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Recent development of organic inorganic hybrid photocatalysts for biomass conversion into hydrogen production

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Over the last few years, photocatalysis using solar radiation have been explored intensely to investigate the possibilities of producing fuels. The production and systematic usage of solar fuels can reduce the use of fossil-based fuels which are currently the primary source for the energy. It’s time for us to exploit renewable sources for our energy needs to progress towards a low-carbon society, this can be achieved by utilizing green hydrogen as the future energy source. Solar light assisted hydrogen evolution through photocatalytic water splitting is one of the most advanced approach but non-spontaneous chemical process and restricted by kinetically demanding oxidation evolution reaction. Sunlight has one of the essential sources for Photoreforming (PR) of biomass waste into solar fuels, lucrative fine chemicals Hydrogen production through photoreforming of biomass can be considered energy neutral as it requires only low energy to overcome the activation barrier and an alternate method for water splitting reaction. Towards the perspective of sustainability and zero emission norms, the hydrogen production from biomass derived feedstocks is an affordable and efficient process. The widely used photocatalyst materials such as metal oxides, sulphides and polymeric semiconductors still possess challenges in terms of performance and stability. Recently, a new class of materials has emerged as organic inorganic hybrid (OIH) photocatalysts which have the benefits of both components, with peculiar properties and outstanding energy conversion capability. This paper work examines the most recent progress in the photoreforming of biomass and its derivatives using OIH as an excellent catalysts for hydrogen evolution. The fundamental aspects of PR mechanism and different methods of hydrogen production from biomass are discussed. Additionally, an interaction between both the composite materials from the atomic level has deeply been discussed upon recent literature. Finally, an opportunity and future perspective for the synthesis and development of OIH catalysts has discussed briefly about biomass photo-reforming.

1. Introduction

In recent years, there has been phenomenal improvement in the standard of living of mankind with the advancement in the arena of science and technology. Unfortunately, rising energy demand and a faster product life cycle have led to the depletion of energy along with environmental and waste issues. To solve these issues, it is highly essential to look forward to sustainable and efficient energy sources. Photocatalytic hydrogen production is receiving worldwide attention as hydrogen has the potential to evolve as a fuel for the post fossil era. Solar energy conversion into chemical fuel is considered an effective alternative technology for addressing fuel shortages and environmental concerns. Hydrogen has emerged as a adaptable choice for carbon-free transportation, energy source, and other sectors as countries around the world aim for a carbon-free society driven by sustainable economy.\textsuperscript{1} However, almost all the hydrogen produced comes from non-renewable fuel sources like coal, oil and natural gas.\textsuperscript{2} More than 96% of H\textsubscript{2} produced globally is from steam reforming of fossil fuels and less than 2% of annual hydrogen production are from electrolysis using renewable electricity.\textsuperscript{3} Non-renewable resources cannot be considered as feasible sources as they cannot be restored within the timescale and their carbon dioxide emission contributes to global warming. Sustainable hydrogen generation from renewable sources can be a promising and eco-friendly way to address global energy problems and minimize the reliance on fossil fuels. This can only be made into the act by changing our strategy in resource generation, usage, and disposal.\textsuperscript{4} Currently, human being follows the fossil-based methods which could offer financial benefits, but in the long run, this will be a challenge for our objective to conserve limited resources and reduce the emission of hazardous gases. To move towards a carbon-free society, there should be a slow and steady turnaround in the production and utilization of energy and materials. The energy domain, which includes transportation, power and industry, is responsible for more than 75% of greenhouse gas emissions.\textsuperscript{5} To reduce the emission of carbon into the atmosphere, a few methods are used, such as using renewable energy sources than fossil fuels,

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reducing the use of electricity and fossil fuels in industries and public sectors, capturing CO₂ as a derivative of fossil fuel combustion before entering the atmosphere. But these methods have their own limitations and they cannot be considered as a long-term remedy towards a green economy. Renewable energy sources, such as solar, wind, and hydropower, are widely used for energy production, despite their low conversion efficiency. In this aspect, green hydrogen can be considered as an energy carrier for the future. To produce hydrogen, solar energy should be considered because it is the ultimate source of renewable energy. More than 48% of the sunlight spectrum consists of UV – Visible radiations. So, the most effective and promising approach for resolving energy and ecological challenges is the successful conversion of visible sunlight into chemical energy stored in hydrogen, which has grabbed a lot of attention recently. Green hydrogen is a clean, flexible energy source that supports the zero carbon emission norms. H₂ contains an approximate energy of 122 KJ g⁻¹, which is considerably higher than gasoline (47 KJ/g), coal (15 KJ/g), natural gas (40 KJ/g) or any other fossil-based fuels. Hydrogen is light, flammable, and storable. It has high-energy content and can be used for various purposes such as carbon-free fuel production, production of fertilizers, and metallurgy. Therefore, it's necessary to produce green hydrogen from never-ending sources to look forward to a clean, sustainable society.

One of the most advanced approaches for hydrogen evolution is the photocatalytic water splitting using solar energy. The reduction and oxidation of H₂O to H₂ and O₂ occur simultaneously in this process. The burning of the hydrogen fuel produced using solar radiations does not lead to the emission of CO₂ gases as the carbon cyclized is closed. The photocatalytic water splitting (WS) is being developed as a sustainable technology that can bring a change to offset the 830 Mt of annual CO₂ emission due to steam reforming of fossil fuels by producing clean hydrogen. Many large-scale photocatalytic hydrogen production processes with decent yields have been developed recently, which include NiSCd, Zn₁₋ₓS catalyst and Na₂SO₃ as scavenger yields 10,400 μmol/m²/hr, another notable achievement is attained by Cu/TiO₂ photocatalyst with glycerol producing 1240 μmol/L of hydrogen. The photooxidation process can be avoided by using a hole scavenger (sacificial agent) which scavenge the holes before it undergo oxidation. They are typical scavenging agents like ethyl alcohol, methanol, sulfides or thiosulfates. For an effective functioning of the scavenger the redox potential should be above the oxidation level of catalyst, which facilitates the smooth transfer of hole to the sacrificial agents. Even though it’s widely encouraged, large-scale production of hydrogen still faces a few issues such as reusability of photocatalyst, use of expensive metals as sacrificial agents, separation of O₂ and H₂ mixture and inefficient use of visible light. WS is a non-spontaneous chemical process [Change in Gibbs free energy, (ΔG°) = +237 kJ mol⁻¹ at 25 °C] and it is restricted by kinetically and energetically demanding oxidation evolution reaction. The difference in energy is responsible for maximum limit of wavelength of the photons irradiated which is responsible for initiation of reaction. The energy can be calculated using the equation ΔE° = ΔG°/nF, where n represents number of exchanged electrons and F is Faraday constant. In case of water splitting reaction ‘n’ has a value of 2, ΔE° calculated as 1.23 V. Depicts that the photon should possess a minimum energy of 1.23 eV with wavelength shorter than 1008 nm (λ = hc/ΔE). Those reactions having positive Gibbs free energy normally have high activation energy i.e., the thermodynamic barrier of WS is -1.23 V, so electrons require high energy to carry out the chemical reaction. The overpotential which is necessary to overcome the kinetic restrictions, which significantly increased especially on the half-oxidation. The larger overpotential showcases the wider band gap which depicts higher charge transfer also leading to absorption of shorter wavelength radiations. The absorption of ultraviolet radiation by the photocatalyst to get enough energy to drive the reaction bus as the quantity of UV is limited, this exhibits less water conversion efficiency. To get a higher productivity for photocatalytic reactions, it is critical to use visible radiation (44 percent), which accounts for the majority of sunlight radiation. So, only a few visible light absorbing photocatalysts is used for the WS reaction.

