$, the better light absorption (less light scattering) and the higher number of photoexcited charge generation in the ultrasonicated sample.

Photocatalytic Experiments

Photocatalysis was carried out in a borosilicate glass photoreactor (total volume 7.74 mL) in a water bath thermostated at 25°C. In a typical experiment, the suspensions were prepared by mixing for 10 min $^{NCN}CN_x$ (such as the ultasonicated form) or CDs and NiP (or H_2PtCl_2 and $H_8N_2MoS_4$ as precursors for Pt and MoS_2 , respectively) in aqueous 0.1 M KPi solution (at pH 4.5, 3 mL) containing an electron donor (4-MBA or 100 mg lignocellulosic substrates) in a photoreactor equipped with a stirrer bar (total solvent volume 3 mL). The container was then tightly sealed with a rubber septum and purged with N_2 containing 2% CH_4 as the internal gas chromatography standard.

The photoreactor was stirred and kept at a constant temperature (25°C) with continuous water circulation through a water-jacketed reservoir during the light experiments.

The vials were then irradiated using a calibrated solar light simulated (Xe lamp, 100 $mW\ cm^{-2}$, 1 Sun, Newport Oriel) whilst stirring. The solar light simulator was equipped with an air mass 1.5 global filter (AM 1.5G) and water filter to remove the infrared irradiation.

Use of $^{NCN}CN_x$

Optimising Performance of Activated $^{NCN}CN_x$

The photocatalytic activity of the photoreforming system to produce H_2 was optimised with respect to the activity of $^{NCN}CN_x$ using 4-MBA as an electron donor, NiP as H_2 evolution catalyst and irradiation by simulated solar light (AM1.5G, 100 $mW\ cm^{-2}$) at room temperature. An optimised specific activity of 39 mmol H_2 ($g\ ^{NCN}CN_x$) $^{-1}\ h^{-1}$ was obtained, which is twice the highest activity previously reported with respect to any CN_x .

Simultaneous proton reduction and 4-MBA oxidation to 4-MBA_d was investigated using bulk and activated $^{NCN}CN_x$ through sonication (data not shown). The activated (sonicated) $^{NCN}CN_x$ samples showed more than three times higher photocatalytic activity than previously reported bulk $^{NCN}CN_x$ samples. Thus, sonication was demonstrated as a means to activate $^{NCN}CN_x$. After 2 h of irradiation, the system becomes limited by the availability of the electron donor and complete and selective 4-MBA conversions to 4-MBA_d was achieved in less than 6 hours. Here, the bulk was sonicated for 10 min. as described previously.

The conditions of ultrasonication were optimised systematically for achieving high photocatalytic performance. The parameters are duration and temperature of ultrasonication, as well as concentration of $^{NCN}CN_x$ and solvent used during ultrasonication. As shown in Table 1, over the first 4 hours, the photocatalytic H_2 production rate and the NiP-based turnover number are enhanced by approximately 5 times after ultrasonication of 10 and 30 minutes. The material shows similar photocatalytic activity when ultrasonicated

for 10 and 30 minutes, and thus 10 min ultrasonication was chosen as the optimum sonication time.

Table 1 - Changes in H₂ production with change in ultrasonication time

Entry	Sonication time / min	TON cat / mol H ₂ (mol cat) ⁻¹ (4 h)	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol (4 h)	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity / μmol H ₂ (g CNx) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CNx) ⁻¹ h ⁻¹
	0	48.30	3.51	0.48	0.04	18.94	3.96	378.80	79.13
	1	102.18	6.77	1.02	0.07	59.70	8.64	1194.05	172.84
	10	236.58	14.90	2.57	0.16	91.08	13.38	1821.67	267.68
	30	74.82	7.38	0.75	0.07	42.60	7.10	851.90	141.92

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production with bulk and 1, 10 and 30 min ultra-sonicated ¹⁵N₂CN_x (0.5 mg) and NiP (10 nmol) in aqueous potassium phosphate buffer, KPi, (0.1 M, pH 4.5, 3 mL) containing 4-methyl benzyl alcohol, 4-MBA, (30 μmol). The suspension was assembled in a photoreactor with a total volume of 7.74 mL.

Ultrasonic acoustic cavitation can lead to a dramatic increase in the temperature of ultrasonicated suspension (see Han *et al.*) so the effect of sonication temperature on the photocatalytic performance of NCNCN_x was investigated. In this case, the temperature of dispersion after 10 min ultrasonication was 40°C. Another dispersion was kept at 25°C using a water circulator throughout 10 min ultrasonication. As the difference between ultrasonication at 40°C and 25°C was insignificant, the water circulator setup was not used in later experiments.

There was no significant enhancement in photocatalytic performance when ultrasonication was carried out at 0°C. This suggests that there is a temperature threshold for cavitation, i.e. ultrasonic acoustic cavitation can only happen within a definite temperature range, which has been observed for water cavitation (Niemczewski). Bath sonication (without the mechanical shearing of a tip) at 40°C was applied for comparison, and this led to no enhancement in the photocatalytic activity of NCNCN_x , because it generates cavitation of a relatively low concentration and thus smaller magnitude of mechanical force, due to its relatively low frequency (Jiang *et al.*). This indicates that the enhancement in photocatalytic activity is not thermally induced. Table 2 contains the data from these experiments.

A range of solvents have been reported as the optimum dispersion media for ultrasonication of NCNCN_x (Yang *et al.* and Hong *et al.*). Accordingly, the photocatalytic performances of NCNCN_x dispersions in KPi, isopropanol (iPrOH), methanol (MeOH) and water were tested (see Figure 6). There is no significant difference in the photocatalytic activity of NCNCN_x dispersions in different solvents, thus KPi buffer was chosen, as it provides a stable pH at which the optimal NiP activity is achieved (Kasap *et al.*).

Table 2 - Changes in H₂ production with changes in sonication temperature

Entry	Sonication temperature / °C	TON cat / mol H ₂ (mol cat) ⁻¹ (4 h)	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol (4 h)	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹
	0	55.04	6.26	0.55	0.06	46.92	2.40	938.37	48.00
	25	219.04	15.85	2.19	0.16	128.99	8.02	2579.85	160.41
	40	286.36	14.45	2.86	0.14	91.08	13.38	1821.67	267.68
	40*	31.47	4.99	0.31	0.05	22.77	2.47	455.45	49.42

*Standard sonication bath.

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production with 10 min ultra-sonicated ^{NCN}CN_x (0.5 mg) at 0°C, 25°C, 40°C and NiP (10 nmol) in KPi (0.1 M, pH 4.5, 3 mL) containing 4-MBA, (30 μmol). Control experiment for 10 min sonication of ^{NCN}CN_x using standard sonication bath at 40°C is also shown.

Table 3 - Changes in H₂ Production with Changes in Solvent

Entry	Sonication concentration / mg mL ⁻¹	Sonication Solvent	TON cat / mol H ₂ (mol cat) ⁻¹ (6 h)	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol (6 h)	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹
	1	iPrOH	221.87	21.27	2.22	0.21	92.67	2.64	1853.50	52.85
	1	MeOH	235.21	14.29	2.35	0.14	101.34	3.62	2026.79	72.33
	1	H ₂ O	246.94	30.77	2.47	0.31	119.19	9.71	2383.72	194.24
	1	KPi	286.36	14.45	2.86	0.14	72.20	8.01	1821.67	267.68
	5	KPi	261.85	15.70	2.62	0.16	72.71	5.21	1454.18	104.24

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production using 10 min ultra-sonicated ^{NCN}CN_x (0.5 mg) in KPi, isopropanol, methanol or water with NiP (10 nmol) in KPi (0.1 M, pH 4.5, 3 mL) containing 4-MBA, (30 μmol). Control experiment with different sonication concentration is also presented.

Further experiments were also conducted to compare EDTA with KPi as reaction solutions for the photosynthesis reaction, using both bulk and sonicated $^{NCN}CN_x$. The results are shown in Table 4. The $^{NCN}CN_x$ photocatalyst is useable in different solvent systems, and the sonicated sample is superior to the bulk sample in each of the different solvent systems.

5

In some studies, a relatively large loading of $^{NCN}CN_x$ was used in photocatalyst experiments and ultrasonication of dispersions at a higher concentration was therefore needed. The effect of dispersion concentration on photocatalytic performance was studied. As shown in Table 5, despite a 5-fold increase of dispersion concentration from 1 to 5 mg mL⁻¹, the H₂ production was barely affected.

10

Table 4 - Changes in H₂ production with Changes in Solvent

Entry	Solvent	^{NON} CN _x	TON cat / mol H ₂ (mol cat) ⁻¹ (4 h)	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol (4 h)	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity / μmol H ₂ (g CNx) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CNx) ⁻¹ h ⁻¹
	KPi	Bulk	48.30	3.51	0.48	0.04	18.94	3.96	378.80	79.13
	KPi	Sonicated	275.39	13.62	2.75	0.14	91.08	13.38	1821.67	267.68
	EDTA	Bulk	56.38	10.75	0.56	0.11	22.78	2.17	455.54	43.34
	EDTA	Sonicated	172.90	0.08	1.73	0.02	70.18	4.22	1403.58	84.48

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production with bulk and 10 min ultra-sonicated ^{NON}CN_x (0.5 mg) and NIP (10 nmol) in KPi, (0.1 M, pH 4.5, 3 mL) containing 4-MBA, (30 μmol) or in aqueous ethylenediamine tetraacetic acid (EDTA) (0.1 M, pH 4.5, 3 mL) solution.

Table 5 - Changes in H₂ production with Changes in Sonication Concentration

Entry	Sonication concentration / mg mL ⁻¹	Sonication Solvent	TON cat / mol H ₂ (mol cat) ⁻¹ (6 h)	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol (6 h)	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity / μmol H ₂ (g CNx) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CNx) ⁻¹ h ⁻¹
	1	KPi	286.36	14.45	2.86	0.14	72.20	8.01	1821.67	267.68
	5	KPi	261.85	15.70	2.62	0.16	72.71	5.21	1454.18	104.24

* Photocatalytic hydrogen production with ^{NON}CN_x (0.5 mg) dispersed at an initial concentration of 5 mg/mL and 1 mg/mL, NIP (10 nmol), 4-MBA (30 μmol) in KPi (0.1 M, pH 4.5, 3 mL) under 1 sun irradiation (AM 1.5G) at 25°C.

The photocatalytic reaction conditions were further optimised systematically for specific activity with respect to carbon nitride, and high TOF_{NiP} and high TON_{NiP} with respect to NiP, as well as the yield of H_2 production and alcohol conversion to oxidation product (determined after 6 h of irradiation).

5

The loading of NiP catalyst was varied at various $^{\text{NCN}}\text{CN}_x$ loadings, 0.5 mg and 5 mg, with 4-MBA (30 μmol), and the hydrogen evolution was monitored for the first 6 hours. As shown in Table 6, the total H_2 evolution and percentage of conversion of 4-MBA to the oxidation product 4-MBA_d raised significantly as the amount of NiP catalyst increased from 10 nmol to 100 nmol, where >99% selective alcohol conversion was also observed. Although the production of H_2 and 4-MBA_d starts to be limited by the availability of 4-MBA electron donors at NiP loadings above 100 nmol, the first-hour rate of H_2 production kept climbing. The maximum TOF_{NiP} , $254.16 \pm 18.97 \text{ mol H}_2 (\text{mol NiP})^{-1} \text{ h}^{-1}$, and maximum TON_{NiP} , $700.91 \pm 20.24 \text{ mol H}_2 (\text{mol NiP})^{-1}$, are obtained when 30 nmol NiP and 5 mg $^{\text{NCN}}\text{CN}_x$ were added to the system (Table 6). The TOF_{NiP} is higher than many previously reported NiP systems with carbon-based photosensitiser, and it is comparable to the reported N-doped carbon dot system (Hutton *et al. Chem. Soc. Rev.* 2017). Both TOF_{NiP} and TON_{NiP} are in good agreement with previously reported $^{\text{NCN}}\text{CN}_x$ -NiP and the RuP-NiP systems (Kasap *et al.*; Gross *et al.*).

20

Similar optimisation was carried out at $^{\text{NCN}}\text{CN}_x$ loading of 0.5 mg. Under these conditions, higher material specific activities were obtained. It is clearly shown that the specific activity increases dramatically as the amount of NiP increases at both $^{\text{NCN}}\text{CN}_x$ loadings. This growth of specific activity does not reach saturation until NiP loading reaches 400 nmol when 0.5 mg $^{\text{NCN}}\text{CN}_x$ is in the system.

25

Table 6 shows the changes in hydrogen productions with changes in the relative and absolute amounts of the $^{\text{NCN}}\text{CN}_x$ photocatalyst and the NiP co-catalyst.

Table 6 - Changes in H₂ production with changes in ^{NCN}CN_x Loading

Entry	NiP / nmol	CN _x / mg	TON cat / mol H ₂ (mol cat) ⁻¹ (6 h)	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol (6 h)	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity/ μmol H ₂ (g CN _x) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹
	100	0.1	20.33	0.19	2.03	0.02	3.20	0.17	3964.80	14.73
	10	0.1	235.69	23.60	2.36	0.24	41.43	0.41	4143.34	414.30
	10	0.5	286.36	14.45	2.86	0.14	72.20	8.01	1443.98	160.21
	30	0.5	205.54	30.65	5.62	0.89	72.68	10.31	4360.66	618.31
	50	0.5	192.88	44.93	9.23	1.90	56.19	10.92	5619.48	1091.56
	100	0.5	194.66	16.56	19.47	1.66	45.72	4.50	9143.43	899.75
	200	0.5	140.44	13.45	28.09	2.69	64.07	109.19	25629.17	4367.63
	100	0.1	20.33	0.19	2.03	0.02	3.20	0.17	3964.80	14.73

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production with 10 min ultra-sonicated ^{NCN}CN_x and NiP at various loadings in KPi (0.1 M, pH 4.5, 3 mL) containing 4-MBA, (30 μmol).

Table 7 - Changes in H₂ production with changes in ^{NCN}CN_x Loading

Entry	NiP/ nmol	CN _x / mg	TON cat / mol H ₂ (mol cat) ⁻¹ (6 h)	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol (6 h)	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹	Aldehyde / μmol (6 h)	± σ / μmol	Alcohol Conversion / % (6 h)	± σ / %
	300	0.5	98.38	2.01	29.51	0.60	57.47	2.07	34480.06	1242.86	29.76	0.19	99.18	0.63
	400	0.5	79.22	0.26	31.69	0.10	49.14	0.33	39310.09	263.09	29.85	0.05	99.51	0.18
	10	5	209.19	18.57	2.09	0.19	105.73	12.33	211.46	24.66	5.50	0.48	18.35	1.60
	20	5	625.00	62.24	12.50	1.24	148.83	16.79	595.31	67.15	9.74	1.05	32.47	3.50
	30	5	700.91	20.24	21.03	0.61	254.16	18.97	1524.98	379.34	17.03	1.40	56.78	4.66
	50	5	511.90	17.56	25.60	0.88	142.32	1.75	1423.24	17.53	24.24	1.12	80.81	3.74
	100	5	299.90	19.84	29.99	1.98	110.77	5.09	2215.41	101.81	29.12	0.93	97.07	3.11
	200	5	158.40	5.68	31.68	1.14	85.15	4.79	3406.15	191.80	29.84	0.07	99.47	0.22
	0	0.5	-	-	0.00	0.00	0.00	0.00	0.00	0.00	0.92	0.10	3.08	0.33
	FeCl ₃	0.5	-	-	0.00	0.00	0.00	0.00	0.00	0.00	0.72	0.05	2.39	0.16
	NiCl ₂	0.5	-	-	1.15	0.24	-	-	383.49	81.24	1.18	0.07	3.93	0.23

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) simultaneous H₂ and 4-MBA oxidation to 4-methyl benzaldehyde (4-MBA) with 10 min ultra-sonicated ^{NCN}CN_x and NiP at various loadings in KPi (0.1 M, pH 4.5, 3 mL) containing 4-MBA, (30 μmol).

To date, the highest activity of carbon nitride photocatalytic system, from urea-derived CN_x with Pt catalyst and TEOA as sacrificial electron donor, was reported to be approx. 20 mmol H₂ g⁻¹ h⁻¹ (Martin *et al.*). In contrast, a specific activity of 39.310 ± 0.263 mmol H₂ g⁻¹ h⁻¹ was achieved in the designed system (with 400 nmol NiP and 0.5 mg ^{NCN}CN_x) in this work.

At the loading of 300 nmol NiP and 0.5 mg ^{NCN}CN_x, a 3-fold enhancement of first-hour H₂ production rate was observed for ultrasonicated ^{NCN}CN_x, compared to the bulk material (see Table 7 above).

The control experiment in absence of NiP showed no H₂ production, indicating the catalyst is an essential component to the photocatalytic system (see Table 7). Degradation of **NiP** under UV/Vis solar irradiation (λ < 400 nm) has been reported (Matindale *et al.*), and the inferred degradation product is Ni(II), which can act as H₂-evolving catalyst.