2. Scientific Analysis of Photoreforming

To bring in a solution, photocatalytic reactions with ΔG° < 0 are studied. These total reactions involve hydrogen production on one electrode while hole scavengers such as triethanolamine, methanol, and lactic acid are used, which work on the other electrode and offer a faster rate than the oxygen evolution reaction. Photoreforming (PR) is an alternative method for hydrogen production from water and organic substrates, which has the potential to overcome the outstanding constraints. In PR, the photocatalyst absorbs radiation from the solar spectrum and electrons in the lower energy level (valence band) are excited to the highest energy level (conduction band). Consequently, an electron and a hole is evolved. Most of these pairs will recombine without any further reaction. If not, these holes and electrons are carried to the surface of photocatalytic material. Strategies such as heterojunction design, construction of intramolecular donor acceptor system, spin polarization regulation and excitation dissociation regulation are used to inhibit charge transfer recombination in photocatalysts. The formation of heterojunction facilitate efficient charge separation and charge carrier transfer through the interface. The D-A system allows high speed charge transfer within the photocatalyst. The free electrons increases by regulating the dissociation of electron hole pair into free carriers. The charge recomination reduced and efficiency of electron transfer increased via controlling the electron spin polarization. Even though these strategies exhibits the ability to inhibit the recombination of excitons, these strategies has its own limitations. The incorporation of electron donors or electron acceptors with organic linkers may reduce the length of the conjugated system making it difficult for the migration of electron between donor and acceptor. Defects like lattice mismatch can exist between the two semiconductors that make up a heterojunction photocatalyst, and the defects become the recombination centre of
photon generated carriers. The exciton dissociation and electron spin polarization regulation are not much explored, the mechanisms need to be further studied.\textsuperscript{27} The electrons and holes reduce water to hydrogen and oxidize organic substrates into small molecules, respectively.\textsuperscript{28} These substrates can be plastic waste, food materials, and biomass. This can effectively aid in avoiding the use of costly sacrificial agents while offering effective conversion of waste materials.\textsuperscript{29} PR can be implemented at room temperature with solar energy as the external energy source to produce clean hydrogen fuel. PR brings forward a different approach of both introducing a method for waste disposal and producing useful organic materials. The thermodynamic energy barrier of PR mechanism for most of the organic substrates is energetically neutral. For example, the photoreforming of ethylene glycol needs $\Delta G^\circ$ of +9.2 kJ/mol (standard electrode potential = -0.01 V) at room temperature.\textsuperscript{28} PR prefers substrates having minimal complexity, high polarity/hydrophilicity, water solubility, and functional groups that adsorb to the surface of photocatalyst according to studies with simple molecules.\textsuperscript{30}

\[ 2H^+ + 2e^- \rightleftharpoons H_2 \quad E^0 = 0 \ V \text{ vs } RHE \] (1)

\[ C_6H_{12}O_6 + 6H_2O \rightleftharpoons 6CO_2 + 24H^+ + 24e^- \quad E^0 = -0.001 \ V \text{ vs } RHE \] (2)

\[ H_2O \rightleftharpoons \frac{1}{20_2} + 2H^+ + 2e^- \quad E^0 = +1.23 \ V \text{ vs } RHE \] (3)

\[ H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2 \quad \Delta E^0 = -1.23 \ V \] (4)

\[ C_6H_{12}O_6 + 6H_2O \rightleftharpoons 12H_2 + 6CO_2 \quad \Delta E^0 = +0.001V \] (5)

A desirable substrate for PR should contain as many of these characteristics as feasible and also be generated from non-recyclable waste materials. H$_2$ is currently in the growing stage and it’s having a low market value, alternative PR products are sought after, and the specific photocatalytic processing of renewable feedstocks into lucrative organic valuables is a seriously debated topic.\textsuperscript{31}

2.1 Photo-reforming feedstock

On a global basis, there is an increasing attention in developing waste-to-energy resolutions for municipal solid waste (MSW), fuelled by ecological concerns regarding inadequate disposal techniques.\textsuperscript{32} Waste produced by industries exceeds largely than those produced at the municipal level but due to the shortage in the availability of global statistics on production and disposal of industrial wastes, we will concentrate mainly on the MSW statistics. Every year, about 2 billion tonnes of MSW are produced around the world. By 2050, global garbage production is expected to increase by 70%, which is estimated to 3.4 billion tonnes. More than 70% of MSW is sent to landfill sites or disposed of by open dumping.\textsuperscript{33} Recycling accounts for 13% of the world’s municipal solid trash. Every year, 93.9 million tonnes of MSW are recycled or composted.\textsuperscript{34} The absence of appropriate waste management has a significant impact on public health and society, it is estimated that implementing trash prevention, recovery and recycling measures may cut global carbon emissions by 20 percent.\textsuperscript{35} Food waste and biomass (46%), paper products (17%), and plastic (12%) make up the majority of MSW globally, with textile, metal, leather, and other trash are accountable for the remaining 25%. The 75% of MSW components contains organic substrates and can be potentially used for the PR. This review will be focussing on producing clean hydrogen and organic substrates from waste materials and thereby evaluating the possibility of fuel production and waste management simultaneously.

The most suitable waste component available for PR is biomass, which includes sucrose, glucose starch and wood.\textsuperscript{36} Around 4 Gt of Biomass waste is annually produced from various sources like farming and industry residues. The biomass derived substrates like carbohydrates and alcohols can be used to produce hydrogen from sewage food, beverages, and paper industry waste materials. Lignocellulose, a combination of cellulose, hemicellulose, and lignin,
is the main component of biomass. Hardwoods have more cellulose and hemicellulose content (78%) compared to softwoods (70%), whereas softwoods have higher lignin content (29.2%) than hardwoods (21.7%). Cellulose and hemicellulose are long chain carbohydrates (C_{n}H_{2n}O_{n} or C_{5}H_{10}O_{5}) that can undergo PR because of the polarity and hydroxyl functional group present. The hydrophobic nature of lignin makes it difficult for photo-reforming. Around 55 - 95 wt.% of chemical content can be reformed from various biomass sources, depending upon the photocatalyst used. The practicability of biomass derived substrates has been carried out using different carbohydrates, organic acids, and other derivatives. The amount and type of the substrate, the reaction media, and temperature all influence the yield of hydrogen. The position of lower and higher energy bands of the photocatalyst has a major role in the selectivity of the product. Band gap engineering is widely carried out to obtain the desired product as chemicals and reaction pathways as the oxidation half is controlled by the holes of the photocatalyst. X-ray photon spectroscopy is used to obtain the band gap of photocatalyst used. Various methods have been carried out for band gap engineering such as vacancy creation, quantum dots, heterojunctions, and solid solutions. This allows the exploitation of the band gap of the catalyst to improve its activity and efficiency. Cocatalyst loading is also an effective method to improve the photo-oxidation. The loadings of cocatalyst such as (Pt, Au, Ag) boost the electron transportation and charge separation. By boosting photoinduced electron and hole separation, the inserted metal species can speed up the reaction process. These metals contain active sites for the electrons which are photogenerated thereby inducing a charge separation. To improve biomass functionality of the catalyst, procedures like enzymatic exfoliation, acid/base addition, and increased ionic liquid solubilization have been utilized with photocatalysis. The initial step in converting biomass to hydrogen is to use TiO\(_{2}\) with Pt and RuO\(_{2}\) serving as a reduction and oxidation co-catalysts, respectively. The starch and cellulose yields 320 \(\mu\)mol/20 h and 244 \(\mu\)mol/20 h of hydrogen using RuO\(_{2}\)/TiO\(_{2}\)/Pt photocatalyst. The photocatalytic fuel production has been carried from this pioneer work, but most of the studies are based on TiO\(_{2}\) materials. Even though TiO\(_{2}\) is responsive and of low cost, its large band (3.2 eV) resists it from absorbing solar radiation to only UV light. CsS has also been considered as the conventional photocatalyst in PR of biomass but its toxic nature and vulnerability to corrosion is considered as the drawback.

2.2. Methods of hydrogen production from biomass

Hydrogen evolution through biomass can be classified as thermochemical and biological processes. The former can be described as four processes of (i) combustion (ii) pyrolysis (iii) liquefaction and (iv) gasification (Fig. 2). The thermochemical process involves the decomposition of biomass thermally, with or without the aid of a catalyst. The product obtained in thermal decomposition such as biomass gasification is usually carried out with the help of an external heat (combustion). It is controlled by major parameters such as temperature, rate of heat, time for reaction and used catalyst. The process of biomass gasification includes the partial oxidation of the substrate, that produces gaseous products.

![Fig. 2 Different biomass reforming processes for hydrogen production.](image)

The formation of tar and ash formation during the process is the major disadvantage of gasification. The use of some additives such as dolomites, char can be used to resolve the former problem and fractionation and leaching can be used to avoid formation of ash in the reactor. Its advantages include the low-cost production and better yield. Coal gasification is widely and efficiently used but it is highly dependent on hazardous fossil fuels. The high installation and maintenance cost is also a drawback for coal gasification. Steam methane reforming is also a relatively stable and efficient form of hydrogen production, but the production of CO\(_{2}\) and high operating temperature are the main challenges.

On the other hand, biological processes are mainly classified into (i) direct and indirect bio-photolysis, (ii) hybrid system, (iii) dark fermentation, and (iv) photo-fermentation they are eco-friendlier and less energy consuming. Hydrogen producing microbes, like nitrogenase and hydrogenase, carry out these operations. Direct bio-photolysis of producing hydrogen is a process that converts sunlight to chemical energy stored in hydrogen, using microalgae photosynthetic systems. Even though the consumption of the substrate is high, the efficiency is very low. Indirect bio-photolysis involves the conversion of solar light by multiple steps mechanism and the yield obtained is comparatively higher than the direct bio-photolysis. Fermentation can be carried out to produce hydrogen in the presence of light and dark condition by bacteria at 30°C - 80°C. Methane fermentation under aerobic condition is one of the major methods, but the yield of hydrogen is low. The fermentation is kinetically slow, but the disposal of fermentation waste is an issue. Even though the biological conversion requires low energy input, it is only carried out on a small scale and produces by-products.

3. Photocatalyst Materials

Scientists have been using with different photocatalytic materials for hydrogen production from biomass and its derivatives to find a new path for fuel generation other than splitting of water. In 1980, the first reported hydrogen production from carbohydrates is published using RuO\(_{2}\)/TiO\(_{2}\)/Pt photocatalyst using 500 W Xenon light.
Hydrogen is also produced from other biomass sources like starch, dead flies, cellulose, algae and waste materials using similar methods.\textsuperscript{57, 48} Researchers have encouraged the use of doped TiO\textsubscript{2} (metal and non-metal doped TiO\textsubscript{2}) (simple and mixed oxides), sulphides (cadmium, zinc), carbon nanomaterials, covalent-organic frameworks (COFs), metal-organic frameworks (MOFs), hybrid inorganic-organic mesoporous materials, polymeric semiconductors, co-catalysts (metal/metal oxide) for solar absorption. This shows the wide possibility of biomass conversion to hydrogen. Widespread research is underway to develop fine band gap materials and metal-free materials for H\textsubscript{2} generation via photo-reforming, with the goal of enhancing visible light photocatalytic performance while also improving selectivity toward important compounds and H\textsubscript{2} evolution (Fig. 3). Extensive work has been carried out with titania based materials due to their high stability, non-toxicity, abundance, and efficiency.\textsuperscript{49, 50} In order to compensate the large band gap and the inability to absorb the light from visible region, TiO\textsubscript{2} could be loaded with cocatalyst (Pt, Pd, Au) and visible light sensitizers (CdS, C\textsubscript{6}N\textsubscript{4}) to enhance the photocatalytic efficiency for hydrogen production.\textsuperscript{50, 51} Doping with different transition metals can increase catalytic efficiency mainly by the reduction the electron hole pairs recombination and the enrichment of surface active sites.\textsuperscript{52} As an example, the photocatalytic conversion of cellulose has been carried out and large yield could be obtained from cellulose immobilized TiO\textsubscript{2}/Pt at 195 \textmu mol.\textsuperscript{53} Photocatalysis and acid hydrolysis of cellulose biomass into hydrogen has been carried out in sulphuric acid medium using Pt/TiO\textsubscript{2} as the catalyst. The reaction yields 123 \textmu mol of hydrogen with 0.6 M H\textsubscript{2}SO\textsubscript{4} concentration and a production of 1320 \textmu mol/h \textgreek{g} \textsubscript{cat} was obtained using raw biomass paper pulp in the same condition.\textsuperscript{54} Pd loaded TiO\textsubscript{2} has also been studied in the photo-reforming of biomass. The surface bound cocatalyst can enhance the photocatalytic reaction by binding electrons to its surface and facilitates the hydrogen evolution reaction.\textsuperscript{55, 56}

Fig. 3 Photocatalytic water splitting and oxidation mechanism.\textsuperscript{57} Copyright 2020, International Journal of Hydrogen Energy.

The deposition of Au metal on the photocatalyst surface has also been effectively used for hydrogen evolution from biomass.\textsuperscript{58, 59} The positions of the valence band and the conduction band of the material have a vital role in the HER and OER because these define the suitable energy of absorbed light radiation (Fig. 4).

Photo-reforming of ethanol is reported using Au/TiO\textsubscript{2}, the gold particles are supported on the photocatalyst by deposition precipitation method. Under UV irradiation, H\textsubscript{2} generation yields are extremely high (30 mmol g\textsuperscript{-1} h\textsuperscript{-1}) and the yield rises versus the increase of gold loading.\textsuperscript{61} Once the radiations fall on the photocatalyst surface the reduction of Au\textsuperscript{3+} to Au (0) is carried out by the electron, this leads to the alignment of Fermi levels of both TiO\textsubscript{2} and Au. It is responsible for the quenching of electron-hole recombination. Another study shows using high-pressure Hg lamp of 125 W, the photocatalytic reforming of glucose using Au/TiO\textsubscript{2} photocatalyst yields 1.37 mmol/h of hydrogen.\textsuperscript{62} A report shows that the photo-reforming of methanol has been carried out using different metal cocatalysts on TiO\textsubscript{2}.\textsuperscript{63} Here Pt achieves the highest activity and the specific activity order is given by Pt > Au > Pd > Rh > Ag > Ru. This can be explained due to the higher overpotential for the production of H\textsubscript{2} on TiO\textsubscript{2} and also due to the work function of noble metals.\textsuperscript{64} The former is the reason for the very low inactivity of TiO\textsubscript{2} and the latter will lead to the construction of a strong Schottky barrier formed at catalysts interface junction.\textsuperscript{65} The work function of platinum metal is higher and thus produces more yield in hydrogen evolution compared to other metals. The Schottky barrier is responsible for the decrease in the creation of the electron-hole pairs and shows better photocatalytic activity.\textsuperscript{66} The photocatalytic reaction’s efficiency still much below and challenging for practical implementation due to the high recombination rate of electron-hole pairs and the photocatalyst’s inadequate active sites, both of which leads to the low quantum yield and photocatalytic efficiency.\textsuperscript{67} Alternate methods in which the use of nickel sulphides and oxides are carried out to avoid the use of costly noble metals for photo-reforming of biomass material to hydrogen. It is reported that when TiO\textsubscript{2} is modified with nickel sulphide and sulphate, the hydrogen yield is 181 \textmu mol from cellulose. The sulphate particles act as a solid acid catalyst which facilitates the hydrolysis of cellulose, this will lead to the availability of soluble glucose to the catalyst which quench the holes and donate electrons. The nickel sulphide act as cocatalyst and trap electrons for the reaction.\textsuperscript{68} When nickel oxide is used, a graphic over-layer is added at the interface, this helps improve the
conversion efficiency successfully. This carbon layer is responsible for the weakening of O-H bonds of the substrates used. The hydrogen produced is reported as 270 μmol/gcat/h at low temperature and 4150 μmol/gcat/h at high temperature. 60Cadmium sulphide is another commonly used substance, which is recognized for their capability for absorbing visible light due to their high molar extinction coefficient in the visible area. The overall photocatalytic efficiency can also be increased by modification techniques such as surface plasmon resonance. This enhances photostability, create new sites on the surface, suppresses electron–hole recombination.70 Activity can further be enhanced by loading the material with cocatalyst metals.

CdS nanosheets loaded with nickel co-catalyst will reduce charge recombination, leading to the production of H2 and value-added compounds from biomass. For Au/CdS nanorod catalyst, a yield of 90 μmol h−1 gcat−1 hydrogen from glucose is obtained using visible radiation, which confirms the self-reducing ability of Au26 to Au increases the separation and transportation of photogenerated excitons.71 Another report shows that the lignocellulosic biomass is used to evolve hydrogen by using a stable CdS/SiC composite material at high temperature. The yield obtained is 321 μmol h−1 gcat−1 of hydrogen when Pt is used as the cocatalyst for the reaction using a cellulose as the substrate.72 The valorisation of cellulose is carried out using CdS/CdOx quantum dots provides high yield of hydrogen. It is noting that the reaction is implemented without use of any cocatalyst material or CdS photo-corrosion in the basic medium.73

Fig. 5 The band gap position of a few metal-free photocatalyst is depicted in the figure.74 Copyright 2017, Green Chemistry.