Therefore, a control experiment without NiP but in presence of NiCl₂ was performed, and it yielded small amounts of H₂ and 4-MBA_d over 6 h (see Table 7).

Another experiment used FeCl₃ in place of NiP to rule out the possibility of Fe deposition from the homogeniser tip during ultrasonication, however there was no measurable H₂ evolution (see Table 7). Hence, the improvement in photocatalytic performance must be attributed to improved activity of ^{NCN}CN_x rather than the catalyst. In all three control experiments, even the one with no metal at all, some 4-MBA_d production was observed. This means that ^{NCN}CN_x can still generate excited electron-hole pairs and drive the 4-MBA oxidation, even in absence of any catalyst.

The kinetics of electron transfer processes in the ^{NCN}CN_x-NiP photosystem were extensively studied for the bulk material using transient absorption spectroscopy (TAS), and the electron transfer to NiP was identified as the rate-limiting step (Kasap *et al.*).

The bulk ^{NCN}CN_x was exploited for time-delayed 'dark' photocatalysis (Kasap *et al.*; Lau *et al. Angew. Chemie Int. Ed.* **2017**). The colour of ^{NCN}CN_x changes from yellow to blue upon irradiation in presence of a suitable electron donor such as 4-MBA. This blue state has a lifetime of up to hours and is representative of trapping of long-lived electrons in ^{NCN}CN_x. Upon addition of an electron acceptor such as the H₂-evolving catalyst NiP in dark, a decay of this blue colour as well as H₂ evolution was observed, suggesting the photogenerated electrons are transferred from ^{NCN}CN_x to the NiP and reductively produce H₂ in absence of light. This means that ^{NCN}CN_x can efficiently decouple photon reduction and 4-MBA oxidation, allowing these two processes to be studied independently.

This property of NCNCN_x was utilised to investigate the mechanistic changes of the photosystem upon ultrasonication of the materials. The data collected in the experiments described below is shown in Table 8.

- 5 As NCNCN_x is irradiated for a longer time, the more electrons are stored in the heptazine framework, the more H_2 can be produced until saturation is reached. As shown in Table 8 H_2 yield increases from 2.0 μmol to 2.5 μmol as the irradiation length increases from 2 hours to 4 hours; however, no further rise in H_2 yield was observed when irradiation increased to 18 hours, suggesting saturation is reached.

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When the photosystem was irradiated for only 30 minutes before addition of NiP, 60% more H_2 was yielded from the ultrasonicated NCNCN_x than from the bulk material, suggesting that there are more photoexcited electrons stored in ultrasonicated NCNCN_x and the reductive quenching of the photogenerated holes in the ultrasonicated material by 4-MBA is faster

15 than in bulk. The initial H_2 evolution rate of ultrasonicated NCNCN_x was approx. 33% faster than bulk although the total amounts of electrons trapped in them are the same. This indicates that the rate-limiting electron transfer from NCNCN_x to NiP was accelerated, which led to improved photocatalytic performance.

Table 8 - Dark H₂ production

Entry	CN _x	TON cat / mol H ₂ (mol cat) ⁻¹	± σ / mol H ₂ (mol cat) ⁻¹	H ₂ / μmol	± σ / μmol	TOF max / h ⁻¹	± σ / h ⁻¹	Activity/ μmol H ₂ (g CN _x) ⁻¹ h ⁻¹	± σ / μmol H ₂ (g CN _x) ⁻¹ h ⁻¹	Aldehyde / μmol	± σ / μmol	Alcohol Conversion / %	± σ / %
0.5 h irradiation, move to dark and inject 50 nmol NiP													
	Sonicated	24.06	1.44	1.20	0.07	22.51	1.30	225.06	12.95	0.86	0.24	2.87	0.81
	Bulk	16.27	0.55	0.81	0.03	15.57	0.59	155.75	5.94	0.70	0.03	2.32	0.10
2 h irradiation, move to dark and inject 50 nmol NiP													
	Sonicated	36.83	5.09	1.84	0.25	24.27	1.69	242.71	16.91	1.97	0.22	6.56	0.73
	Bulk	34.17	0.69	1.71	0.03	19.50	1.17	195.01	11.71	1.60	0.16	5.33	0.53
0.5 h irradiation, move to dark and inject 50 nmol NiP													
	Sonicated	54.01	4.07	2.70	0.20	26.95	0.91	269.47	9.06	3.24	0.71	10.81	2.37
	Bulk	48.21	5.14	2.41	0.26	20.04	1.23	200.44	12.30	2.14	0.41	7.13	1.36
4 h irradiation, move to dark and inject 100 nmol NiP													
	Sonicated	25.81	2.79	2.58	0.28	16.29	1.01	325.73	20.17	3.06	0.08	10.21	0.28
	Bulk	25.56	2.90	2.56	0.29	12.21	0.48	244.11	9.55	2.32	0.24	7.72	0.80
18 h irradiation, move to dark and inject 50 nmol NiP													
	Sonicated	62.40	3.60	3.12	0.18	17.84	1.88	178.43	18.82				
	Bulk	52.79	3.82	2.64	0.19	15.34	0.49	153.36	4.89				

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) dark H₂ production with bulk and 10 min ultrasonicated ^{NCN}CN_x (5 mg) in KPi solution (0.1 M, pH 4.5, 3 mL) containing 4-MBA (30 μmol) in the absence of NiP. The samples were irradiated under 1 sun (100 mW cm⁻², AM1.5G, 25°C) for (a) 30 min, (b) 2 h and (c) 4 h, moved to dark and **NiP** (in KPi solution) was injected under anaerobic conditions.

Photocatalysis - α -Cellulose

Biomass conversion is both an affordable and sustainable approach to produce hydrogen. So far, only systems comprising of noble and toxic metals as light harvesters and catalysts have been reported for photocatalytic reforming of biomass, and most of these have involved pre-treatment of the biomass under alkaline conditions (Young Park *et al.*; Roy *et al.*). Described below is the use of carbon nitride photocatalyst for hydrogen evolution from lignocellulosic biomass under mild conditions with no pre-treatment. The carbon nitride photocatalyst was used together with a co-catalyst for photocatalytic reforming of biomass over a wide spectrum of pH values.

The loadings of biomass, carbon nitride and NiP were optimised with respect to hydrogen production. Cellulose is the main component of wood-derived biomass (Sun *et al.*), so it was used in all initial optimisations. α -Cellulose, the most unreactive form of cellulose also with the highest degree of polymerisation (DP = 1450) (Sweet *et al.*), was chosen. In all initial optimisations, the ultrasonicated $^{NCN}CN_x$ -NiP photosystem (3 mL, 0.1 M KPi, pH 4.5) was used based on the merit of its high specific activity.

The data in Table 9 shows photocatalytic hydrogen evolution at different loadings of α -cellulose. Since $^{NCN}CN_x$ is a heterogeneous photosensitiser and α -cellulose is a nearly insoluble electron donor, stirring becomes critical for photocatalytic hydrogen evolution in this system. Increasing the α -cellulose loading scarifies stirring efficiency while lower α -cellulose amount reduces electron donor availability; thus, 100 mg is the optimum loading for a balance between providing effective stirring and sufficient electron donor. Table 9 shows that the H_2 evolution at different loadings of $^{NCN}CN_x$ and NiP. The system with 0.5 mg $^{NCN}CN_x$ and 50 nmol NiP gave a high specific activity of $1694.87 \pm 104.89 \mu\text{mol } H_2 (\text{g } ^{NCN}CN_x)^{-1} \text{ h}^{-1}$, whereas the highest H_2 production over 4 h was observed with 5 mg $^{NCN}CN_x$ and 50 nmol NiP. The latter (5 mg ultrasonicated $^{NCN}CN_x$, 50 nmol NiP and 100 mg lignocellulosic substrate) was used in the following photocatalytic experiments, unless specified otherwise.

Table 9 - Changes in H₂ Production with Change in CN_x and Substrate Loading

Entry	Substrate loading / mg	CN _x type	CN _x loading / mg	NiP / nmol	H ₂ / μmol (4 h)	$\pm \sigma$ / μmol	Activity / $\mu\text{mol H}_2$ (g CN _x) ⁻¹ h ⁻¹	$\pm \sigma$ / $\mu\text{mol H}_2$ (g CN _x) ⁻¹ h ⁻¹
	50	NCNCN _x	5	20	0.67	0.00	58.40	2.24
	100	NCNCN _x	5	20	0.77	0.02	54.51	2.55
	150	NCNCN _x	5	20	0.58	0.04	41.34	7.31
	100	NCNCN _x	5	50	2.62	0.09	252.94	26.14
	100	NCNCN _x	0.5	50	1.43	0.02	1694.87	104.89
	100	Bulk NCNCN _x	5	50	1.91	0.07	131.76	3.52
	100	Bulk H ₂ NCN _x	5	50	8.81	3.89	0.13	0.04

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production with bulk ¹⁵N₂CN_x, bulk and 10 min ultra-sonicated ¹⁵N₂CN_x and NiP at different concentrations in KPi (0.1 M, pH 4.5, 3 mL) containing α -cellulose.

Moreover, the photocatalytic reforming of cellulose was studied using previously reported $\text{H}_2^{15}\text{N}\text{CN}_x\text{-NiP}$ and bulk $\text{NCN}\text{CN}_x\text{-NiP}$ photosystems (Caputo *et al.*; Martindale *et al. Angew. Chemie Int. Ed.* **2017**). As the data in Table 9 shows, the $\text{H}_2^{15}\text{N}\text{CN}_x$ system produced a trace amount of H_2 after 4 h of irradiation while bulk and ultrasonicated NCNCN_x systems

5 respectively yielded approximately 20 or 30 times more. This enhancement in photocatalytic performance is attributed to improved charge separation as well as efficient substrate oxidation brought by the insertion of the cyanamide groups (Zhang *et al.*; Lau *et al. Nat. Commun.*).

- 10 Different H_2 -evolving catalysts were investigated for photocatalytic reforming of α -cellulose. Pt, the benchmark H_2 -evolving catalyst, as well as MoS_2 and the molecular catalyst NiP were used, and the results are presented in Table 10. NiP shows the best activity amongst all for first 24 h, demonstrating the first example of molecular catalyst-based biomass reformation system. After 24 hours of irradiation, the activity of NiP terminated due to UV-induced
- 15 degradation caused by ligand displacement and ligand oxidation caused by photogenerated holes (Martindale *et al. Angew. Chemie* **2016**). NCNCN_x can be easily platinised by *in situ* photodeposition of H_2PtCl_6 (Lau *et al. Nat. Commun.* **2016**), which accounts for the relatively slow H_2 -evolving rate of the first day. Similarly, MoS_2 can be generated by *in situ* photodeposition of $[\text{MoS}_4]^{2-}$ precursor (Nguyen *et al.*). Both the $\text{NCN}\text{CN}_x\text{-MoS}_2$ and the
- 20 $\text{NCN}\text{CN}_x\text{-Pt}$ photosystems outperform the $\text{NCN}\text{CN}_x\text{-NiP}$ system over long term due to their robustness.

Table 10 - Change in H₂ Production with Change in Catalyst

Entry	Catalyst	Activity / $\mu\text{mol H}_2 (\text{g CN}_x)^{-1} \text{ day}^{-1}$	$\pm \sigma$ / $\mu\text{mol H}_2 (\text{g CN}_x)^{-1} \text{ day}^{-1}$	Time / day	H ₂ / $\mu\text{mol (24 h)}$	$\pm \sigma$ / μmol
	NiP	748.34	23.99	1	3.74	0.12
				2	3.74	0.12
				3	3.74	0.12
				4	3.74	0.12
				5	3.74	0.12
				6	3.74	0.12
	Pt	172.28	22.66	1	0.86	0.11
				2	2.40	0.12
				3	3.79	0.23
				4	5.12	0.12
				5	5.99	0.05
				6	7.30	0.15
	MoS ₂	356.28	5.64	1	1.75	0.13
				2	3.56	0.06
				3	4.72	0.23
				4	5.93	0.25
				5	6.88	0.37
				6	7.67	0.52

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production with 10 min ultra-sonicated ^{NCN}CN_x (5 mg) and NiP (50 nmol), H₂PtCl₂ (4 wt.%) or H₈N₂MoS₄ (4 wt.%) in the presence of α-cellulose (100 mg) in KPi (0.1 M, pH 4.5, 3 mL) over 6 days.

Photocatalysis - Lignocellulose

Lignocellulose is the most abundant constituent of biomass (Azadi *et al.*), and it is composed of cellulose, hemicellulose and lignin. Cellulose is in the form of microfibrils, which are coated with hemicellulose to form an open network whose empty spaces are filled up with lignin (Rubin *et al.*). Cellulose, the major component, is a polymeric chain of glucose units mainly linked by β (1→4) glycosidic bonds (van Wyk *et al.*). Cellobiose and glucose are respectively the disaccharide and monosaccharide units of cellulose. Hemicellulose is a branched polysaccharide of various pentose and hexose sugars. In this project, xylan, a type of hemicellulose that accounts for up to a third of carbohydrate content in many lignocellulosic materials (Hinman *et al.*), and consist of xylose units, was used as the representative hemicellulose.

Lignocellulose components (α -cellulose, xylan and lignin) as well as their subunits were used as electron donors for photocatalytic H_2 evolution, and the data are presented in Table 11. As expected, the photocatalytic reforming yields of the subunits are much higher than those of α -cellulose, hemicellulose and lignin.

5

Cellobiose, the only disaccharide substrate, showed lower PR yield than the monosaccharides, which is consistent with previous reports.³⁵ $3.74 \pm 0.12 \mu\text{mol}$ and $4.92 \pm 0.17 \mu\text{mol}$ H_2 were produced from α -cellulose and xylan respectively over 24 h. Lignin is strongly light-absorbing and its UV-Vis spectrum shows a broad peak at 300 nm and a shoulder at 350 nm (Wakerley *et al.*), the region over which the photosensitiser $^{NCN}CN_x$ absorbs most strongly. Therefore, due to this competition for light absorption in the UV-vis region, no measurable amount of H_2 was produced from this $^{NCN}CN_x$ -NiP photosystem with lignin as an electron donor at 100 mg loading. However, changing lignin loading to 0.5 mg resulted in H_2 production of $0.42 \pm 0.03 \mu\text{mol}$ over 24 h, due to reduced concentration and light absorption.

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Some of these experiments were repeated using H_2PtCl_2 in place of NiP. The results are shown in Table 12 in relation to the use of α -cellulose, xylan and lignin as substrates. These results are reported in an aqueous mixture at 10 M KOH, after a basic pre-treatment of the substrate.

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Table 11 - H₂ Production with ^{NCN}CN_x and Changes in Substrate

Entry	Substrate type	H ₂ / μmol (4 h)	$\pm \sigma$ / μmol	Activity / $\mu\text{mol H}_2 (\text{g CN}_x)^{-1} \text{ h}^{-1}$	$\pm \sigma$ / $\mu\text{mol H}_2 (\text{g CN}_x)^{-1} \text{ h}^{-1}$	H ₂ / μmol (24 h)	$\pm \sigma$ / μmol
	α -cellulose	2.62	0.09	252.94	26.14	3.74	0.12
	xylan	3.89	0.23	136.59	5.51	4.92	0.17
	lignin	0	0	0	0	0	0
	lignin*	0.20	0.03	40.84	6.76	0.42	0.03
	cellobiose	8.03	0.68	510.74	54.01	14.17	1.73
	glucose	13.94	0.27	1117.55	80.21	32.05	4.76
	xyllose	8.30	0.81	552.83	53.93	19.86	2.27
	galactose	13.16	0.69	761.88	11.42	28.05	2.52
	α -cellulose	2.62	0.09	252.94	26.14	3.74	0.12

*0.5 mg lignin is used.

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production using 10 min ultra-sonicated ^{NCN}CN_x (5 mg) and NiP (50 nmol) in the presence of lignocellulosic substrates (100 mg) in KPi (0.1 M, pH 4.5, 3 mL).