In order to achieve a more sustainable and eco-friendly means to produce H2 from biomass sources, the use of metal-free photocatalyst is used potentially. These photocatalysts are basically derived from elements like chalcogens and carbon-based derivatives. This includes graphic carbon nitride, boron carbides, graphene oxides, carbon quantum dots, and other organic compound photocatalysts have exhibited promising applications in energy conversion (Fig. 5).74 These materials are known for their unique characteristics such as good thermal and electrical conductivity, stability, bonding effects to produce active sites and tunable structures. The most widely used metal-free photocatalyst is g-C3N4 towards hydrogen production using visible light. g-C3N4 is known for its versatile morphology and stability, but its low surface and rate of charge recombination is considered as demerits.75 Photo-reforming of lignocellulose using cyanamide functionalized carbon nitride shows good H2 production in presence of visible light. A maximum yield of 2.62 μmol is obtained under alkaline medium. The same reaction is carried out using saw dust, a yield of 202 μmol/h/gcat of hydrogen is obtained. The activity is mainly because of the ability to transfer holes formed to electron donating substrates by the cyanamide surface.76

3.1. Organic – Inorganic Hybrid Materials (OIH)

To improve the performance of conventional photocatalyst materials organic-inorganic hybrid materials (OIH) have been deeply explored. The development and synthesis of novel catalysts having higher activity and versatile properties for photocatalytic applications are rapidly emerging in the research of material studies and industrial developments. Towards this objective, the flexibility to regulate the structural properties is an important criterion in the development of catalytic materials. If observed closely, nature has always followed a mechanism by which it combines materials even at lower scale, resulting in formation of “hybrid materials”. Bone and wood are examples of naturally occurring organic inorganic composites, the former is composed of protein and minerals and the latter contains cellulose fibre in lignin matrix. Organic-inorganic hybrids, which showcase the features of both organic (variety,flexibility) and inorganic (conductivity, surface area) material, evolves as a new division of photocatalytic material (Fig. 6). The concept of OIH material is basically the combination of organic and inorganic components into a single material integrating inorganic material with organic molecules is an attractive pathway to manufacture functional hybrid materials with tunable properties. Systematic synthesis of hybrids of desired size and structure, and tuning of optoelectronic properties which might improve the photocatalytic productivity.77 The advancement of inorganic organic hybrid materials has inspired a large number of researchers towards this field. At the peripheral level, these hybrids will be either homogeneous or heterogeneous composites. The homogeneous arrangement consists of monomers and miscible constituent, but the heterogeneous composite has a component with dimension range between few angströms (Å) to nanometres (nm). OIH can be classified into two types depending upon the type of interactions between the components.

In type 1, the physical interactions such as hydrogen bonding, Van der Waals or ionic interactions are only allowed between the organic and inorganic components which provide stability to the structure.
Both organic and inorganic contain some functional groups (polyamides, polycarbonates) which is responsible for the interaction. On the other hand, in type 2, chemical bonding such as covalent or non-covalent bond is responsible for the interaction between the two different phases. The miscibility between the two phases can be obtained by adding compatibilizers. Compatibilizers are macromolecules which is used to enhance interfacial adhesion between both the organic and inorganic components. These hybrid materials are promising towards catalytic applications.

Fig. 6 Representation of interpenetrated organic-inorganic composites. Copyright 2019 Springer.

The development of photovoltaics is responsible for the evolution of photo conductive polymers and their widespread usage. The morphologies and properties of OIH materials can be adjusted on a large-scale parameter and it can be reduced to very small sizes. The preparation of these materials are difficult due to its heterogeneous structures. So, it’s highly essential and a tough task to design an OIH material with efficient photocatalytic activity. The initial works on these materials were based on inorganic semiconductors and organic components. The latter can either be molecular catalysts or dyes (organic) which can act as photocatalysts or sensitzers (Fig. 7). Organic macromolecular polymers can also be used due to its characteristics such as hydrophobic and hydrophilic nature. These polymers will not act as photocatalyst but can be protective films which aid the hybrid with their properties. Here it is noting that the polymer is not considered as a part of the photocatalytic system, it just improves the activity of the entire system. When conjugated polymers are used, their conducting properties may contribute to the photocatalytic features. The delocalization of the alternating double and single bonds in conjugated polymers are responsible for the photocatalytic properties. Recent literature reveals that hybrid graphene-inorganic semiconductor materials are having the potential to evolve as the modern material in the field of photocatalyst and composite industries.

3.2 Organic–Inorganic Hybrid Materials for Photocatalytic H₂ Production

Fig. 8 Organic–Inorganic Hybrid Materials for Photocatalytic H₂ production.

3.2.1 Carbon Nitride materials for Photo-reforming of Biomass Derivatives

The metal-free carbon nitride (C3N4) is a conjugated polymer which contains tertiary nitrogen’s heptazine (C6N7) 2D linked network units has evolved as a promising photocatalyst. Its characteristic properties include low preparation cost, highly stable (550 degrees, in both acid and base), synthesized from earth abundant chemicals, unique band gap ($E_{CB}$: -1.1 eV, $E_{VB}$: +1.6 eV) and respond to 400 nm – 700 nm (visible) region. As g-C$_3$N$_4$ possess these many magnificent features, it is a strong contestant for gaining the tag of ‘green photocatalyst’ than other semiconductors such as CdS, BiVO$_4$, MoS$_2$, etc. by the scientific community. The availability of primary and secondary nitrogen at edges and hydrogen bonded heptazine gives many catalytically active centres for the biomass substrate. In recent studies, 2D carbon containing materials are widely used in the biomass reforming as they have good mobility of electrons, enhanced activity, large surface area and ability to form hybrid structures with other materials (Fig. 8). The adsorption of biomass on to the C$_3$N$_4$ sheets is facilitated due to the electron rich 2D conjugated structure. The band gap 2.7 eV makes it suitable for the

Fig. 7 Representation of energy level diagram of a few inorganic semiconductors and conjugated polymers and the type of charge transfer mechanism in hybrid semiconductor material. Copyright 2019, Chemical Society Reviews.
visible light absorbing photocatalyst for biomass reforming. The synthesis strategies play vital role to control structure which include regulating size and morphology of the material. Two kinds of strategies have been carried for the synthesis of CNN which involves bottom up and top-down approaches. The previous methods are involved the use of precursor containing nitrogen compound with template assisted bulk g-C$_3$N$_4$ precursor under thermal oxidation or chemical exfoliation. Different strategies has been followed to control the morphology of the materials such as introduction of co catalyst, formation of heterojunction with targets to improve light absorption. DFT data shows the valence band of g-C$_3$N$_4$ comprises 2p state nitrogen and the conduction band consist of hybridization of carbon 2p and 2p state of nitrogen. So, the photogenerated holes will be present in the nitrogen sites. The photogenerated electrons suffer from the high recombination of electron-hole pairs because of the hybridization of nitrogen 2p and 2p carbon states in CB, which reduces the photocatalytic activity. Strong covalent bonding holds the carbon and nitrogen atoms together, forming layers of honeycomb-like structure. The Van der Waals’s force between the layers of CN provides better stability in acidic or alkali solvents. CNN is synthesized from nitrogen rich sources such as melamine, urea, thiourea and dicyandiamide through the process of thermal polycondensation and polyaddition (Fig. 9). More importantly the polymeric nature of the material helps in achieving modulation and fictionalization at molecular level. The synthesis of CNN hollow spheres with high crystallinity via molten salt method where cyanuric acid-melamine used as the precursor. The presence of heptazine units of CN is served as a support matrix which allows it to merge with semiconductors, quantum dots and nanoparticles. Modification methods such as nanostructure design, heterostructure construction, electronic structure modulation and loading of cocatalyst have been fruitfully illustrated in water splitting and biomass-photo reforming. A report shows that the lignocellulose photo-reforming exhibits a yield of 262 μmol h$^{-1}$ g$_{cat}^{-1}$ with pristine polymeric carbon nitride.

The mechanism is carried out by constructing carbon nitride curly sheets with includes the surface in plane heterostructure which reduces recombination of charge (charge separation) and optimization of the electronic band gap of the catalyst. The efficiency still improves to 4092 μmol/h g$_{cat}$ where Pt (cocatalyst) is used. The same material is used for the water splitting, which produces an yield of 22043 μmol/h g$_{cat}$ of hydrogen. The potential and efficiency of CN based materials have been already well established in the field of photo-reforming of biomass. A further enhancement of activity is obtained by following certain modification techniques such as surface functionalization, elemental doping and construction of hybrid heterostructures (Fig. 10). Among these the modifications through the modulation of hybrid heterostructures will help to increase the photocatalytic activity of the material as the recombination of photogenerated electron-hole pairs are minimized. The incorporation of various composites will increase the biomass conversion efficiency. The use of metal complexes, metal nanoparticles, and semiconductors in hybrid carbon nitrides for successful hydrogen production from biomass will be briefly described.

**Fig. 9** Structure of graphitic carbon nitride with a) Triazine, b) tris-triazine, and c) schematic representation of preparation of g- C$_3$N$_4$ by thermal polymerization of various precursors. The C, N, H, O, and S atoms are depicted by black, blue, white, red, and yellow balls respectively.

**Fig. 10** Different hybrid heterostructures of carbon nitride.

The use of metals with g-C$_3$N$_4$ will enhance the hydrogen evolution reaction. The metal will use its surface plasmon resonance (SPR) phenomenon to increase the absorption of solar radiation with a greater efficiency. The same metal can also play the role of cocatalyst which lowers the activation energy thereby increasing the rate of hydrogen production in the presence of a scavenger (methanol, EDTA). Metals like Pt, Au, Ag, Rh and Ni are widely used as cocatalyst to increase the efficiency of C$_3$N$_4$ for the hydrogen evolution. Jiang et al. was able to synthesis low-cost g-C$_3$N$_4$ surface modified using renewable bio-oil from pine saw dust. The oxygen containing functional groups (C=O, C=O), helps in improving the separation of holes and electrons, thereby enhances photocatalytic activity. The maximal yield of hydrogen obtained is about 1654 μmol/h g$_{cat}$ at 180 °C. The currently used biomass sources like raw lignocellulosic materials have a few drawbacks such as low solubility and inert behaviour towards chemical reactions. These are avoided by an extent with the use of methods like acid hydrolysis and ball milling. This review will be concentrated not only on raw biomass but also on biomass derived substrates like alcohols, acids, aldehydes, and glucose which is also a feasible source for hydrogen production. Industrial biomass waste products can be
used as a source of hydrogen production substrate. The ethanol obtained from biomass sugar fermentation, glycerol produced from biofuels and methanol from the syngas are few examples. Amines are biomass derivatives which is getting a lot of attention these days. Triethanolamine (TEOA), triethylamine (TEA) is highly preferred in the H₂ production as they are used as scavengers in the reaction mechanism. Alcaudia et al. has reported that g-C₃N₄ could be hybridized with TiO₂ by hydrothermal method. The reaction is carried out using 3 wt.% of triethanolamine, the yield of hydrogen obtained is 1042 μmol/g/h as Pt as cocatalyst. The heterojunction CₓNₓ-TiO₂ formed could give higher yield compared to pristine CₓNₓ and TiO₂, respectively. This shows that the coupling of both materials could increase the spatial charge separation of holes and electrons, this is supported by XPS data.³⁷

Xiaohu et al. (2015) carried-out hydrogen production using poly(3-hexylthiophene) in graphitic carbon nitride solution. The reaction yield is varied when different sacrificial reagents are used.

The surface heterojunction which contains 3 wt.% of P3HT yields 3045 μmol/h of hydrogen when ascorbic acid is utilized as a scavenger. The catalyst when used with TEOA and EDTA produces a yield of 320 μmol/h and 44 μmol/h respectively. The surface heterojunction catalysis mechanism is depicted in Fig. 11. The ability to absorb extensive range of light and highly effective charge transfer among poly(3-hexylthiophene) and g-C₃N₄ is accountable for the efficient photocatalytic activity of polymer-polymer catalyst. The efficiency of poly(3-hexylthiophene)-g-C₃N₄ decreases with higher composition of poly(3-hexylthiophene). This is attributed to two reasons, the hydrophobicity of P3HT is responsible for the agglomeration of the polymer which make to its float above the solution surface finally decreases the absorption of light. The other reason is the activity of the co-catalyst is screened by the excess of P3HT, leading to decreased activity.³⁸

Andera Speltini et al. (2018) described hydrogen production using aqueous biomass with stimulated light radiation. Oxidized graphitic carbon nitride (o-g-C₃N₄) is decorated with Pt, Cu-Ni co-catalysts in the presence of biomass and carbohydrates. The oxidized material (o-g-C₃N₄) with Cu-Ni co-catalysts 912 μmol/h and with Pt yield is 1170 μmol/h. The usage of starch as the sacrificial agent has a large impact in the H₂ evolution. The photoreforming basically involves the biomass act as the scavenger of the oxidizing group and metal act as the photoreforming site. The potential uses of these low-cost materials can be used for the development of low environmental impact methods of hydrogen production.³⁹

Another report by Xinxing Wu et al. (2020) demonstrated an ideal path for the photocatalytic reforming with CoO/g-C₃N₄ for hydrogen evolution. The photo-reforming of phosphoric acid swollen cellulose (PASC) yields 178 μmol/h/gcat of hydrogen. The higher activity is due to the interaction of PASC with photocatalyst, this is confirmed by the quartz crystal microbalance analysis.

The PR of raw lignocellulosic biomass wheat straw gives higher results on pre-treatment methods. The same study has shown an advantage of producing lactic acid which value-added chemicals. So, this study widely opens the sunlight driven biomass valorisation to produce both hydrogen and value-added chemicals simultaneously (Fig. 12).⁵⁰

Fig. 11 Plausible mechanism of hydrogen production using visible light over the surface heterojunction catalyst.⁸⁸ Copyright 2019, International Journal of Hydrogen Energy.

Fig. 12 Schematic representation of photo-reforming of wheat straw to produce hydrogen and lactic acid by photocatalysis.⁵⁰ Copyright 2020, ACS.

The PR of raw lignocellulosic biomass wheat straw gives higher results on pre-treatment methods. The same study has shown an advantage of producing lactic acid which value-added chemicals. So, this study widely opens the sunlight driven biomass valorisation to produce both hydrogen and value-added chemicals simultaneously (Fig. 12).⁵⁰

Fig. 13 Mechanism of photocatalytic reforming of glucose on ZnS/Co-Ni.⁵⁰ Copyright 2019, Journal of colloid and interface science.
Xinyuan Xu et al. (2019) carried the photocatalytic hydrogen evolution using glucose as the substrate. In this study, ZnS nanoparticles (10-15 nm) were hybridized with g-C₃N₄ derived from various components such as melamine, urea, and dicyandiamide. These two produce a heterojunction which performs reforming of biomass. The best yield was obtained from g-C₃N₄ produced from melamine. The hydrogen evolution reaction shows a productivity of 210 µmol/g with Pt as co-catalyst carried under 300 W Xenon lamp light source. The electron and hole transfer mechanism of the photocatalyst is represented in Fig. 12. The photoluminescence spectra show that introduction of ZnS with g-C₃N₄ reduce the charge carrier recombination. It is responsible for the enhanced hydrogen generation during photoreforming of glucose.

3.2.2 Metal Organic Framework Based Photocatalysts for Biomass Photo-reforming

The valorisation of the biomass to obtain fine chemicals and fuels has a diversified advantage than the fossil-based products. The utilization of metal-organic frameworks (MOFs) as photocatalyst is explored in recent times for the photo-reforming mechanism. They are basically coordination polymers with porous structure obtained by using organic ligands and metal atoms (Fig. 14). MOFs have advantages like large surface area, tuneable and uniform porosity.

Fig. 14. The components, structures, characteristics and applications of MOFs. Copyright 2018, Science Bulletin.

MOFs composites can be prepared using metal nanoparticles, metal oxides, polymers, graphene, quantum dots, carbon nanotubes (Fig. 15). The hydrogen production with MOFs is an ideal way for clean energy generation. Efficient hydrogen production from water containing sacrificial energy donor using visible light is obtained by metal loaded MOFs. The water splitting mechanism is really a conventional way of hydrogen production and is studied using MOF to a larger extent. The Pt cocatalyst incorporated MOFs, Zr₂[(µ₃-O)₄(µ₂-OH)]₄(bpdcl)₅[Li]₀.₆₈ and Zr₂[(µ₂-O)₄(µ₂-OH)]₄[Li]₉, 6DMF, are efficient photocatalysts to obtain hydrogen fuel. This review emphasis the methods by which hydrogen is produced by biomass and its derivatives. The hydrogen production from biomass substrates such as lignocellulose is not much explored using metal-organic framework materials yet. Mingjin Luo et al. (2018) exploited photo-catalysts based on metal-organic frameworks. In this literature 2D MOF [M(TylP)₄]ₙ(TylP=5-(1,2,4-triazol-1-yl)isophthalic) is used as the photocatalyst material. Both Mn-MOF and Co-MOF have been loaded with Au nanoparticles and carried photocatalytic reaction. The MOF could be synthesized by hydrothermal method at 120°C followed by high temperature reduction (Fig. 16).

Fig. 15 The composites of MOFs and functional materials.

Fig. 16. Mechanism of Mn-MOF-Au loading reduction at 500°C. Copyright, 2018 Phase Transitions.

A turnover frequency of 576 µmol/h/gcat has been calculated for Mn₂[TylP]₄ catalyst, which is higher than what is offered by the Co-MOF. Aqueous solution of triethylamine (TEA) is used as the scavenger. The study shows that on adding the co-catalyst nanoparticle the photocatalytic efficiency further increases. Thus, MOF as a heterogeneous catalyst opens a new arena for the hydrogen evolution reaction.

Fig. 17 Structure of various MOFs (MIL-125(Ti), UiO-66 (Zr), Cu₃(BTC)₂, ZIF-8 (Zn)). Copyright 2019, ChemPhysChem.