Table 12 - H₂ Production with H₂PtCl₂ and Changes in Substrate

Entry	Substrate	Substrate mass/ mg	Activity/ $\mu\text{mol H}_2$ (g CNx) ⁻¹ day ⁻¹	$\pm \sigma$ / $\mu\text{mol H}_2$ (g CNx) ⁻¹ day ⁻¹	Time / day	H ₂ / μmol (24 h)	$\pm \sigma$ / μmol
	α -cellulose	100	1065.37	52.32	1	5.33	0.26
					2	11.36	0.03
					3	18.54	0.20
					4	26.83	0.58
					5	32.27	0.25
					6	39.50	1.11
					7	40.63	1.33
					8	48.85	3.13
					9	56.41	2.79
					10	63.47	3.30
					11	62.32	1.30
					12	69.78	1.39
	xylan	50	1447.21	34.35	1	7.24	0.17
					2	13.03	0.27
					3	26.31	1.82
					4	35.07	1.36
					5	47.78	3.11
					6	55.45	2.72
					7	63.63	2.36
					8	75.09	1.85
					12	122.55	9.34

Entry	Substrate	Substrate mass/ mg	Activity/ $\mu\text{mol H}_2$ (g CNx) ⁻¹ day ⁻¹	$\pm \sigma$ / $\mu\text{mol H}_2$ (g CNx) ⁻¹ day ⁻¹	Time / day	H ₂ / μmol (24 h)	$\pm \sigma$ / μmol
	lignin	0.5	350.33	11.37	1	1.75	0.06
					2	2.86	0.20
					3	4.87	0.37
					4	6.36	0.43
					5	7.70	0.63
					6	8.85	0.74
					7	9.11	0.76
					8	9.56	0.98
					12	13.62	1.28

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production using 10 min ultra-sonicated ¹⁵N₂CN_x (5 mg) with H₂PtCl₂ (4 wt. %) and cellulose, xylan or lignin in 10 M KOH. All the samples were pre-treated in 10 M KOH prior to injection of ¹⁵N₂CN_x and H₂PtCl₂.

Photocatalysis - Biomass

The photocatalytic reforming of raw biomass was also investigated. Three natural lignocellulosic materials (bagasse, wooden branch and sawdust) and two waste materials (waste paper and cardboard) were used as electron donors for photocatalytic H₂ evolution and the 24-hour H₂ production yields are shown in **Table 13**. Lignin is the most challenging component of lignocellulose for photoreforming, and paper, wood and bagasse have lignin content of <15%, 18-35% and 20%, respectively (Sun *et al.*; Lavarack *et al.*). However, the difference in lignin content does not dictate the trend in H₂ production in these photosystems. Sawdust is the only powder and it stirs the best with the heterogeneous photosensitiser, so it achieved the highest PR yield. Cardboard, turned into small crumbs after grinding, is the second best, while the remaining samples, paper, bagasse and wooden branch, remain as large pieces after grinding. Therefore, the bulkiness of solid biomass has a more significant impact than the lignin content on photocatalytic H₂ evolution in the case of this ^NCN_x-NiP photosystem.

Table 13 - H₂ Production with Change in Substrate

Entry	Substrate type	H ₂ / μmol (4 h)	$\pm \sigma$ / μmol	Activity/ $\mu\text{mol H}_2$ (g CNx) ⁻¹ h ⁻¹	$\pm \sigma$ / $\mu\text{mol H}_2$ (g CNx) ⁻¹ h ⁻¹	H ₂ / μmol (24 h)	$\pm \sigma$ / μmol
	sawdust	2.36	0.43	117.87	21.59	3.89	0.34
	paper	0.85	0.04	42.67	1.98	1.42	0.20
	cardboard	0.94	0.05	46.90	2.47	2.95	0.16
	bagasse	0.70	0.08	34.85	3.79	1.30	0.08
	wooden branch	0.71	0.01	35.65	0.34	0.91	0.04

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production using 10 min ultra-sonicated ¹³C₆N₆ (5 mg) and NiP (50 nmol) in the presence of raw biomass substrates (100 mg) in KPi (0.1 M, pH 4.5, 3 mL).

Photocatalysis - Pre-Treatment

Since the conversion of lignocellulose materials is often hindered by the crystallinity of cellulose, a variety of physical, physio-chemical, chemical and biological pre-treatment methods, e.g. pyrolysis, gas explosion, ozonolysis and use of cellulase, have been studied to make cellulose accessible for hydrolysis to improve its solubility (Sun *et al.*; Kumar *et al.*). In this project, a combination of hydrolysis at extreme pH ranges and irradiation was used as the pre-treatment (Chosdu *et al.*).

The cellulose pre-treatment was explored over a broad range of pH. Pt was chosen instead of NiP because the photocatalytic performance of NiP is largely impaired at extreme pH (Caputo *et al.*). In addition, using the benchmark Pt H₂-evolving catalyst can provide a direct comparison between this ^{NCN}CN_x-Pt photosystem and many previously reported systems (Kuehnel *et al.*). In the following experiments, α-cellulose was suspended in different solvents and stirred for 24 h under 1 sun irradiation (AM 1.5G) at 25°C before the addition of H₂PtCl₆ and ^{NCN}CN_x.

Table 14 illustrates the photocatalytic H₂ evolution performance of the ^{NCN}CN_x-Pt photosystem with α-cellulose pre-treated at different pH values. The system with no pre-treatment is shown by the orange line for comparison. Pre-treatment at pH 15 (with 10 M KOH) gives the highest H₂-evolving activity. The total H₂ production yield over 6 days is 39.50 ± 1.11 μmol, which is twice as that of pre-treatment with 5 M KOH and is 4 to 5 times higher than that of systems in more acidic conditions. This is consistent with previous studies that showed cellulosic material is more easily solubilised in more alkaline conditions (Budtova *et al.*).

Table 14 - Changes in H₂ Production with Changes in Pre-Treatment

Entry	Catalyst	Conditions	Activity/ $\mu\text{mol H}_2$ (g CNx) ⁻¹ day ⁻¹	$\pm \sigma$ / $\mu\text{mol H}_2$ (g CN _x) ⁻¹ day ⁻¹	Time / day	H ₂ / μmol (24 h)	$\pm \sigma$ / μmol
	Pt	H ₂ SO ₄ , pH 2	178.06	5.47	1	0.89	0.03
					2	2.44	0.03
					3	3.97	0.06
					4	6.29	0.09
					5	7.76	0.35
					6	10.16	0.42
	Pt	KP _i , pH 4.5	172.28	22.66	1	0.86	0.11
					2	2.40	0.12
					3	3.79	0.23
					4	5.12	0.12
					5	5.99	0.05
					6	7.30	0.15
	Pt	10 M KOH, pH 7 [±]	941.94	57.97	1	4.71	0.29
					2	6.92	0.59
					3	8.40	0.19
					4	9.38	0.07
					5	10.20	0.07
					6	11.08	0.02

Pt	1 M KOH	497.41	31.77	1	2.49	0.16
				2	4.33	0.05
				3	5.94	0.09
				4	7.40	0.40
				5	8.22	0.47
				6	9.82	0.23
Pt	5 M KOH	458.04	24.36	1	2.29	0.12
				2	5.17	0.30
				3	9.48	0.41
				4	13.88	0.97
				5	17.48	1.32
				6	20.73	1.96
Pt	10 M KOH	1065.37	52.32	1	5.33	0.26
				2	11.36	0.03
				3	18.54	0.20
				4	26.83	0.58
				5	32.27	0.25
				6	39.50	1.11

‡Pre-treatment with 10 M KOH for 24 h, followed by neutralization to pH 7.

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production using 10 min ultra-sonicated ¹³C₆H₅COOH (5 mg) with H₂PtCl₆ (4 wt. %) and α-cellulose (100 mg) in 1, 5, 10 M KOH, pH 2 H₂SO₄ or pH 4.5 KPi solution (0.1 M, pH 4.5, 3 mL). All the samples were pre-treated prior to injection of ¹³C₆H₅COOH and H₂PtCl₆.

The conversion yield determined with different α -cellulose loadings in the presence of $^{NCN}CN_x$ indicates that 22% conversion is reached after 6 days of irradiation in 10 M KOH solution (see Table 15). This is more than twice (9.7%) the yield reported previously with a CdS/CdO_x photocatalyst system (Wakerley *et al.*).

Table 15 - Changes in H₂ Production with Changes in Pre-Treatment

Entry	α -Cellulose / mg	Anhydroglucose monomers ^[a] / μ mol	Theoretical Maximum H ₂ ^[b] / μ mol	H ₂ / μ mol	Conversion / %
	1.65	10.18	122.16	14.4	11.79
	0.81	5	60	13.22	22.03

* Photoreactors were prepared using 10 min ultra-sonicated $^{NCN}CN_x$ (5 mg) with H₂PtCl₂ (4 wt %) and cellulose (1.65 or 0.81 mg) in 10 M KOH. The samples were pre-treated in 10 M KOH prior to injection of $^{NCN}CN_x$ and H₂PtCl₂. Percentage conversion yields were calculated after irradiating (AM 1.5G, 100 mW cm⁻², 25°C) the samples for 6 days.

[a] Moles of anhydroglucose monomer units are calculated by dividing the total amount of α -cellulose used with the molecular mass of an anhydroglucose repeating unit (162.14 g mol⁻¹)

[b] The theoretical maximum H₂ is calculated based on the assumption that maximum 12 equivalent of H₂ can be produced per anhydroglucose unit in α -cellulose structure.

Unlike many reported systems that can only photocatalytically reform cellulose in extremely alkaline conditions (Wakerley *et al.*; Kawai *et al.*), this $^{NCN}CN_x$ -Pt photosystem can operate over a wide range of pH with reasonable yield. This can be attributed to the stability of $^{NCN}CN_x$ as well as facilitated electron transfer to Pt (Kasap *et al.*; Lau *et al. Nat. Commun.* **2016**).

Photocatalysis - Polymer Substrates

$^{NCN}CN_x$ (5 mg) was used together with NiP (50 nmol) to produce hydrogen from a range of polymer substrates (100 mg) in KPi solution (0.1 M, pH 4.5, 3 mL). The substrates included PET (polyethylene terephthalate), PUR (polyurethane) and PS (polystyrene). The reaction was irradiated under 1 sun for 24 hours (100 mW cm⁻², AM1.5G, 25°C).

The results are shown in Figure 10.

Carbon Dots

Synthesis of CDs

CDs were prepared as previously described by Martindale *et al. Angew. Chemie Int. Ed.* **2017**, or as described below, from biomass organic precursors.

Pyrolysis of organic precursors under air to form CDs was optimized for high photocatalytic activity by varying the calcination temperatures and times (data for thermogravimetric analysis, TGA, and photocatalytic screening not shown). All organic precursors were calcinated in muffle Carbolite furnaces for 4 days under air, at optimum temperatures, to obtain CDs with good photocatalytic properties.

Namely, α -cellulose and cotton wool were treated thermally at 320°C, xylan at 250°C, lignin at 300°C, cotton pads and T-shirt at 340°C, *G. Nivalis*, *G. Elliptica* and *T. Baccata* at 230°C, *Elaeagnus X ebbingei* at 275°C and olive leaves at 250°C. The samples after carbonization, were used in their crude form for all types of characterization, without any further treatment.

Cotton contains mainly cellulose (≤ 93 –97%) with the remaining part consisting mostly of hemicellulose ($\leq 7\%$) (Chen; Zhu *et al.*). It was therefore an excellent carbon source for this purpose, and cotton-derived CDs were prepared from four-day pyrolysis of commercial cotton wool, pads and recyclable cotton fabric (T-shirt) at 320, 340 and 340°C, respectively.

CDs from cotton resources have been prepared previously for ion detection, imaging, patterning and sensing applications (Wen *et al.*; Wang *et al.* and Alves *et al.*), either by hydrothermal or strong-acid mediated approaches. However, the synthesis of such materials with great potential in photocatalysis, via facile and simple calcination approaches, is unprecedented.

To demonstrate the potential of various biomass sources for CDs synthesis, inedible plant waste was also used as precursors. The species selected are in great abundance in various climates, have no special growth requirements, and can be obtained at no cost when the plants complete their life-cycle and/or from tree trimming. More specifically, pruning of the olive trees worldwide, results in 25 kg of waste/tree annually (Herrero *et al.*; Peralbo-Molina *et al.*; Abaza *et al.*).

The optimal conditions for CD synthesis from crude biomass depends on the relative content of the samples in α -cellulose, xylan and lignin as well as their morphology (George *et al.*; Zhang *et al.*). The TGA traces of the plants show three main bands: xylan degrades first at 210–300°C, followed by α -cellulose (300–350°C), and lignin as a shoulder at higher temperatures (380–430°C) (Carrier *et al.*; Biagini *et al.*; Barneto *et al.*). Olive leaves show additional bands between 460 and 490°C, possibly due to the presence of other polyphenols in the sample (Abaza *et al.*).

Deconvolution of the xylan, cellulose and lignin bands in the TGA plots allowed to determine the relative fractional areas (RFAs) for each component (cellulose, lignin and xylan; (Table 16). The calcination temperature of the sample was optimized below the decomposition temperature of the dominating component, and CDs with the best

photocatalytic activity were obtained upon the following heat treatment; 230°C for *G. Nivalis*, *G. Elliptica* and *T. Baccata*, 275°C for *Elaeagnus X. ebbingei* and 290°C for olive leaves. Calcination resulted in color change to black and shrinkage for all leaves, but the overall macroscopic morphology remained unchanged (images not shown).

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Table 16 - Decomposition Temperatures and Relative Fractional Areas (RFAs) of xylan, α -cellulose and lignin in crude biomass samples as determined by TGA

Precursor	Xylan		Cellulose		Lignin	
	$T_{\max}$ (°C)	RFA _x ¹	$T_{\max}$ (°C)	RFA _c ¹	$T_{\max}$ (°C)	RFA _l ¹
<i>G. Nivalis</i>	209.6	0.21	317.7	0.55	434.0	0.23
<i>Cyprus Olive Tree</i>	268.1	0.30	332.4	0.43	402.8	0.27
<i>G. Elliptica</i>	240.4	0.34	303.0	0.31	412.4	0.35
<i>T. Baccata</i>	233.7	0.41	308.5	0.14	381.3	0.45
<i>ElaeagnusX. ebbingei</i>	299.3	0.56	344.4	0.14	413.5	0.30

10 ¹ Relative Fractional Area; Ratio of the area of a single component divided by the overall areas of all components; RFA_x= $A_x / (A_x + A_c + A_l)$; RFA_c= $A_c / (A_x + A_c + A_l)$; RFA_l= $A_l / (A_x + A_c + A_l)$ (x: xylan, c: α -cellulose, l: lignin).

Analysis and Characterisation of CDs

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All CDs were characterized by X-ray photoelectron spectroscopy (XPS) upon drop casting the CD aqueous solutions on clean fluorine-doped indium tin oxide (FTO)-coated glass slides, at RT, under atmospheric pressure. The spectra were collected at NEXUS (Newcastle University, UK). Analysis was performed using a K-Alpha (Thermo Scientific, East Grinstead, UK) spectrometer utilizing a monochromatic Al K α X-ray source (1486.6 eV, 400 μ m spot size, 36 W). High resolution (HR) spectra were collected at a pass energy of 40 eV with 10 sweeps. Measurements were taken at 3 points on each sample surface. The data were processed using CasaXPS.

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25 Fourier Transform Infrared (ATR-FTIR) spectra were recorded on a ThermoScientific Nicolet iS50 FTIR spectrometer, in the range of 400 to 4000 cm⁻¹ and analyzed using the Omnic software. Raman measurements were carried out on a Horiba LabRAM HR Evolution microscope using a 473 nm laser.

30 ¹H and ¹³C NMR spectra for all CD samples were measured using a 400 MHz Bruker NMR spectrometer in D₂O.

The optical properties of the CDs were investigated with a Varian Cary 50 UV/vis spectrophotometer, in the wavelength range between 250 and 850 nm (in water), using quartz cuvettes with 1 cm pathlength. The X-ray diffraction (XRD) patterns for all materials were recorded with a PANalytical BV X'Pert PRO, at a scan rate of 0.9 min⁻¹.

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The Transmission electron microscopy (TEM) images of the carbonaceous materials were obtained on a JEOL 200-CX instrument operating at 120 kV. For this purpose, a droplet from the aqueous solutions of the samples, was placed on a carbon-coated holey grid and dried under atmospheric pressure.

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Thermogravimetric analysis (TGA) measurements, were performed with a Mettler Toledo TGA analyzer, under a nitrogen atmosphere, at a scan rate of 10°C/min and in the temperature range from 50 to 800°C.

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XPS confirmed that the carbonaceous photoabsorbers synthesized from pure biomass components contain predominantly C and O species. In particular, the high-resolution (HR) C 1s XPS spectrum of α -cellulose CDs displays peaks at 284.8 eV, 286.3 and 288.5 eV (Figure 3(a), top), which correspond to C=C, C–O (alkoxy and epoxy) (Yang *et al.*; Qin *et al.*) and C=O groups, respectively (Martindale *et al. Angew. Chem. Int. Ed.* **2017**; Oza *et al.*; Young Park *et al.*; Roy *et al.*). This suggests nanoparticles with a graphitic sp² core structure, decorated with alkoxy, epoxy, and carboxyl functionalities. Carboxylates (531.8 eV, 89.5 %) are the predominant surface functionalities, which coexist with C–O groups (534.1 eV, 10.5 %) but to a less extent, as indicated by their relative area ratio in the HR O 1s spectrum (data not shown).

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Xylan and lignin-derived carbonaceous materials show a significantly higher surface coverage by alkoxy/epoxy groups (532.6-532.7 eV, 63-65%) compared to carboxylates (531.3 eV, 29-37%). (Qin *et al.*; Yang *et al.*; Qu *et al.*).