The ease of tailoring the framework and addition of functional components made MOFs a competitive and promising in large number of applications. The structure of a few MOF is
represented in Fig. 17. MOFs are extensively used organic pollutants degradation, CO₂ gas reduction and metal reduction in the wastewater. This implies that photocatalytical activity of MOFs is more efficient than that of traditional semiconductor-based photocatalyst materials. The synthesis of MOFs is carried out through the liquid phase and solid phase reaction mechanisms. The latter is more simplistic and less time consuming. The general methods which largely used for the MOFs synthesis are evaporation method, vapour diffusion method, gel crystallization, solvothermal, electrochemical and sonochemical methods. The mechanism, structure are the main factors which determine the photocatalytic efficiency of MOFs and other practical applications. The stability of the MOFs are often subjected to criticism as it is highly unstable in the aqueous conditions, which is considered as its major drawback. Even though MOFs are used to produce hydrogen from water, it is not yet explored in the photoreforming of biomass to produce fuels. This application has a wide future scope and is not yet fully explored.

Vladimir V. et al. (2021) has reported hydrogen production using different organic inorganic hybrid niobates Ca₃Nb₂O₈·ROH, which contain n-alkoxy groups of primary alcohols inserted in the interlayer region. The photocatalytic hydrogen production is carried out using methanol solution using UV radiation. The activity was recorded for bare and Pt as cocatalyst. The highest hydrogen evolution is produced by the ethoxy derivative Pt cocatalyst, HCa₃Nb₂O₈EtOH/Pt, in different of n-alkoxy derivatives. The apparent quantum efficiency in the 220–350 nm region is 20.6 percent. Using precalcined Nb₂O₅, CaO, and K₂CO₃ as starting materials, the alkaline layered perovksite-like niobate KCa₃Nb₂O₈ (KCN₃) could be created using the traditional ceramic process. The alkxy derivatives (R) are synthesized by grafting the corresponding alcohols into HCN₃·yH₂O interlayer space. The crystallinity of the samples and stability was confirmed by TGA (Fig. 18a, b). The organic alteration has been proved to be a successful method of increasing the niobates photocatalytic behaviour for light-driven hydrogen evolution using aqueous methanol.

The results indicate high efficiency of niobates for hydrogen generation from aqueous methanol using solar radiatins has achieved because of the organic modification. The hybrid samples seem to be unstable under photocatalytic conditions, and the organic counterpart undergoes degradation during the reaction. Demetra S. Achilleos et al. (2020) reported a process that uses carbon dots (CDs) synthesised using calcination of cellulose, commercial precursors like aspartic acid or citric acid as photocatalyst which absorbs light for lignocellulose conversion into hydrogen and other organic components (Fig. 19). The photocatalytic system operates in ambient pH (2-8) at mild pressure and temperature. Carbon dots may be directly generated from biomass in a sustainable synthesis, and their solubility makes them compatible with insoluble biomass substrates.

They also have good photophysical features, such as a large proportion of long-lived charge carriers and the ability to quench light both reductively and oxidatively. The homogeneous carbon dots are synthesized via scalable and controlled calcination of cellulose or using citric acid and aspartic acid as commercial precursors for biomass PR. The nonpoisonous, compatible CDs and Ni bis(diphosphine) [cocatalyst] are used as light absorbers. The highest hydrogen production is shown by galactose (8.8±0.2 μmol) and glycerol (8.5±0.1 μmol) (Fig. 19b) after 24h reaction. The turnover numbers of NiP (TON) are 177±4 and 170±2, respectively. The EDTA is used as the sacrificial agent. These metal-free systems could preserve their photocatalytic activity even in untreated seawater. This opens up new possibilities for the creation of energy-independent and zero-carbon society.  

Beltram et al. (2016) showed the evolution of hydrogen from light and biomass derived alcohols using hierarchical MWCNTs / Pd-TiO₂ hybrid catalytic material. CNTs have been emerging as an active support in large number of catalytic reactions because of their optical, electronic, and thermal properties. The recent improvement includes usage of titanium oxide and carbon nanotubes (CNTs) to produce inorganic nanocarbon material with higher efficiency. In photocatalytic reactions, studies show that CNTs as good material
which can take away the photoexcited electrons and reduces recombination of charge thereby increasing the speed of the reaction.

The work is carried out using functional MWCNTs, Pd nanoparticles, and TiO$_2$ on photo-reforming of ethanol and glycerol using simulated sunlight radiation. The inorganic-nanocarbon hybrid is synthesized using benzoic acid functionalized MWCNTs, palladium nanoparticles with mercapto-undecanoic acid and titanium tetra (n- butoxide).

The insitu formed diazonium salt of benzoic acid is radically added which is used to access nanotube blocks (Fig. 21a). THF solution of Ti(n-OBu)$_4$ is added to Pd-MUA obtain Pd-TiO$_2$ precursors (Fig. 21b). Hydrolysis with water or THF and followed by calcination gives CNTs/Pd-TiO$_2$ (Fig. 21c). The hydrogen yield is reported when ethanol is used for 20-CNTs/Pd-TiO$_2$ and 10-CNTs/Pd-TiO$_2$ is 120 mmol g$^{-1}$ cat h$^{-1}$ and 14 mmol g$^{-1}$ cat h$^{-1}$ respectively. Quantum efficiency (QE) of 10-CNTs/Pd-TiO$_2$ and 20-CNTs/Pd-TiO$_2$ are 17% and 21% respectively at 365 nm, it shows decent photocatalytic efficiency of the material. In case of glycerol, lower hydrogen production is observed in case of both the catalyst. The performance is 95 mmol/g$^{-1}$ cat h and 149 mmol/g$^{-1}$ cat h, respectively. The hydrogen produced in the reaction by H$^+$ reduction by the electrons, from the TiO$_2$ conduction band and are transferred to Pd nanoparticles in which they undergo further reaction (Fig. 22). The catalyst is found to be stable for over 24 hr.  

Alicia Moya et al. (2015) has reported hydrogen evolution using mesoporous CNT-TiO$_2$ composite. The hybrid material synthesized by using electrospinning and sol–gel methods showcase a mesoporous structure of crystalline, interlinked inorganic nanoparticles (Fig. 21 a-c). This features a novel synthesis technique in which a large suitable polymer links the sol and the nanocarbons in the compound before calcination, and the polymer is removed by annealing the fibres in air, causing the sol to densify into a porous network of interconnected TiO$_2$ particles. The photocatalytic activity is studies using ox-CNT-TiO$_2$ material, electron spun TiO$_2$ nanofibres and TiO$_2$ nanoparticles which produces a hydrogen evolution of 1218.5, 880 and 88.2 µmol/h respectively using Pt as cocatalyst under UV radiation. The oxygen vacancies and interface in the material has a crucial part in the structural evolution of the electron spin sample. The oxygen vacancies and interface in the material has a crucial part in the structural evolution of the electron spin sample.
A proposed method for $\text{H}_2$ synthesis with simultaneous scavenging of photogenerated holes by alcohol is schematically represented. Copyright 2016, Green Chemistry.

The sample shows higher activity due to the presence of oxygen vacancies, the catalyst has a mesoporous structure of interlinked nanocrystals with a large $\text{TiO}_2$ – $\text{TiO}_2$ interface to enhance charge transfer, and CNTs hybridised with $\text{TiO}_2$ nanocrystals to form a metal semiconductor junction with CNTs acting as electron acceptors, which improves charge separation and stability.

3.4 Biomass Derived Substrates

The hydrogen production from water splitting in ambient conditions using solar radiation is considered as the cheapest, efficient and eco-friendly means of fuel production. On the other hand, the biomass forms an alternative substrate for the photoreduction to form hydrogen with the addition of value-added chemicals. The use of raw material biomass is hardly explored in photocatalytic hydrogen production, but biomass derivatives are widely used as substrates for the same purpose. The remaining part of the review will focus on the feasibility and potential of biomass derivatives such as monomeric substrates for the photocatalytic hydrogen synthesis using OIH materials. Numerous monomeric substrates from industrial and agricultural processing can be used to serve as the feedstock of the photoreforming mechanism. This mainly includes the glycerol, methanol and ethanol which is produced via different mechanisms such as biofuel production, syngas production and sugar fermentation respectively. The future objective of the scientist community is to head towards a green chemistry approach where the reaction substrates are expected to be produced from non-energy intensive sources or non-fossil fuels. The substrates which are most reliable and promising for the photocatalytic hydrogen production are aldehydes, alcohols, amines and acids. The use of sacrificial agents is widely used in the photocatalytic hydrogen productions in aqueous solutions. The works about photocatalytic hydrogen production is commonly mentioned via a generic term ‘water splitting’ in publications, which will be methanol or ethanol or any other biomass derivatives as sacrificial agent in the aqueous media for the reaction. Taking into account those works which deals with oxygenated organic substrates derived from the biomass. Even though greater efficiency has been obtained in the field of photoreforming, this area not really explored as a source of hydrogen production. The use of biomass derivatives as substrates in the photoreforming mechanism will be briefly analysed in the following section.

![Fig. 22](image-url)
1) lattice fringe and the tight interface across nanocrystals of anatase. and (e) CNT hybridized with nanocrystals of TiO$_2$.Copyright 2015, Applied Catalysis B: Environmental.

Claudia G. Silva et al. (2014) reported the photocatalytic hydrogen production from methanol and saccharides by using carbon nanotubes-TiO$_2$ catalysts. CNT-TiO$_2$ catalyst was synthesized using a composite procedure. The one pot method consisting of oxidation of CNT and preparation of composite leads to the development of materials having efficient productivity due to the good interaction between TiO$_2$ and CNT interface. Incipient wetness method is used to incorporate Pt, Au, Pd and Ir nanoparticles in (TiO$_2$ and CNT-TiO$_2$)ox. The activity is higher in metal loaded catalysts than those non-loaded catalysts. This can be explained by the low overpotential for hydrogen production on metal added photocatalyst than the bare catalysts. The material treated at higher temperature (673 K) shows higher efficiency than those at low temperature (473 K) because the metal particles are sintered and the metal support interface is stronger. The highest yield is obtained for the Pt/(CNT-TiO$_2$)ox catalyst for hydrogen production of 30.6 μmol in water/methanol solutions (Fig. 24). Saccharides are effective sacrificial donors for HER. It is observed that the efficiency of hydrogen generation with Pt/(CNT-TiO$_2$)ox increases with the decreasing complex molecular structure of saccharides. The electrons from TiO$_2$ and CNT are expected to be photoexcited. Electrons from VB are excited to CB of TiO$_2$, then transferred to Pt nanoparticles to generate H$_2$. The high contribution of water proton reduction on the metal particle surface is credited with superior activity in case of fructose, glucose and cellulobiase solutions.

G. Nagaraju et al. (2015) reported photocatalytic water splitting using TiO$_2$-reduced graphene oxide (RGO) photocatalyst via ionothermal method by functionalist ionic liquid. The characterization data of the composite proven that the TiO$_2$ nanoparticles are placed onto the graphene sheets surface (Fig. 25). The reaction is carried out in water and ethanol solution using TiO$_2$-RGO composites. The reaction is carried out in water and ethanol solution using TiO$_2$-RGO composites. The hydrogen yield is given as 3.0 mmol/g through water splitting which is more than the performance of the pristine TiO$_2$ particles. The yield enhancement is described using the synergetic effect of reduced graphene oxide.

The suppression of charge recombination and the improvement in the activity is also due to the electron accepting and electron accepting properties of graphene in the composites.

Miyuki Ikeda et al. (2006) reported the hydrogen evolution using water and methanol mixture with mixture of TiO$_2$ and graphitic silica. A synergic effect on the production of hydrogen is obtained from GS and TiO$_2$ from water methanol mixtures. This synergic effect has been studied by evaluating the hydrogen evolution with different composites of TiO$_2$ using bare GS, SiO$_2$, calcined GS, clay from GS, activated carbon and quartz from GS. It is found that the synergic effect is due to increase of ions of hydrogen in the clay components of GS and accumulation of GS and TiO$_2$ (Fig. 26a). The highest rate of hydrogen production is reported as 22.3 μmol/h, and this rate has been obtained at a GS composition of 50 wt.%., but pure TiO$_2$ or GS give just 0.23 and 0.03 μmol/h (Fig. 26b).

Sundaram Ganesh Babu et al. (2015) reported scalable and economic synthesis of reduced graphene oxide (RGO) with Cu$_2$O-TiO$_2$ composite (surfactant free) catalyst via wet impregnation method aided by ultrasound. The UV-DRS spectroscopical studies show that the incorporation of Cu$_2$O brings a change in the band gap from 3.21 eV to 2.87 eV. The HER is studied in presence of glycerol (sacrificial agent) under visible light.
The incorporation of RGO increases the mobility of Cu$_2$O-TiO$_2$/RGO. The hydrogen evolution rate is 110968 μmol/g/h when 1.0% Cu and 3.0% graphene oxide is used, which is more than that of the previously studied graphene-based photocatalysts. The RGO enhances the efficiency of the photocatalyst compared to bare TiO$_2$ and Cu$_2$O-TiO$_2$, by a factor of 14% and 7% respectively.

Luna Tie et al. (2020) were able to construct a photocatalyst with graphene oxide in microsphere ZnS, which delivered a higher productivity of hydrogen evolution. The preparation of Pt/GO-ZnS photocatalyst could be achieved via two steps: the hydrothermal synthesis of ZnS, followed by the deposition of GO and Pt through in situ mechanism. The combination of ZnS with GO and Pt nanoparticles is a stepwise depositing process as described in the Fig. 28a. The HER is carried out via water splitting with lactic acid as scavenger using 300 W Xe lamp. The results show that the incorporation of GO sheets and Pt nanoparticles improves the efficiency of the catalyst. The improved yield of Pt/GO-ZnS was because of the efficient charge separation and higher visible range absorption, which is credited to the synergetic effects of GO and Pt nanoparticles. The exited electrons in the CB of ZnS are transferred instantly by GO and are transferred to the Pt nanoparticles. The interface is responsible for the smooth mechanism. (Fig. 28b). The catalyst exhibits an yield of 1082 μmol g$^{-1}$ h$^{-1}$ of hydrogen which is much higher than the pristine ZnS catalyst (Fig. 28c).

Yidong Hou et al. (2013) carried out hydrogen evolution reaction using MoS$_2$ with mesoporous graphitic carbon nitride nanojunction. The construction of OIH with MoS$_2$ and g-CN heterojunction is carried out via in situ growth method, which involves both impregnation and sulfidation (Fig. 29a). The structure of MoS$_2$ is similar to that of graphite, this will minimize the lattice difference and MoS$_2$ can be easily grown above the g-CN surface. This kind of arrangement has a few benefits, such as it can increase the accessible space about the interface and reduces the electron transport barrier through the cocatalyst.
depicts the proposed reaction mechanism of photoreforming. This work depicts innovative strategy to control the carbon quantum dots particle size to carry out metal free photocatalysis. Hydrogen production using biomass with organic inorganic hybrid materials and its derivatives are represented in Table 1.

![Image](14x290 to 26x354)

**Fig. 30** a) Illustration of the photoreforming reaction mechanism, b) photocatalysis hydrogen evolution production for the various composites.