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Elemental analysis showed that CDs produced from real biomass samples contained significant amounts of N, with C/N ratios varying between 5.5 to 11.1. XPS analysis of CDs from *G. Nivalis*, *T. Baccata* and *Elaeagnus X. Ebbingei*, showed mainly graphitic N-containing CDs with a pyrrolic (N-5, 399.3 eV) and graphitic quaternary N (N-Q, 400.2 eV) content (Zhang *et al.*; Li *et al.*) (Figure 3(a), bottom). *G. Elliptica*-derived CDs displayed pyridinic (N-6, 398.7 eV) functionalities in addition to graphitic N-Q. The C 1s and O 1s environments are similar for CDs from pure and real biomass precursors. All samples show bands assigned to C=C (284.7-284.8 eV), C–O (Gupta *et al.*) and C=O groups (287.9-288.5 eV). The CDs are surface-covered by C=O groups (531.3-531.7 eV) and C–O (532.8-533eV) moieties, which provide good water solubility to the nanoparticles. The carboxylate content is 67, 64, 61 and 46% for *G. Elliptica*, *G. Nivalis*, *T. Baccata* and for *Elaeagnus X. ebbingei*, respectively.

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FTIR spectroscopy (data not shown) of the CDs confirms the coexistence of C=O, C–OH and O–H functionalities at the CD surface ($\nu = 1319, 1380, 1560$ and $3000\text{--}3500\text{ cm}^{-1}$) with skeletal vibrations from the graphitic core tentatively assigned at 1611 cm^{-1} (Martindale *et al. J. Am. Chem. Soc.* **2015**; Martindale *et al. Angew. Chem. Int. Ed.* **2017**; Roy *et al.*; Mondal *et al.*; Yang *et al.*).

TEM images show that CDs synthesized from α -cellulose and *G. Nivalis* are highly graphitic with an average diameter of 9.4 and 7 nm, respectively (Figure 3(b)). The lattice fringes allow for the assignments of the (100) intralayer spacings ($3.0\text{ \AA}$ for α -cellulose and $2.7\text{ \AA}$ for *G. Nivalis* CDs), which is larger than for graphite ($2.4\text{ \AA}$) (Martindale *et al. Angew. Chem. Int. Ed.* **2017**; Qu *et al.*; Qu *et al.*). CDs derived from *G. Elliptica* and lignin are relatively large colloids with a diameter of 96 and 115 nm, respectively (data not shown).

Raman spectroscopy supports highly graphitic nanostructures for α -cellulose and *G. Nivalis*-derived CDs. Specifically, the D (1579.3 cm^{-1} , defective sp^2 carbon) to G (1320.7 cm^{-1} , intact sp^2 carbon) band intensity ratio (I_D/I_G) for both α -cellulose and *G. Nivalis* CDs is about 0.18 (Figure 3(c)) (Ferrari; Pimenta *et al.*). This value is far lower than what reported previously for other graphitic CD systems (≥ 0.75) (Martindale *et al. Angew. Chem. Int. Ed.* **2017**; Qin *et al.*; Roy *et al.*; Wang *et al.*). The I_D/I_G ratios of our biomass-derived CDs suggests low-defect crystalline structures (Yang *et al.*; Yang *et al.*). *T. Baccata* and *Elaeagnus X. ebbingei* displays I_D/I_G ratios of 0.35 and 0.56, respectively, indicating more defective graphitic structures. The Raman results are in good agreement with XPS analysis, which shows sp^3/sp^2 C ratios of 0.3 and 0.5 for α -cellulose and *G. Nivalis*-derived CDs, respectively, and sp^3/sp^2 C > 0.6 for the other CD samples.

NMR studies confirm predominant sp^2 (C=C, C=N) core environments for the CDs from α -cellulose and *G. Nivalis* (data not shown) with peaks between 120–140 ppm and 7–8 ppm in ^{13}C and ^1H NMR spectra, respectively (Martindale *et al. Angew. Chem. Int. Ed.* **2017**; Gao *et al.*; Yu *et al.*). ^{13}C NMR spectra further show peaks in the 175 to 180 ppm range for surface carboxylates, whereas the absence of signals between 8 and 80 ppm, suggests limited sp^3 character for these CDs, in agreement with the Raman measurements. The other CDs exhibit significantly higher sp^3 character than α -cellulose and *G. Nivalis* CDs.

XRD patterns of CDs indicate variations in the (002) interlayer spacing of the graphitic structures. α -Cellulose CDs show an interlayer spacing of $3.8\text{ \AA}$ ($23^\circ 2\theta$), which deviates from that of pure graphite ($3.3\text{ \AA}$), and suggest material with turbostratic disorder (data not shown) (Bourlinos *et al.*; Zhang *et al.*; Mewada *et al.*).

CDs from *G. Nivalis* show an interlayer spacing closer to that of graphite ($3.5\text{ \AA}$; $25.3^\circ 2\theta$), which is similar to that obtained for the other CDs produce from real biomass (data not shown).

UV-vis absorption spectra (Figure 3(d)) of all CDs show a predominant absorption in the UV region with a featureless tail extending into the visible spectrum (Baker *et al.*). These properties are assigned to π - π^* (C=C, core) and n- π^* (C=O, surface) transitions of the carbonaceous structures (Yang *et al.*). Increased graphitic character results in enhanced absorption, as indicated by the stronger absorption profiles of α -cellulose and *G. Nivalis* CDs, compared to *G. Elliptica*, *T. Baccata*, olive leaf and *Elaeagnus X. ebbingei*-derived CDs. Moreover, CDs from waste biomass, presumably due to N-doping/graphitic N-centres (N-Q), (Figure 3(a), bottom), exhibit a stronger absorption in the visible spectrum compared to α -cellulose CDs. It had been shown that graphitic N centers are associated with electron doping that causes a decrease in the magnitude of the electronic gap (Sarkar *et al.*).

Photocatalytic Experiments

The samples for photocatalytic experiments were prepared in borosilicate glass vials (7.74 mL), by first dissolving 0.03-2.8 mg of the as calcinated α -cellulose CDs and 50 nmol of the hydrogen evolution catalyst (NiP), in aqueous EDTA solutions (0.1 M, 3 mL, pH 6). Next, the vessels were sealed with rubber septa (Subaseal), purged with N₂ containing 2 % CH₄ (internal gas chromatography (GC) standard) for about 20 mins, and irradiated using a Newport Oriel Solar Light Simulator (100 mW cm⁻²) equipped with an Air Mass (AM) 1.5G filter. The samples were kept at 25°C and stirred constantly during irradiation.

Samples of the headspace gas (20 μ L) were taken from the photoreactor and analyzed by gas chromatography (GC) as described above.

The photocatalytic performances of the rest CDs synthesized in this study, were evaluated as described above, upon dissolving 2.2 mg of the as calcinated CDs along with NiP (50 nmol) in EDTA solutions (0.1 M). For the investigation of the photocatalytic activities of the CDs in sea, river and sewage water, the aqueous phases were first passed through a 0.20 μ m filter, to remove any solids and/or microorganisms prior the addition of EDTA and photocatalytic experiments.

Photocatalytic experiments in purified water in the presence of organic pollutants (200 μ mol) and chloride ions (3.2 wt %), were carried out by dissolving 2.2. mg of α -cellulose CDs in phosphate solution (KPi, 0.1 M, pH 6, 3 mL), in the absence of EDTA and in the presence of 50 nmol NiP.

Use of CDs

Photocatalytic biomass reformation into H₂ was also studied using a carbon-based alternative to carbon nitrides, namely carbon nanodots. Carbon nanodots can be cheaply prepared from abundant organic precursors on a large scale (see the review Hutton *et al. Chem. Soc. Rev.* **2017**). The use of these known CDs is described below.

Carbon nanodots were also prepared from biomass organic precursors, and the use of these CDs is also described below.

Photocatalysis - Known CDs

Undoped and amorphous (undoped, a-CDs) and nitrogen-doped and graphitic (N-doped, g-CDs) carbon nanodots in combination with NiP as the H₂ evolution catalyst are active for photoreforming α -cellulose into H₂ under benign conditions (0.1 M KPi, pH 6, 3 mL) (see Table 17).

The CDs used in this work, which include an α -CD (amorphous CD) and a nitrogen-doped CD (g-N-CD; graphitic nitrogen-doped CD), were prepared as described Martindale *et al. Angew. Chemie Int. Ed.* **2017**. The experimental methods for the preparation of these CD photocatalysts are described on pages S1 to S5 of the *Supporting Text* for this reference.

Additionally, CDs were prepared from α -cellulose (α -cell CDs) and these were also used as photocatalysts to degrade α -cellulose and glucose.

Table 17 - H₂ Production with CDs

Entry	CD type	CD amount / mg	Substrate	H ₂ / μ mol (24 h)	$\pm \sigma$ / μ mol
	α -CDs	10	α -cellulose	0.52	0.12
	N-doped CDs	0.5	α -cellulose	1.96	0.40
	α -cell CD	2.2	α -cellulose	4.06	0.98
	α -cell CD	2.2	glucose	6.39	0.64

* Solar light driven (AM 1.5G, 100 mW cm⁻², 25°C) H₂ production using a variety of CDs and NiP (50 nmol) in the presence of lignocellulosic substrates (100 mg) in KPi (0.1 M, pH 6, 3 mL).

Photocatalysis - CDs in Pure Water

CDs prepared from purified and waste biomass were used as photoabsorbers to drive H₂ evolution. Photocatalytic experiments were carried out for 24 hrs, using NiP (50 nmol) as

the H₂ evolution catalysts and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA 0.1 M, pH 6) as the electron donor. All experiments were carried out as described above.

- 5 The quantity of CDs was systematically varied between 0.03 and 2.8 mg (Figure 6) during photocatalytic experiments and optimized for maximum H₂ yield (in μmol), from which the specific activities ($\mu\text{mol H}_2 (\text{g}_{\text{CDs}})^{-1} \text{ h}^{-1}$) and NiP turnovers ($\text{TON}_{\text{NiP}}, \text{mol H}_2 (\text{mol NiP})^{-1}$) were determined.
- 10 α -Cellulose CDs (2.2 mg), after 24 hrs of irradiation, showed the best H₂ yield ($15.6 \pm 0.73 \mu\text{mol}$) and TON_{NiP} (312 ± 14.6) among all photoabsorbers synthesized from purified biomass components (Figure 4(a) and Figure 6). The highest specific activity of $13,450 \mu\text{mol H}_2 (\text{g}_{\text{CDs}})^{-1} \text{ h}^{-1}$, was achieved at 0.03 mg α -cellulose CDs (Figure 4(b)), which outperformed previously reported carbonaceous photocatalysts (CDs and carbon nitrides)
- 15 when combined with noble-metal free catalysts (Table 18) (Martindale *et al. J. Am. Chem. Soc.* **2015**; Hutton *et al.*; Martindale *et al. Angew. Chem. Int. Ed.* **2017**; Caputo *et al.*). These systems reach activities only up to $7,950 \mu\text{mol H}_2 (\text{g}_{\text{CDs}})^{-1} \text{ h}^{-1}$ when N-doped CDs are combined with NiP and EDTA.

Table 18 - Photocatalytic performances of noble-metal free carbonaceous photoabsorbers in water using sacrificial electron donors and molecular as well as noble-metal catalysts.

Entry	Photoabsorbers	Catalyst	ED	H ₂ (μmol)	Activity/ μmol g ⁻¹ h ⁻¹	TON _{cat}	QE/%	Ref.
Noble-metal free carbonaceous								
1	a-CD	NiP	EDTA	0.64	397	64	1.4	1
2	a-CD	NiP	TCEP/AA ^a	10.9	53	1094	n.d.	2
3	g-CD	NiP	EDTA	0.5	1,549	45	n.d.	3
4	g-N-CD	NiP	EDTA	2.8	7,950	277	5.2	3
5	CD(yeast)	Pt	TEOA ^b	n.d	31	n.d.	n.d.	4
6	NH ₂ CN _x	NiP	EDTA	3.32	437	166	0.4	5
7	NCN _x CN _x	NiP	4-MBA ^c	21.3	311	425	15.2	6
8	g-C ₃ N ₄	Pt	TEOA ^b	n.d.	20,000	641	26.5	7

^aTCEP = tris(carboxyethyl)phosphine; AA = ascorbic acid; ^bTEOA = triethanolamine; ^c4-MBA= 4-methylbenzyl alcohol

* NCN_xCN_x is a reference to a bulk sample that has not been ultrasonically treated.

Control experiments in the absence of CDs, NiP and EDTA, resulted in no H₂ generation, suggesting that α-cellulose CDs themselves are not catalytic for H⁺ reduction and do not serve as sacrificial electron donors via autooxidation (Figure 7).

- 5 Although CDs produced from α-cellulose have been reported for use in bioimaging (Shen *et al.*), this is the first example of CDs from a cellulosic precursor being employed in photocatalytic applications.

10 Photocatalytic H₂ generation with CDs synthesized from xylan and lignin in sacrificial EDTA solution, after 24 h of irradiation, showed lower activities than with α-cellulose CDs. Xylan- and lignin-derived photoabsorbers yielded 4.7 ± 0.34 and 0.5 ± 0.07 μmol H₂ after 24 hrs of irradiation (Figure 4(a)) and specific activities of 625 and 87 μmol H₂ (g_{CDs})⁻¹ h⁻¹, respectively (Figure 4(b)). CDs from xylan and lignin are limited and have been previously used only in
15 in energy production (Rai *et al.*; Chen *et al.*; Liang *et al.*).

The distinct photocatalytic activity of CDs produced from different biomass components is presumably associated with the distinct chemical composition, polymeric architecture and microstructure of the biopolymer. α-Cellulose is a linear and crystalline polymer (100,000 g
20 mol⁻¹) made of glucopyranose units, whereas xylan is an amorphous and branched polysaccharide (30,000 g mol⁻¹), made of sugars such as glucose, mannose, xylose and arabinose. Lignin is also amorphous and consists of randomly cross-linked phenolic monomers (p-coumaryl, coniferyl, and sinapyl alcohols) (Lee *et al.*). Our photocatalytic experiments suggest that pyrolysis of a crystalline homopolymer with regular microstructure
25 might support the formation of high-performance CD photocatalysts.

Cotton is predominantly made from α-cellulose with no lignin content (Kräsig *et al.*), and thus cotton wool-derived CDs showed indeed almost identical photocatalytic performance as α-cellulose CDs: 11.8 ± 0.29 μmol H₂ are photo-produced after 6 hrs of irradiation
30 (Figure 4(c)). The photocatalytic performances of CDs derived from cotton pads and a T-shirt, after 6 hrs of irradiation, do not exceed 4.86 ± 0.16 and 1.74 ± 0.17 μmol H₂, respectively (Figure 8). This discrepancy between photocatalytic properties of CDs prepared from α-cellulose precursors may be due to additives in the commercial materials (Rivero *et al.*; Barker *et al.*).

35 The photocatalytic performances of CDs obtained from real biomass samples, leaves of *G. Nivalis*, *G. Elliptica*, *T. Baccata*, *ElaeagnusX ebbingei* and “Cyprus olive tree”, were subsequently studied.

40 Photocatalytic experiments using the leave-derived CDs (Figure 4(c)), after 6 hrs of irradiation, reveal lower H₂ evolution activity than with α-cellulose CDs (11 ± 0.49 μmol H₂, Figure 4(a)), which can be explained by their composite nature (see below).

The best performances were observed for CDs from *G. Nivalis* and olive leaves, which over 6 hrs of irradiation, were driven the production of 6.15 ± 0.11 and 5.29 ± 0.27 $\mu\text{mol H}_2$ (Figure 5 and Table 19), respectively, which is consistent with their highest RFAs for α -cellulose, and lowest for xylan and lignin (data not shown). The H_2 evolution activity of CDs prepared from the other leaves, declined as the RFA of α -cellulose decreases. In particular, after 6 hrs of irradiation, CDs from *G. Elliptica* photo-generate 4.47 ± 0.03 $\mu\text{mol H}_2$, since the RFA of α -cellulose drops to 0.31, whereas that of xylan and lignin increase to 0.34 and 0.35, respectively (Table 19). The H_2 evolution capacities of CDs from *T. Baccata* and *Elaeagnus X. ebbingei* are even lower, and do not exceed the 3.50 ± 0.07 and 3.19 ± 0.15 $\mu\text{mol H}_2$, after 6 h of irradiation, respectively. For both samples, the RFA of α -cellulose decrease to its minimum (0.14) whereas that for lignin and xylan increase significantly (data not shown). The correlation between the RFAs of the components and the photocatalytic performances of the derived CDs gives therefore a qualitative predictor for photocatalytic efficiency (Table 19).

Table 19 - Experimentally and theoretically-determined H_2 evolution capacities of the photocatalytic systems, which use CDs from crude biomass as light-harvesters.

Sample	Photocatalytic Activity ($\mu\text{mol H}_2$)	
	Experimental ¹	Theoretical ²
<i>G. Nivalis</i>	8.74 ± 0.13	9.71
<i>Cyprus Olive Tree</i>	7.93 ± 0.97	8.17
<i>G. Elliptica</i>	6.49 ± 0.03	6.53
<i>T. Baccata</i>	4.70 ± 0.13	4.30
<i>ElaeagnusX. ebbingei</i>	3.94 ± 0.10	4.90

¹ Experimentally-determined H_2 evolution capacities (in μmol), as obtained from photocatalytic experiments using CDs from crude biomass

²Theoretically-determined H_2 evolution capacities, calculated by multiplying the RFA for each component (obtained by TGA) with the capacity of the respective pure constituent to produce H_2 after 24 hrs of irradiation (α -cellulose; 15.6 μmol , xylan; 4.7 μmol and lignin; 0.5 μmol , Figure 4(a)). The derived values for all components were then summed up, to result the overall activity for each plant species.

The results discussed above, suggest that the best photocatalytic performances are associated with CDs of smaller sizes and low-defect graphitic cores, which are bestowed mainly with carboxylates, whereas they contain C-O functionalities in less extend. N-doping

of the CDs from biomass waste, does not seem to have a significant effect in the photocatalytic activities.

Photocatalysis - CDs in Untreated Waste Water

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A major limitation in photocatalysis is the requirement of (i) pure water to avoid catalyst poisoning at high salinities and/or impurities (Li *et al.*), and (ii) an external, costly sacrificial reagent (Pellegrin *et al.*). Given the global shortage of clean water supplies (Service *et al.*), and challenges of water purification in many developing countries, we sought to establish the photocatalytic activity of our biomass-derived CDs in sea, river and sewage water, first in the presence and later absence of EDTA (Figure 5).

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Simulated solar irradiation of the α -cellulose CDs in untreated water for 6 hrs, in the presence of both EDTA and NiP, resulted in the production of 12.57 ± 0.17 and $12.61 \pm 0.58 \mu\text{mol H}_2$ in sea and river water (Figure 5(a)), respectively, which indicates a slight improvement in the photocatalytic performance of the systems in untreated water (14.4 - 14.7%), compared to pure water ($11 \pm 0.491 \mu\text{mol H}_2$, Figure 4(c)). However, under the same conditions, when sewage water was used as the reaction medium, after 6 hrs of irradiation, only $1.12 \pm 0.263 \mu\text{mol H}_2$ were photogenerated, suggesting the intolerance of the NiP catalyst to sewage impurities.

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On the other hand, the photocatalytic properties of α -cellulose CDs in untreated water, in the absence of EDTA but existence of NiP, deviate significantly than those in purified water under the same conditions; 2.85 ± 0.46 and $3.38 \pm 0.23 \mu\text{mol H}_2$ were photo-evolved over a period of 6 hrs in sea and river water (Figure 5(a)), respectively, compared to no H_2 evolution in purified water (Figure 7). This indicated the presence of additives in the untreated aqueous media which could serve as sacrificial electron donors to extract the photogenerated holes (Martindale *et al. Angew. Chem. Int. Ed.* **2017**). On the other hand, elimination of NiP in the presence of EDTA (Figure 9(a)), resulted in no H_2 production neither in pure or untreated water, suggesting that no species (i.e. metal traces) exist in sea, river and sewage water that could drive fuel formation.

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Untreated sea water (Gulf of Mexico) contains a cocktail of organic compounds (Nowell *et al.*), among which benzaldehyde and atrazine can potentially act as electron donors (Figure 9(b)) (Nowell *et al.*). Chloride anions that are abundantly present in seawater can also serve the same role (Iguchi *et al.*). Similarly, untreated river water (River Cam), is rich in organic herbicides/pesticides (River Cam), among which prometryn and terbutryn can quench the photogenerated holes (Figure 9(b)).

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To confirm this, an aqueous α -cellulose CD phosphate solution (KPi, 0.1 M, pH 6, 3 mL), in the absence of EDTA, was bestowed with these species (200 μmol), in the presence of NiP. After 6 hrs of full solar light irradiation (AM 1.5 G, 100 mW cm^{-2}), in the presence of the

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organic pollutants and Cl^- anions, the H_2 yields were in the range between 2.05 ± 0.20 and $4.99 \pm 0.15 \mu\text{mol}$ (Figure 5(b)), which are close to those recorded in the absence of any electron donor in untreated water media (Figure 5(a) and Figure 9(c)). As such, the unwanted toxic substances and/or the abundant Cl^- eliminate the need for additional chemicals to serve as electron donors, allowing simultaneously for fuel synthesis and water treatment. To the best of our knowledge, this is the first time that photogenerated CD holes drive the oxidation of water pollutants, a process that traditionally is catalyzed by reactive oxygen species (Xiao *et al.*).

Next, the photocatalytic performances of the photoabsorbers synthesized from biomass waste, were evaluated in sea (Figure 5(c)) and river water (Figure 5(d)), in the presence of EDTA and NiP. In sea water, after 24 hrs of irradiation, most of the CDs show higher photocatalytic performances (Figure 5(c)) than those measured in purified water under the same conditions (Figure 4(c) and 9(d)).

The only exception are the CDs from *Elaeagnus X ebbingei*, which within error, show the same performances in both pure and sea water. On the other hand, all systems show slightly lower performances in river compared to sea water, except for the CDs from *T. Baccata* and *Elaeagnus X Ebbingei*, which show slightly higher H_2 evolution yields in river water (Figure 5(d) and 9(d)).

These results suggest the robust character of our photocatalytic systems, which maintain their good photocatalytic properties, independently of the purity and origin of the aqueous phase. As such, the toxic water contaminants do not restrict the performances of the CDs by hindering photoabsorption and/or electron transfer, and more importantly do not poison the NiP molecular catalyst. The performances of the photocatalytic systems described herein, even in untreated water media, are believed to be the highest among all photocatalytic systems based on carbonaceous systems reported up-to-date (see Table 17).

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

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Claims:

1. A method for producing hydrogen, the method comprising the step of exposing a photocatalyst to visible and/or ultraviolet light in the presence of an organic substrate and a co-catalyst that is a hydrogen evolution catalyst, wherein the photocatalyst is a carbon-containing catalyst selected from a carbon nitride (CN_x) photocatalyst and a carbon dot (CD) photocatalyst.
2. A method for producing hydrogen, the method comprising the step of exposing a photocatalyst within untreated water to visible and/or ultraviolet light in the presence of a co-catalyst that is a hydrogen evolution catalyst, wherein the photocatalyst is a carbon-containing catalyst selected from a carbon nitride (CN_x) photocatalyst and a carbon dot (CD) photocatalyst.
3. The method of 1 or 2, wherein the catalyst is a carbon nitride photocatalyst.
4. The method of claim 3, wherein the catalyst is a ^{NCN}CN_x photocatalyst.
5. The method of claim 5, wherein the catalyst is a ^{NCN}CN_x photocatalyst having a surface area that is at least 60 m² g⁻¹, such as at least 90 m² g⁻¹.
6. The method of claim 1 or 2, wherein the catalyst is a carbon dot, which is optionally doped.
7. The method of claim 6, wherein the catalyst is a carbon dot, which is optionally doped, such as nitrogen doped, which catalyst is obtained or obtainable by calcination of an organic substrate, such as a biomass.
8. The method of claim 1, wherein the organic substrate is or contains a component having a molecular weight of 200 or more, such as 500 or more, such as 2 kDa or more.
9. The method of claim 1, wherein the organic substrate is selected from α-cellulose, xylan and lignin, such as α-cellulose.
10. The method of claim 1, wherein the organic substrate is a biomass.
11. The method of claim 10, wherein the biomass is selected from wood, paper, cardboard, bagasse, grass and/or sawdust.

12. The method of claim 1, wherein the organic substrate is selected from general waste, plastics, packing materials, waste food, aliphatic polyols, algae, sugars, starches, biomass, sewage and/or domestic waste.

5 13. The method of claim 2, wherein the untreated water is sea water.

14. The method of claim 2, wherein the untreated water is sewage, or river, lake, or canal water.

10 15. The method of claim 2, wherein the untreated water contains a sacrificial electron donor that is an organic compound, such as selected from atrazine, prometryn, terbutryn and benzaldehyde, or an inorganic species, such as chloride.

15 16. The method of claim 1 or claim 2, wherein the hydrogen evolution catalyst is selected from a Ni-, Pt- or Mo-containing hydrogen evolution catalyst.

17. A method of preparing $^{NCN}CN_x$, the method comprising the step of forming a bulk sample of $^{NCN}CN_x$ and subsequently treating the bulk $^{NCN}CN_x$ thereby to increase the surface area of the $^{NCN}CN_x$.

20

18. The method of claim 17, wherein the bulk $^{NCN}CN_x$ is sonicated, such as ultrasonicated, to increase its surface area.

25 19. A method of preparing a carbon dot, the method comprising the step of calcining an organic substrate comprising an oligosaccharide or a polysaccharide, such as calcining at a temperature in the range 250 to 450°C.

20. The method of claim 19, wherein the organic substrate is or comprises a polysaccharide.

30

Fig. 1

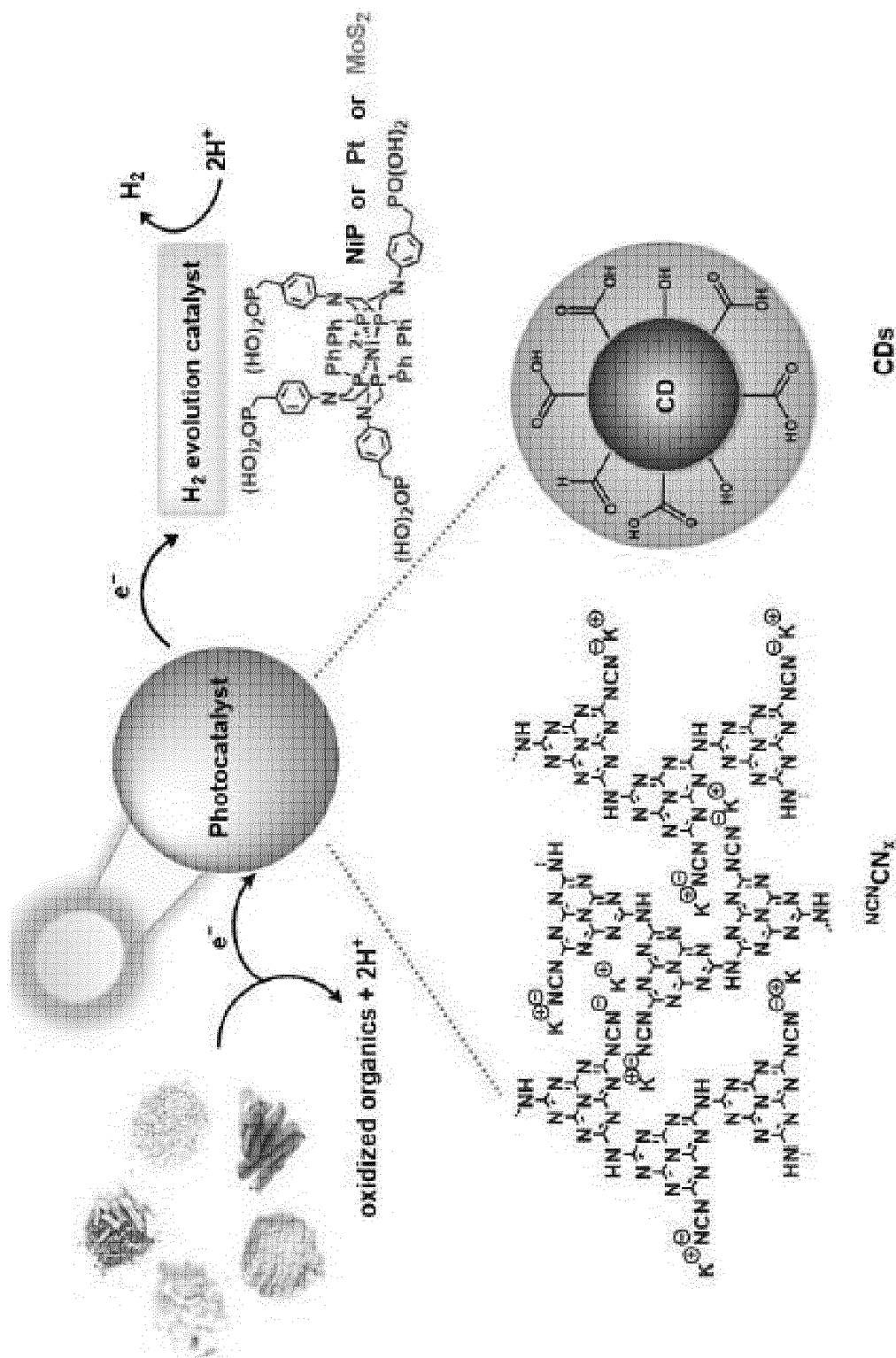
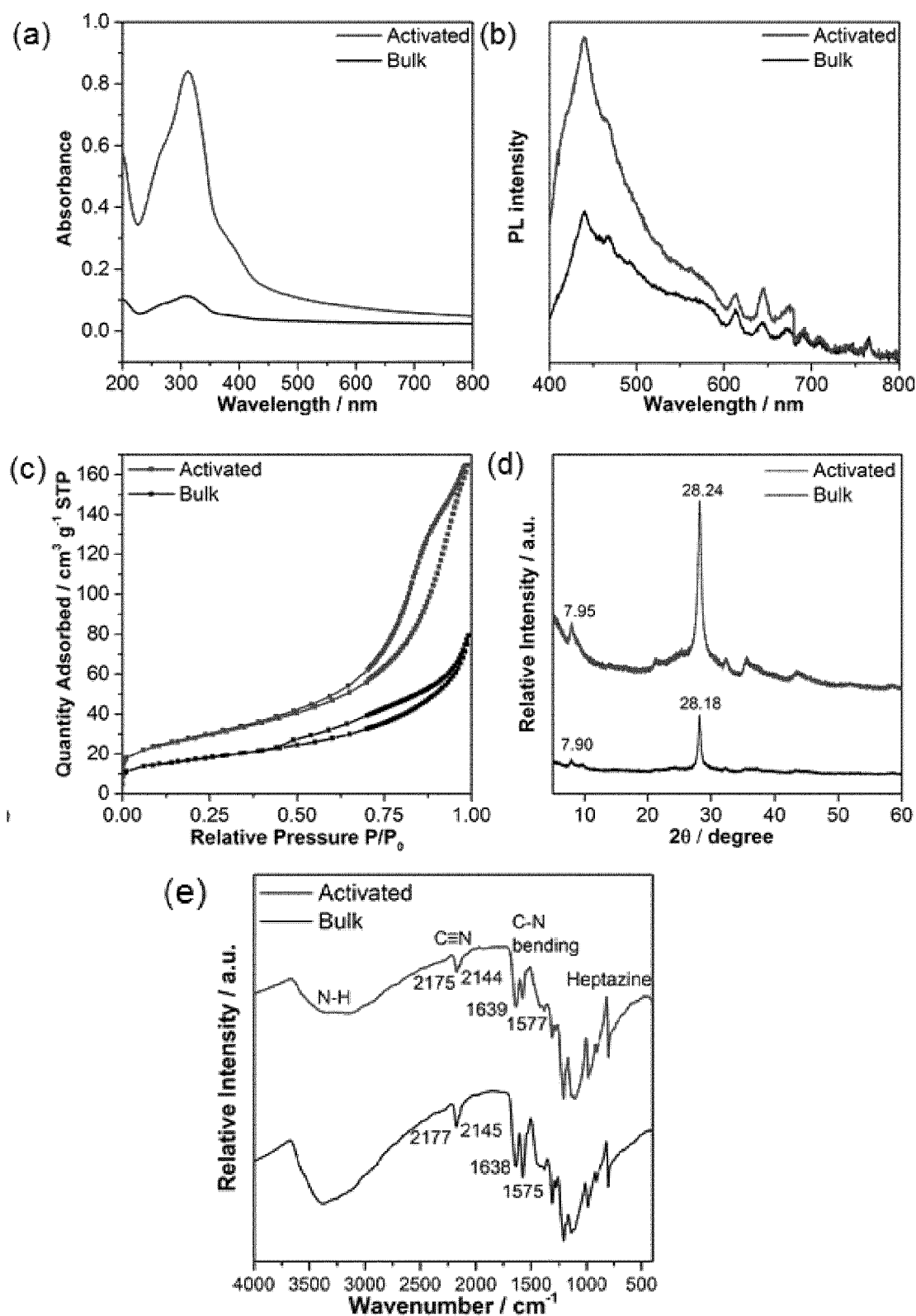