### 4. Perspective and Conclusions

The article deals with the recent developments and scopes of organic inorganic hybrid (OIH) materials in the photo-reforming of biomass and its derivatives. The unavailability of efficient and stable photocatalytic materials for various applications in research area is a major barrier for the innovative and effective research work. Although different types of photocatalytic materials, such as inorganic semiconductors, metal oxides, sulphides, polymers, are widely used in the hydrogen evolution reaction, the class of organic inorganic hybrid materials has been deeply studied in the last few decades. The material used for photocatalytic reactions should possess certain features such as abundant active sites, high surface area, good charge transfer and band structure tunability for the efficient productivity of the hydrogen. The class of OIH material is gaining good attention in the photocatalytic studies due to its stable photocatalytic materials for various applications in the field of research. The stimulation of photocatalyst materials. This can be used to study band structure, charge density and band structure of the photocatalyst. The accurate results regarding the material properties can be obtained by increasing the thickness of the material slab in the simulations, resulting in increasing the computational cost. Machine learning (ML) also one of the developing technology, which used computational algorithms to convert empirical data to usable models. The coupling of photocatalysis domain with ML can pave a way for the growth of catalyst materials. The development of ML models with the existing ideas can lead a pathway to find efficient photocatalysts. It involves the integration of prior theoretical and empirical knowledge to models and use the available data to predict the results. The shortage of reliable data and difficulty in collecting new data’s main challenges in ML. Big data analysis also a similar method which used bibliometric reports on a particular research topic and provide scientific and theoretical information to the scientific community. An information regarding the previous studies conducted in a particular topic results are collected and combined as a database. The difficulty in finding credible and authentic data has the main issue related to big data analysis. Recently, artificial intelligence (AI) also came into this scenario for prediction and stimulation of photocatalyst materials. This can be used to identify various interactive influence of parameters and finding optimum strategy to obtain maximum efficiency of material. The ability of AI to predict without having perfect and complete information and pattern recognition ability can be widely explored the field of research.
computational methods are in initial stage of their growth and should explored deeply to bring out a correlation between the technology and research. On the other hand, we should find a way to overcome the challenges such as difficulty in modelling, collection reliable raw data and computational cost. The growing arena of computation and technology can be well utilized for the effective prediction of stable and productive photocatalyst materials. Hydrogen production and chemical fuels using water is one of the growing research areas in the latest decade. Photon catalytic method is probably the most economical means of hydrogen production compared to other methods such as electro-catalysis, gasification, and pyrolysis. The photocatalytic method of producing hydrogen is getting a great attention and is widely obtained by splitting of water. The same method can be used for water production using biomass as the substrate. This is an effective step to convert waste into valuable fuels. This can be carried out via the photo-reforming of sucrose, glucose, starch, and other biomass derivatives. H2 generation from renewable biomass presents an appealing possibility to fully realize the economic advantages of H2 as a fuel. The photoreforming of biomass substrates has proven thermodynamic and kinetic advantages over the water splitting photoreaction. Still this method is not fully explored by the research community yet. Different photocatalysts have been developed and improved for higher efficiency and stability. OIH materials involves photocatalyst based on carbon nitrate, graphitic oxide, quantum dots, which have been discussed in this review. Still, metal-organic frameworks and covalent organic frameworks are not efficiently used for the hydrogen production from biomass and its substrates. However, the production of usable organics has been already successfully carried out by MOF functional materials. This showcases the wide range of opportunities available for the photocatalytic hydrogen production using OIH materials using biomass and its substrates. Apart from the challenges, biomass photoreforming can be considered as an emerging technology which can influence the production green hydrogen and sustainable method for valuable chemical production. The future work shall focus on designing an efficient, selective and stable hybrid material with appropriate band gap for PR of biomass under sunlight, still under development. It is also an important to use of earth abundant elements as a cocatalyst for better efficiency. The overall objective is to find an efficient, eco-friendly photocatalyst with lower driving force and produces H2 in large scale using raw biomass materials. The ultimate aim is to use photoreforming to produce more valuable chemicals by the use of lower energy radiations which is not suitable for water splitting reactions. This can be an efficient pathway to use photoreforming mechanism for commercial and economical aspects. Although it’s a long journey, we can expect the future works can be based on these ideas and gaps to prepare suitable photocatalytic OIH materials for different applications. Photocatalysis provides potential pathway to substitute the energy consuming method of thermal reforming of biomass to produce hydrogen from solar energy. As hydrogen is renewable, energy efficient source of energy, and it has all sorts of possibility to the future green fuel. A strategy to produce hydrogen in a sustainable, efficient and pollution free method should be developed, photoreforming of biomass using solar energy can be considered as a possible solution.

Fig. 32 Schematic illustration of biomass photoreforming, benefits and challenges.

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Author contributions


Conflicts of interest

There are no conflicts to declare.
<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Photocatalyst</th>
<th>Substrate</th>
<th>Light Source</th>
<th>Reaction Solution</th>
<th>H$_2$ Production rate</th>
<th>AQE</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt/C$_3$N$_4$-TiO$_2$</td>
<td>Triethanolamine</td>
<td>250W, visible light radiation</td>
<td>10 wt.% of TEOA + 3 wt.% Pt</td>
<td>1042 µmol/g/h</td>
<td>-</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>Poly(3-hexylthiophene)/g- C$_3$N$_4$</td>
<td>Triethanolamine</td>
<td>300 W, Xe lamp 420 nm</td>
<td>3 wt.% Catalyst + 1 wt% Pt</td>
<td>320 µmol/h</td>
<td>-</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>Poly(3-hexylthiophene)/g- C$_3$N$_4$</td>
<td>Ethylenediamine tetra-acetic acid</td>
<td>300 W, Xe lamp 420 nm</td>
<td>3 wt.% Catalyst + 1 wt% Pt</td>
<td>44 µmol/h</td>
<td>-</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>Poly(3-hexylthiophene)/g- C$_3$N$_4$</td>
<td>Ascorbic acid</td>
<td>300 W, Xe lamp 500 nm</td>
<td>3 wt.% Catalyst + 1 wt% Pt</td>
<td>3045 µmol/h</td>
<td>59.4</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>Pt/Holey carbon nitride-N-acetylamide</td>
<td>Triethanolamine</td>
<td>300 W, Xe lamp 420 nm</td>
<td>0.8 wt.% Pt, 30 mg catalyst</td>
<td>22043 µmol/g/h</td>
<td>41.2</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>Cu-Ni/o-g-C$_3$N$_4$</td>
<td>Brewery/Dairy effluent 50</td>
<td>Solar Simulator</td>
<td>1-5 wt.% Cu-Ni + starch solution</td>
<td>912 µmol/g/h</td>
<td>-</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>Pt/o-g-C$_3$N$_4$</td>
<td>Brewery/Dairy effluent 50</td>
<td>Solar Simulator</td>
<td>3 wt.% Pt + starch soln</td>
<td>1170 µmol/g/h</td>
<td>-</td>
<td>89</td>
</tr>
<tr>
<td>#</td>
<td>Reactants</td>
<td>Products</td>
<td>Reaction Conditions</td>
<td>Catalyst</td>
<td>Yield</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>---</td>
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<td>---------</td>
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<td>-----------</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>CoO/g-C$_3$N$_4$</td>
<td>Wheat straw</td>
<td>300 W, Xe lamp</td>
<td>1.7 wt.% Co + cellulose</td>
<td>178 µmol/g/h</td>
<td>90</td>
<td></td>
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<tr>
<td>9</td>
<td>ZnS-C$_3$N$_4$</td>
<td>Glucose</td>
<td>300 W, Xe Lamp</td>
<td>1 wt.% Pt + glucose</td>
<td>210 µmol/g/h</td>
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<tr>
<td>10</td>
<td>Mn-MOF-Au</td>
<td>TEA</td>
<td>300 W, Xe Lamp</td>
<td>Pt + TEA</td>
<td>576 µmol/g/h</td>
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<tr>
<td>11</td>
<td>HCa$_3$Nb$<em>5$O$</em>{12}$ROH</td>
<td>methanol</td>
<td>125 W, Hg tube lamp</td>
<td>Pt +1 wt.% methanol</td>
<td>500 µmol/g/h</td>
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<tr>
<td>12</td>
<td>Cellulose -CDs</td>
<td>lignocellulose</td>
<td>-</td>
<td>NiP + 0.1 M EDTA</td>
<td>13450 µmol/g/h</td>
<td>97</td>
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<tr>
<td>13</td>
<td>MWCNTs / Pd- TiO$_2$</td>
<td>ethanol</td>
<td>150 W, Xe Lamp</td>
<td>Pd + ethanol</td>
<td>120 mmol/g/h</td>
<td>98</td>
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<tr>
<td>14</td>
<td>oxCNT-TiO$_2$</td>
<td>methanol</td>
<td>200 W, Hg tube lamp</td>
<td>0.5 wt.% Pt + methanol</td>
<td>1218 mmol/g/h</td>
<td>99</td>
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<tr>
<td>15</td>
<td>oxCNT-TiO$_2$</td>
<td>saccharides</td>
<td>-</td>
<td>Pt + methanol</td>
<td>30.6 µmol</td>
<td>100</td>
<td></td>
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<tr>
<td>16</td>
<td>TiO$_2$ - RGO</td>
<td>ethanol</td>
<td>-</td>
<td>Water + ethanol</td>
<td>3.0 mmol/g</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>TiO$_2$ - graphitic silica</td>
<td>methanol</td>
<td>-</td>
<td>Methanol + water</td>
<td>22.3 µmol/h</td>
<td>102</td>
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<tr>
<td>18</td>
<td>Cu$_2$O-TiO$_2$ / RGO</td>
<td>glycerol</td>
<td>250 W, Xe Lamp</td>
<td>Glycerol + water</td>
<td>110968 µmol/g/h</td>
<td>103</td>
<td></td>
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<tr>
<td>19</td>
<td>GO-ZnS</td>
<td>lactic acid</td>
<td>300 W, Xe lamp</td>
<td>lactic acid + water</td>
<td>1082 µmol/g/h</td>
<td>104</td>
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<tr>
<td>20</td>
<td>The MoS$_2$/mpg-CN</td>
<td>Lactic acid</td>
<td>-</td>
<td>Lactic acid + water</td>
<td>20.6 µmol/h</td>
<td>105</td>
<td></td>
</tr>
</tbody>
</table>
21 CDs - TiO$_2$ methanol 300W, Xe lamp Methanol + water 2.43 mmol/h
References

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