Fig. 2



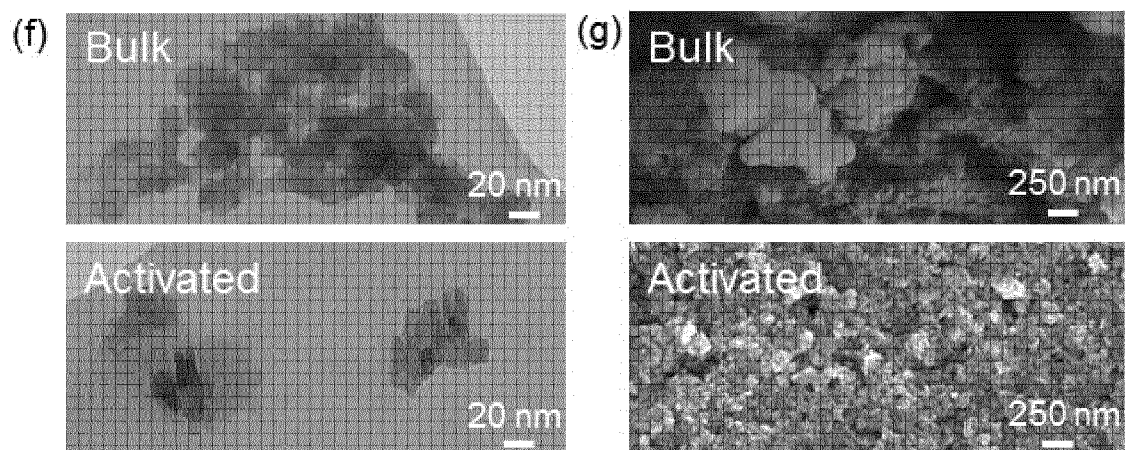
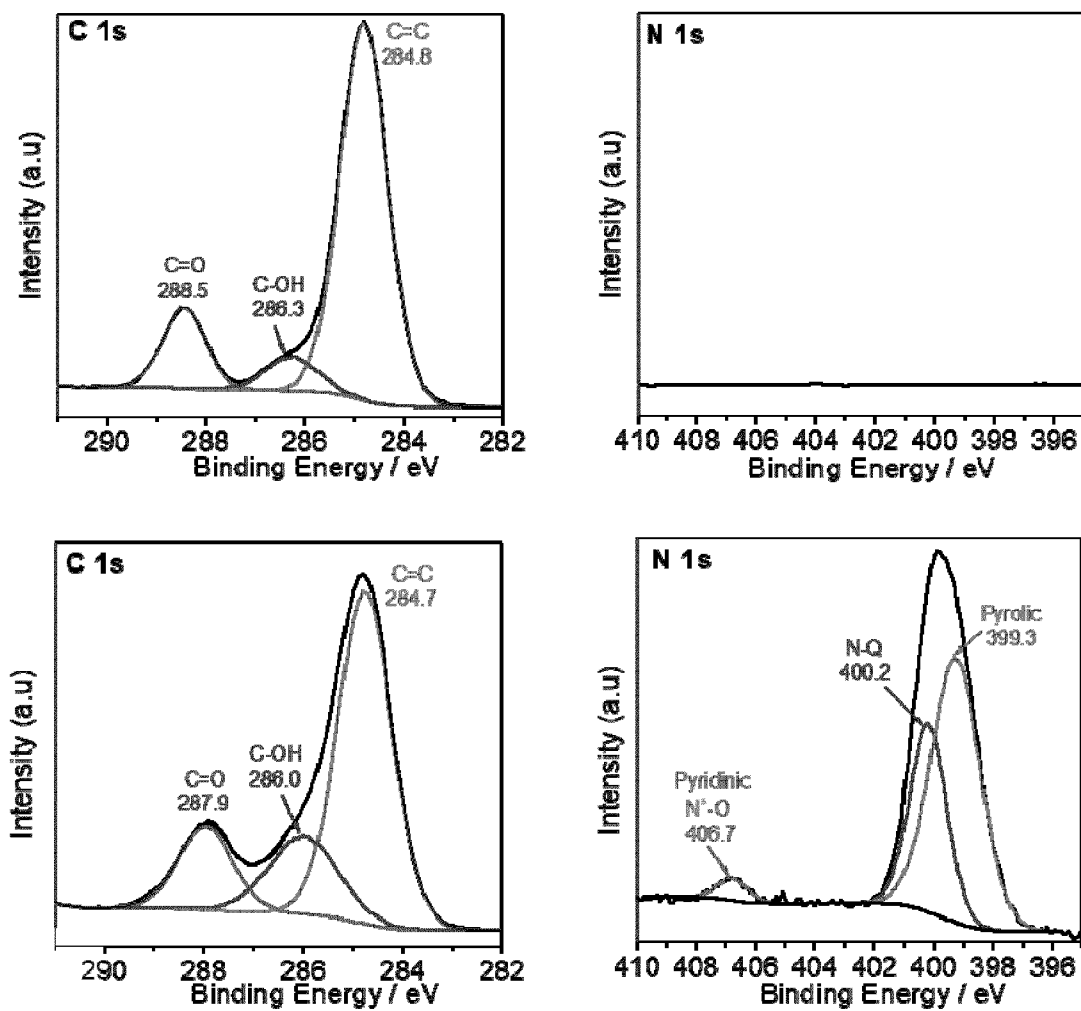
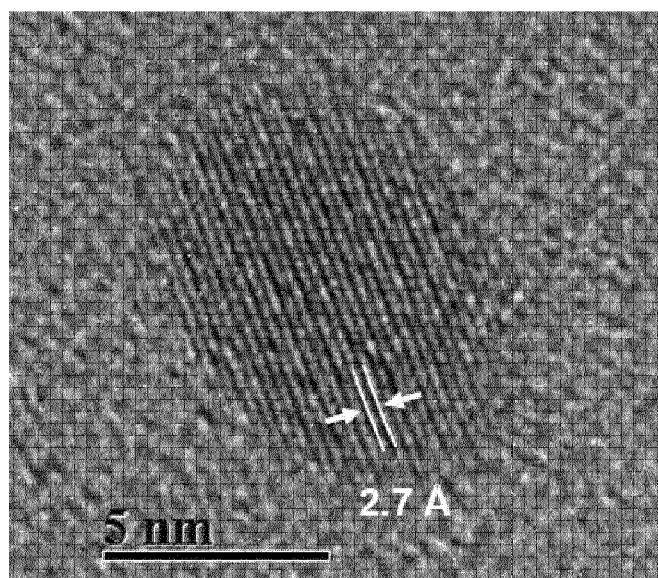
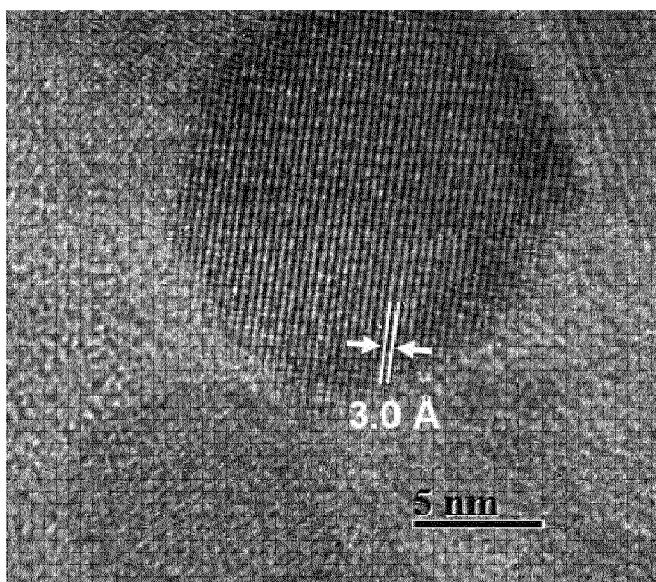


Fig. 3

(a)



(b)

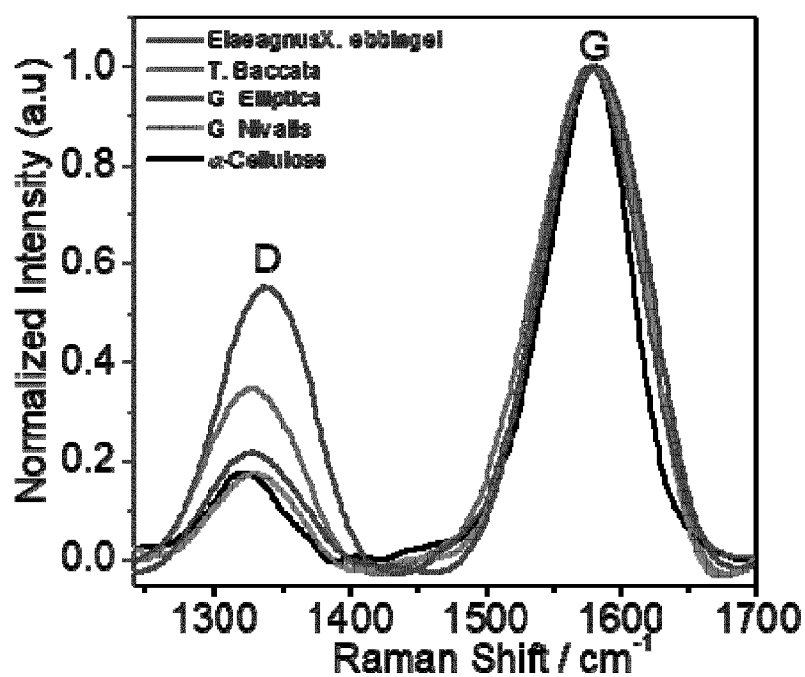
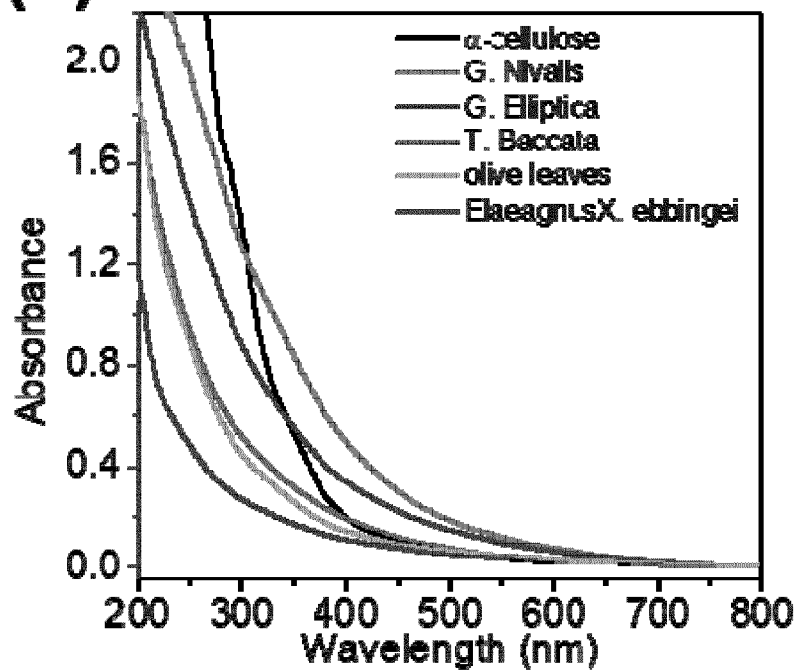
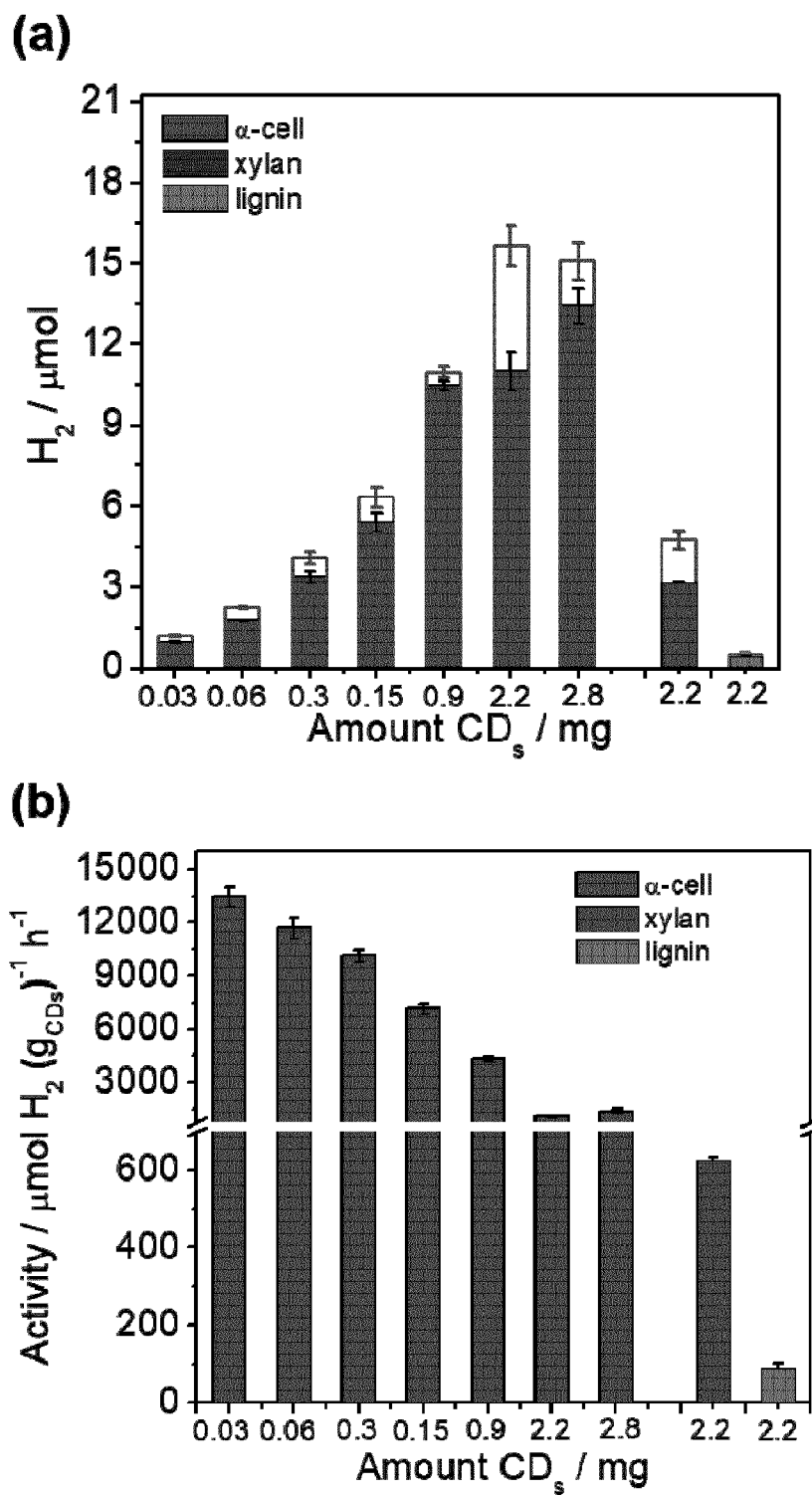
(c)**(d)**

Fig. 4



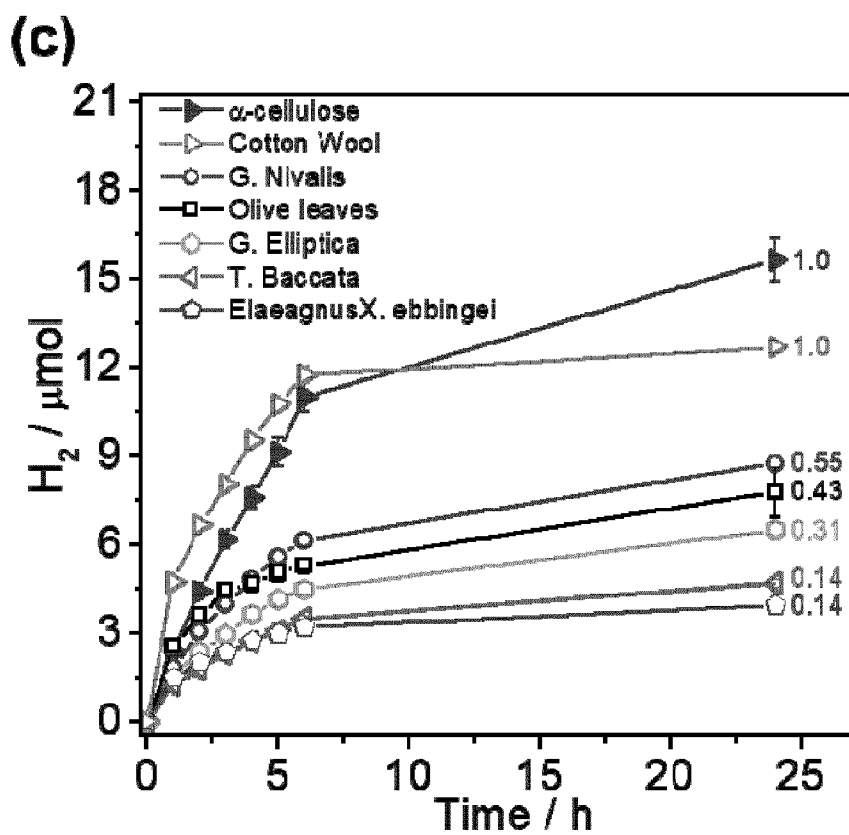
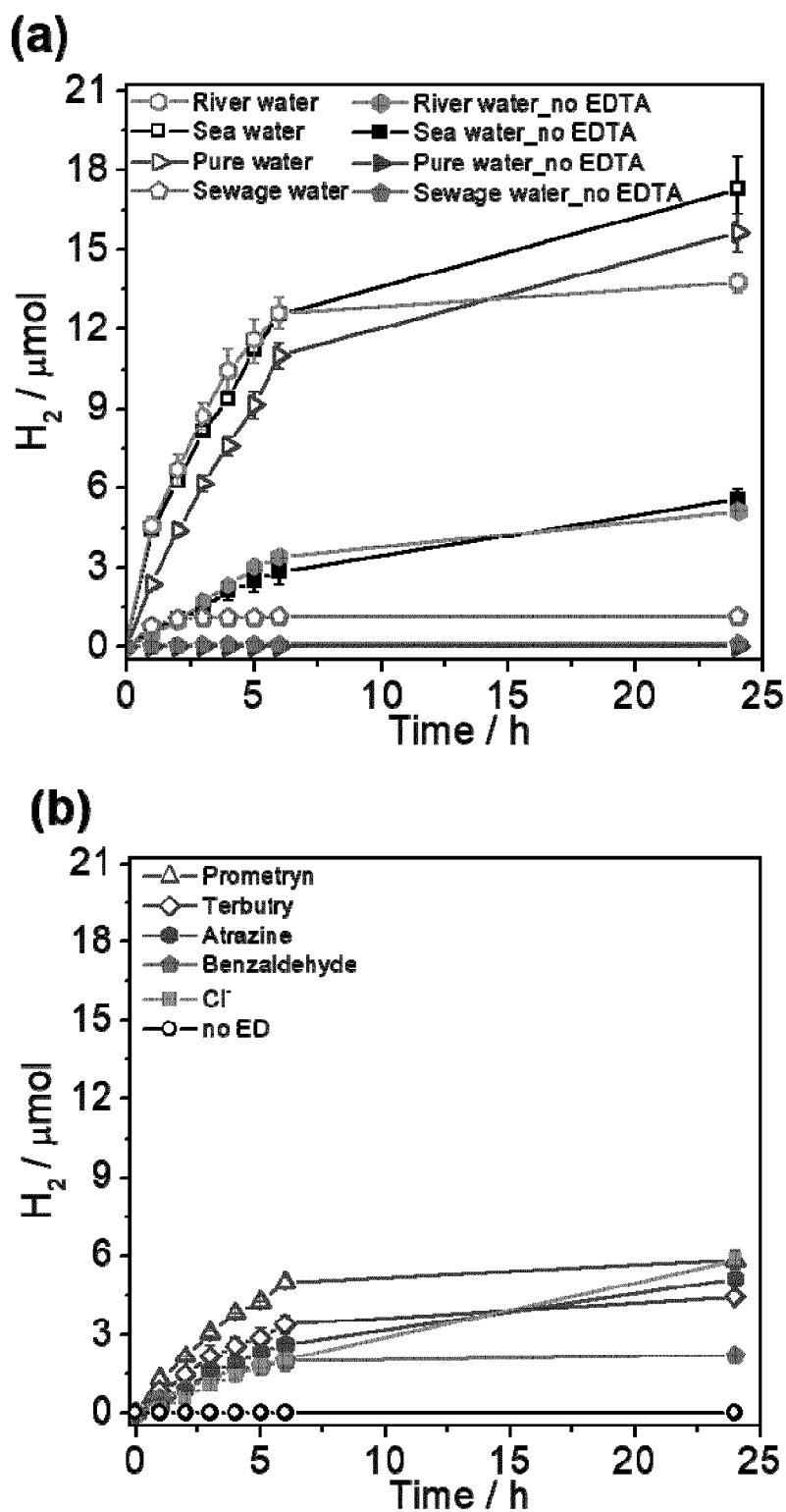


Fig. 5



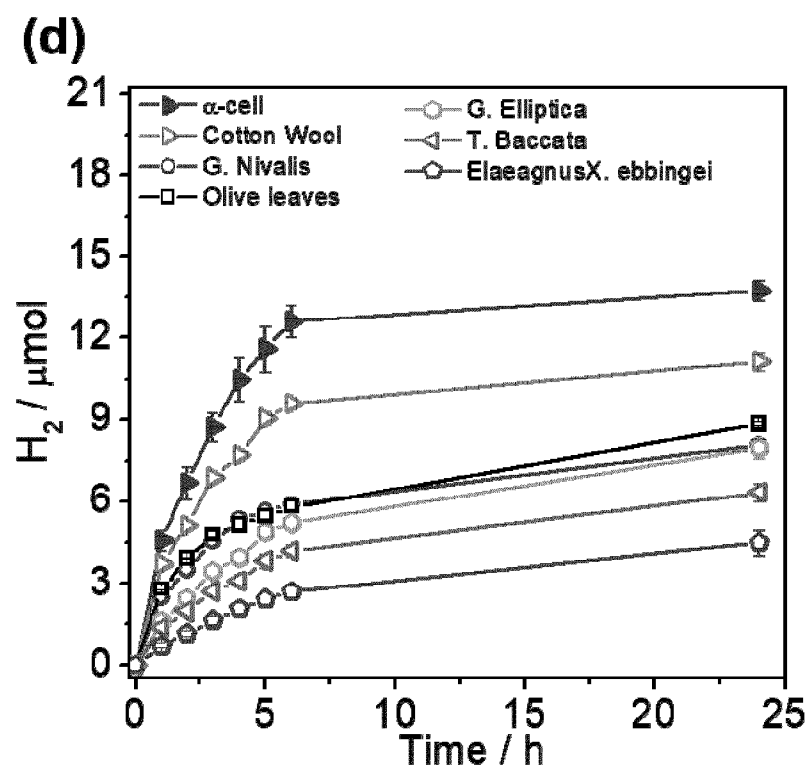
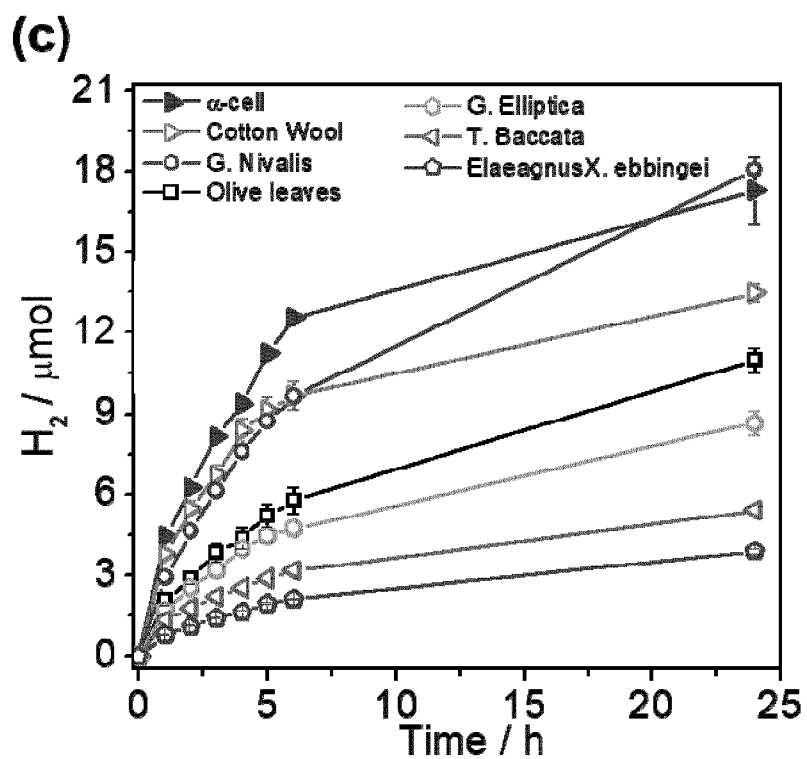


Fig. 6

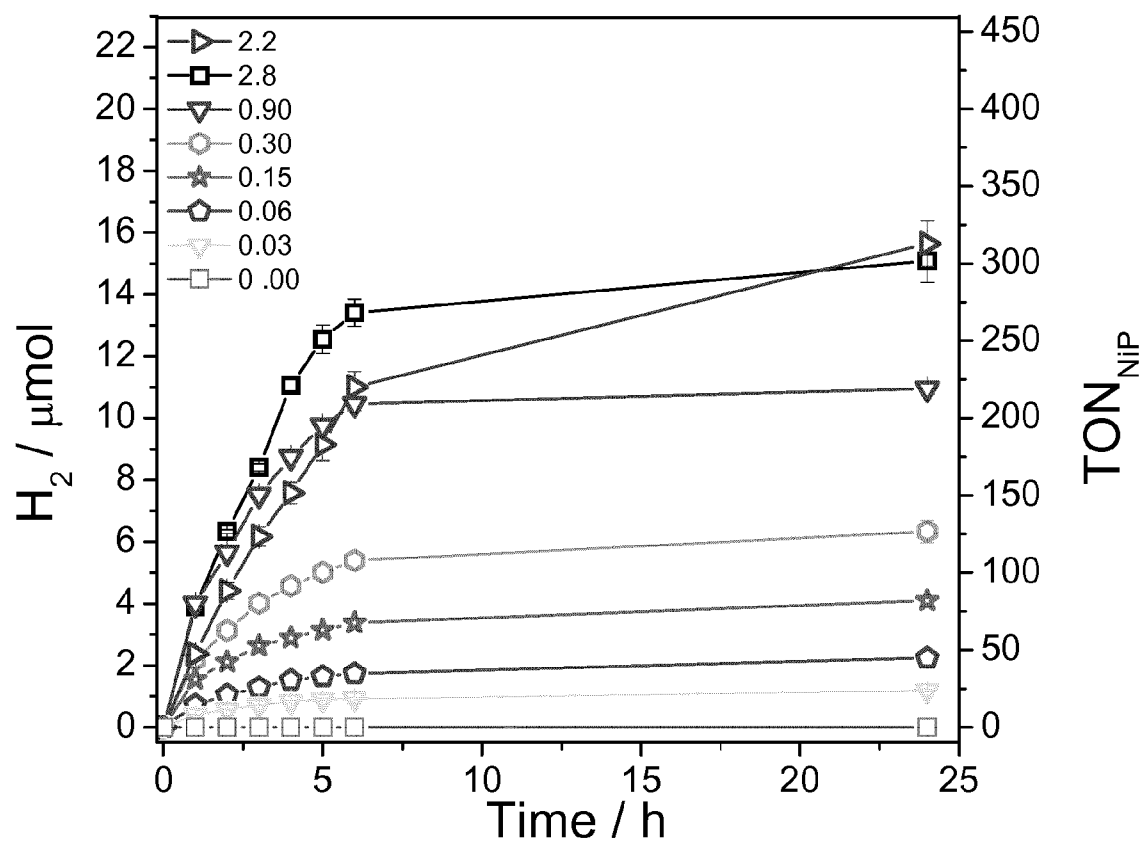


Fig. 7

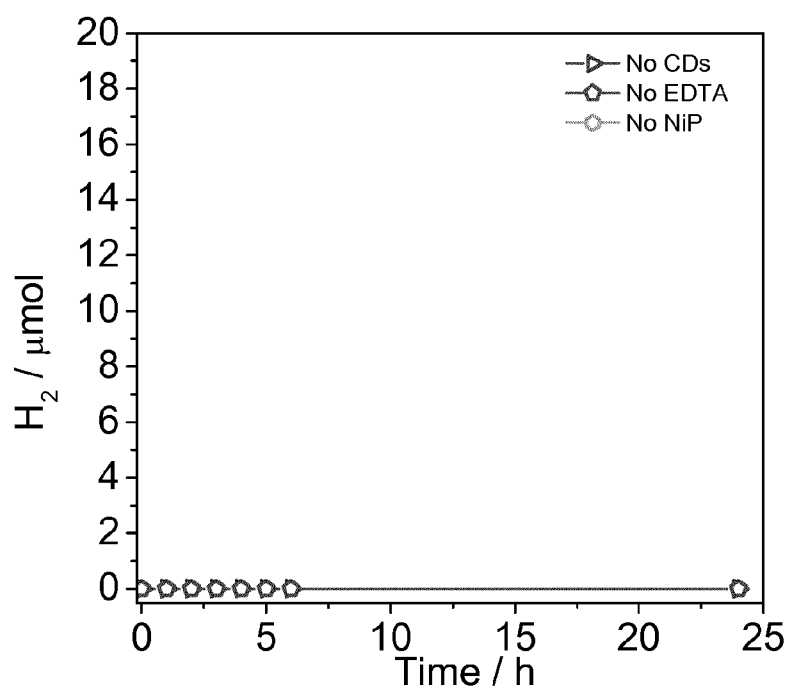


Fig. 8

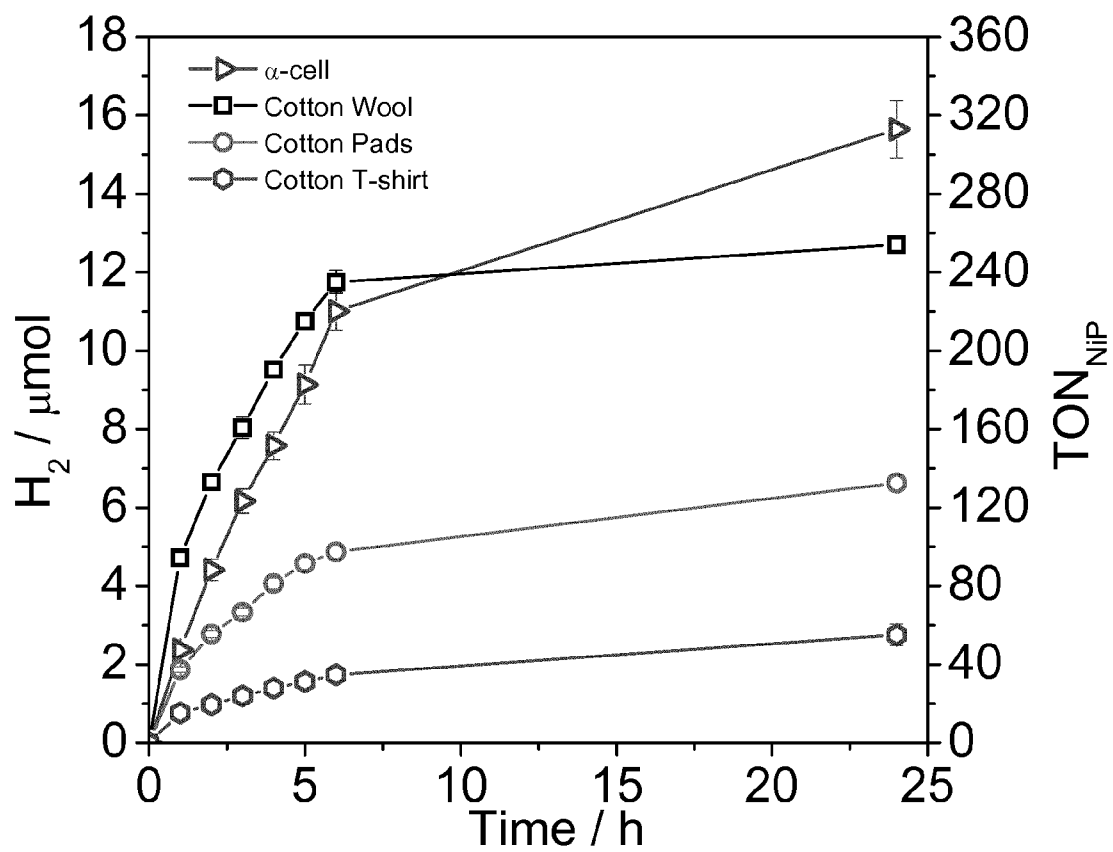
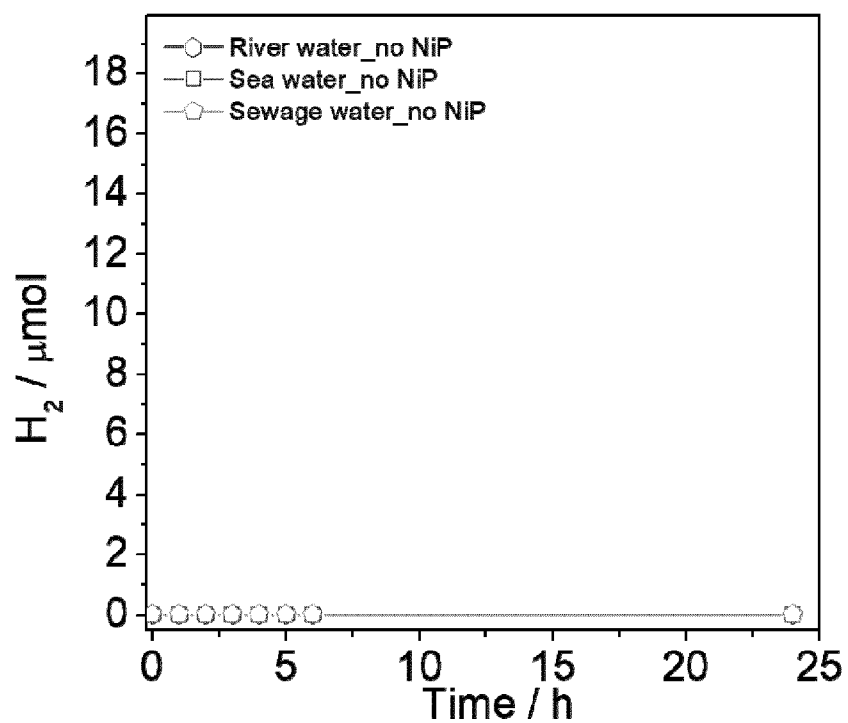
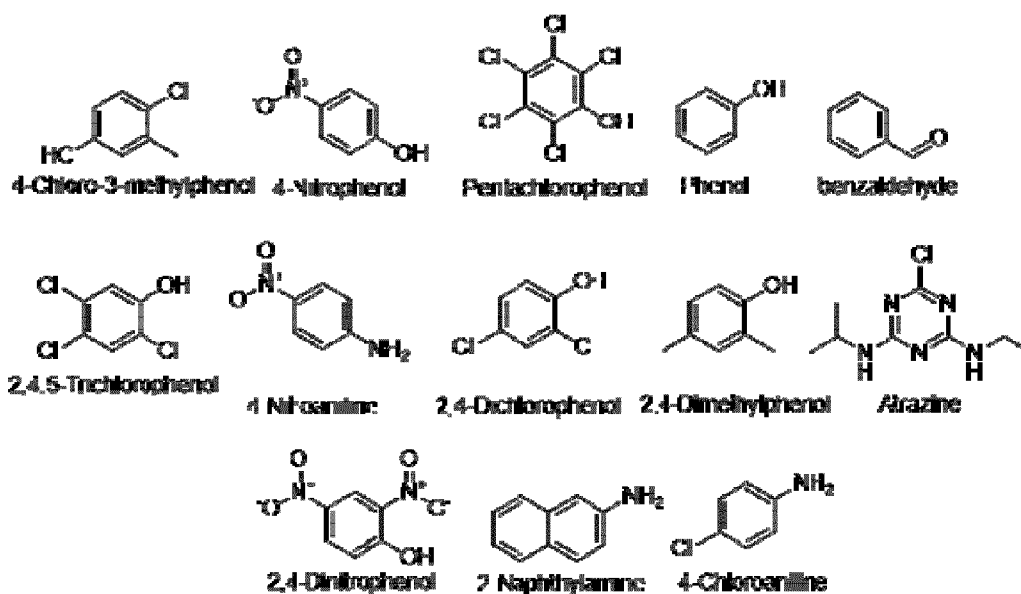
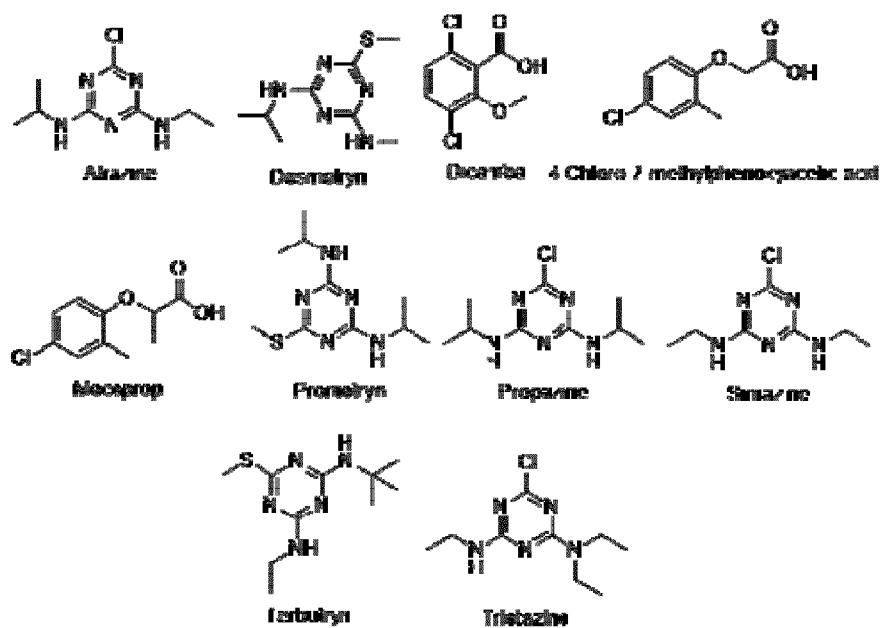
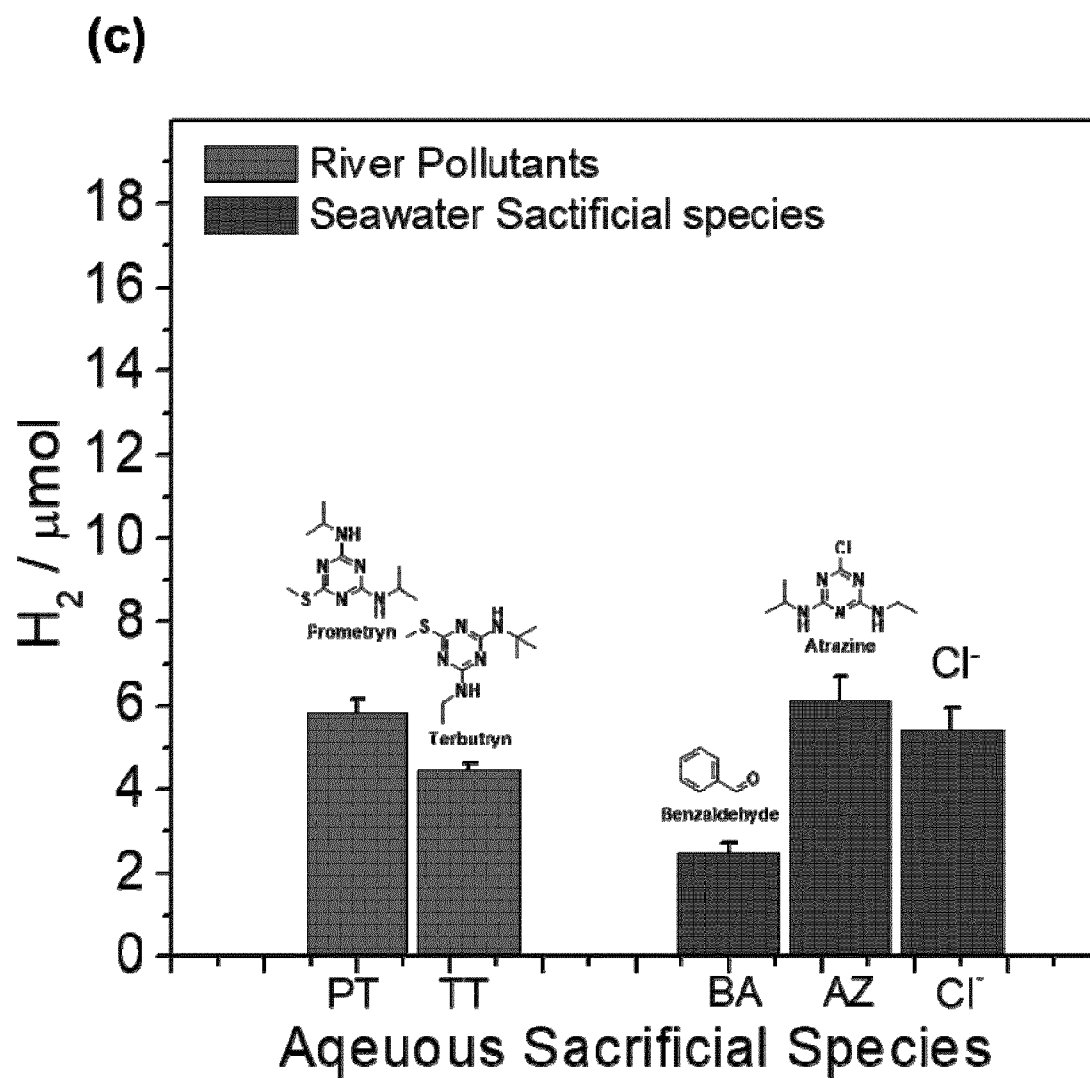


Fig. 9

(a)



(b)**Sea Water****River Water**



(d)

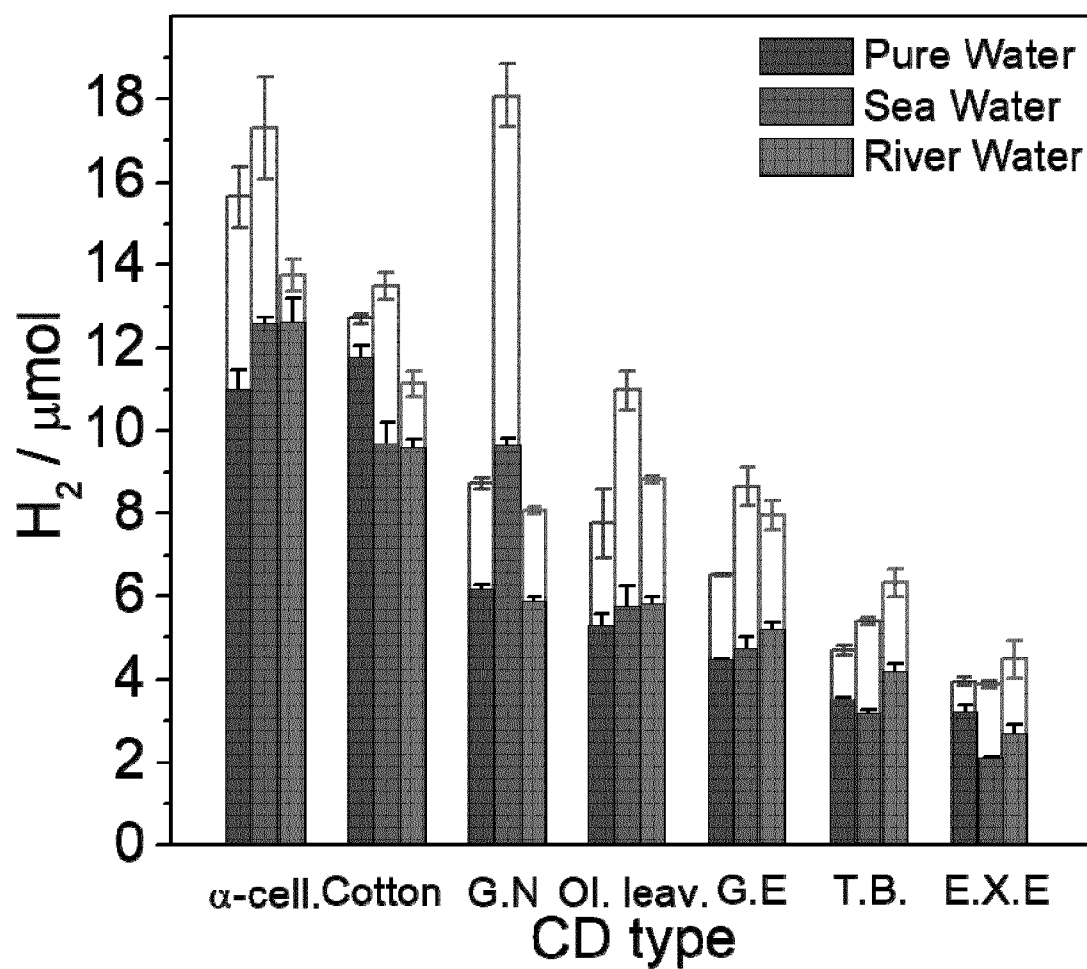
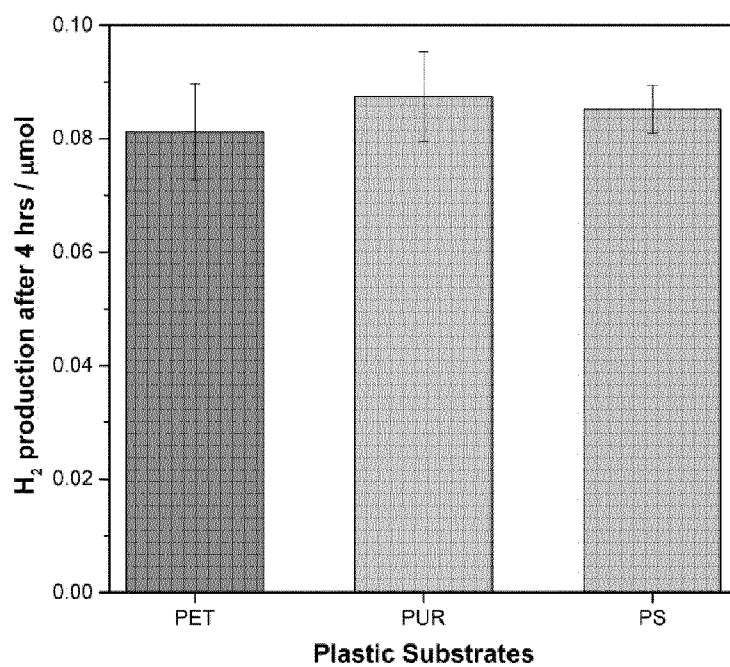


Fig. 10

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/064221

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C01B3/04 B01J27/24	C01B3/22 B01J35/00 B01J35/10 B01J21/18
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) C01B B01J		
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	HATICE KASAP ET AL: "Solar-Driven Reduction of Aqueous Protons Coupled to Selective Alcohol Oxidation with a Carbon Nitride-Molecular Ni Catalyst System", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 138, no. 29, 14 July 2016 (2016-07-14), pages 9183-9192, XP055622827, US	1-5, 16-18
A	ISSN: 0002-7863, DOI: 10.1021/jacs.6b04325 cited in the application page 9184, right-hand column, line 3 - line 16 "RESULT AND DISCUSSION - Preparation and Characterization of the Photosystem" "CONCLUSIONS" "EXPERIMENTAL SECTION - Photocatalytic Experiments" figures 2-4 -/--	6-15
☒ 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 "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "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 "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 "&" document member of the same patent family		
Date of the actual completion of the international search 18 September 2019		Date of mailing of the international search report 27/09/2019
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 Harf-Bapin, E

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/064221

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	----- BENJAMIN C. M. MARTINDALE ET AL: "Solar Hydrogen Production Using Carbon Quantum Dots and a Molecular Nickel Catalyst", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 137, no. 18, 28 April 2015 (2015-04-28), pages 6018-6025, XP055623012, US ISSN: 0002-7863, DOI: 10.1021/jacs.5b01650	1,2,6,7, 10,12-16
A	cited in the application page 6020, last paragraph figures 4-6 "CONCLUSIONS" "EXPERIMENTAL SECTION - Materials" "EXPERIMENTAL SECTION - Photocatalysis Experiments"	3-5,8,9, 11,20
X	----- BENJAMIN C. M. MARTINDALE ET AL: "Clean Donor Oxidation Enhances the H₂ Evolution Activity of a Carbon Quantum Dot-Molecular Catalyst Photosystem", ANGEWANDTE CHEMIE, INTERNATIONAL EDITION, vol. 55, no. 32, 29 June 2016 (2016-06-29), pages 9402-9406, XP055622885, DE ISSN: 1433-7851, DOI: 10.1002/anie.201604355	1,2,6,7, 13-16
A	cited in the application figures 1,3a	3-5, 8-12, 17-20
X	----- XIAOWEI SHI ET AL: "Faster Electron Injection and More Active Sites for Efficient Photocatalytic H₂ Evolution in g-C₃N₄/MoS₂ Hybrid", SMALL, vol. 14, no. 11, 26 January 2018 (2018-01-26), page 1703277, XP055622642, DE ISSN: 1613-6810, DOI: 10.1002/smll.201703277	1-3,10, 12-16
A	"4. Experimental Section - Preparation of g-C₃N₄" "4. Experimental Section - Preparation of g-C₃N₄/MoS₂" "4. Experimental Section - Photocatalytic H₂ Evolution" figures 3B,3C,3D ----- -/--	4-9,11, 17-20

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/064221

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUIJUN YU ET AL: "Carbon quantum dots/TiO ₂ composites for efficient photocatalytic hydrogen evolution", JOURNAL OF MATERIALS CHEMISTRY A, vol. 2, no. 10, 14 March 2014 (2014-03-14), page 3344, XP055622587, GB	1,2,6,7, 10,12-15
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A	DOI: 10.1039/b907612c Retrieved from the Internet: URL:https://pubs.rsc.org/en/content/articlepdf/2009/cc/b907612c [retrieved on 2019-09-17] paragraph bridging the left and right columns on page 5118 -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/064221

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 107597166	A	19-01-2018	NONE
