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The emerging role of biochar in the carbon materials family for hydrogen production

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Abstract

The energy crisis is at the top of global priorities. It left us with an option to progress with highly efficient materials for energy conversion, production, and storage systems. Carbon nano-allotropes have more accessible, and modifiable surface with excellent surface area, conductivity, catalytic activity, and other features. Biochar synthesized from renewable organic material viz. biomass (plants, animal waste), has beneficial physicochemical features (surface functionalities, porosity, adsorption capacity, etc.) and agronomic properties. They are influenced by several factors like the type of thermal treatment and feedstocks. Modification of biochar is an excellent option to obtain synergistic effects and sustainable materials. The current comprehensive review article will focus on biochar, selected nanocarbons (fullerene, carbon dots, nanotubes, nanodiamonds, graphene, and graphdiyne), and their hybrids for hydrogen evolution. Particular emphasis will be on biochar as these materials could be easily generated from different wastes. **Biochar can have graphitized or non-graphitized carbon atoms. They can have carbon fragments resembling fullerene. This can be a potential low cost biocarbon alternative to graphene and fullerene and we are well aware of the importance of graphene and fullerene.**

Future projections in this paper may lead to an added foundation for “trash to treasure”/ “waste to wealth” and “waste to fuel” research and also contributes towards real-world applications in the clean fuel and sustainable energy sector.

Keywords: Carbon allotropes; Nanohybrid; Trash to treasure; Sustainable development; (Photo)catalysis; Green carbon.

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1. Introduction and Scope of the Review

A list of ten world's problems includes (i) energy, (ii) water, (iii) food, (iv) environment, (v) poverty, (vi) terrorism and war, (vii) disease, (viii) education, (ix) democracy, and (x) population in which energy is on the top. Energy can play a significant role in solving all of the mentioned issues [1]. When it comes to clean fuel and energy, hydrogen production and storage come into the picture. In view of functional material commercialization, several parameters must be addressed, such as reproducibility, ease of synthesis, toxicity, abundance of precursors, cost-effectiveness, stability and recyclability [2].

A carbon atom can exist in sp , sp^2 , and sp^3 hybridizations [3,4]. There are numerous carbon allotropes (Figure 1), such as graphite, diamond, fullerene, carbon nanotubes (CNTs), graphene, carbon nanohorns (CNHs) and carbon nanooxions (CNOs). Biochar is an amorphous, carbon-rich porous material [5], obtained by thermochemical treatment of the biomass, and which could be ranked among the large carbon allotrope series. The latter can be employed as such, chemically/physically modified or hybridized with other materials. They possess fascinating high surface area, electrical and thermal conductivity, catalytic activity and chemical stability [4]. For these reasons, they are utilized in several fields, including the energy sector [6], encompassing heterogeneous catalytic hydrogen production needed to meet the demand for a greener 21st century [7].

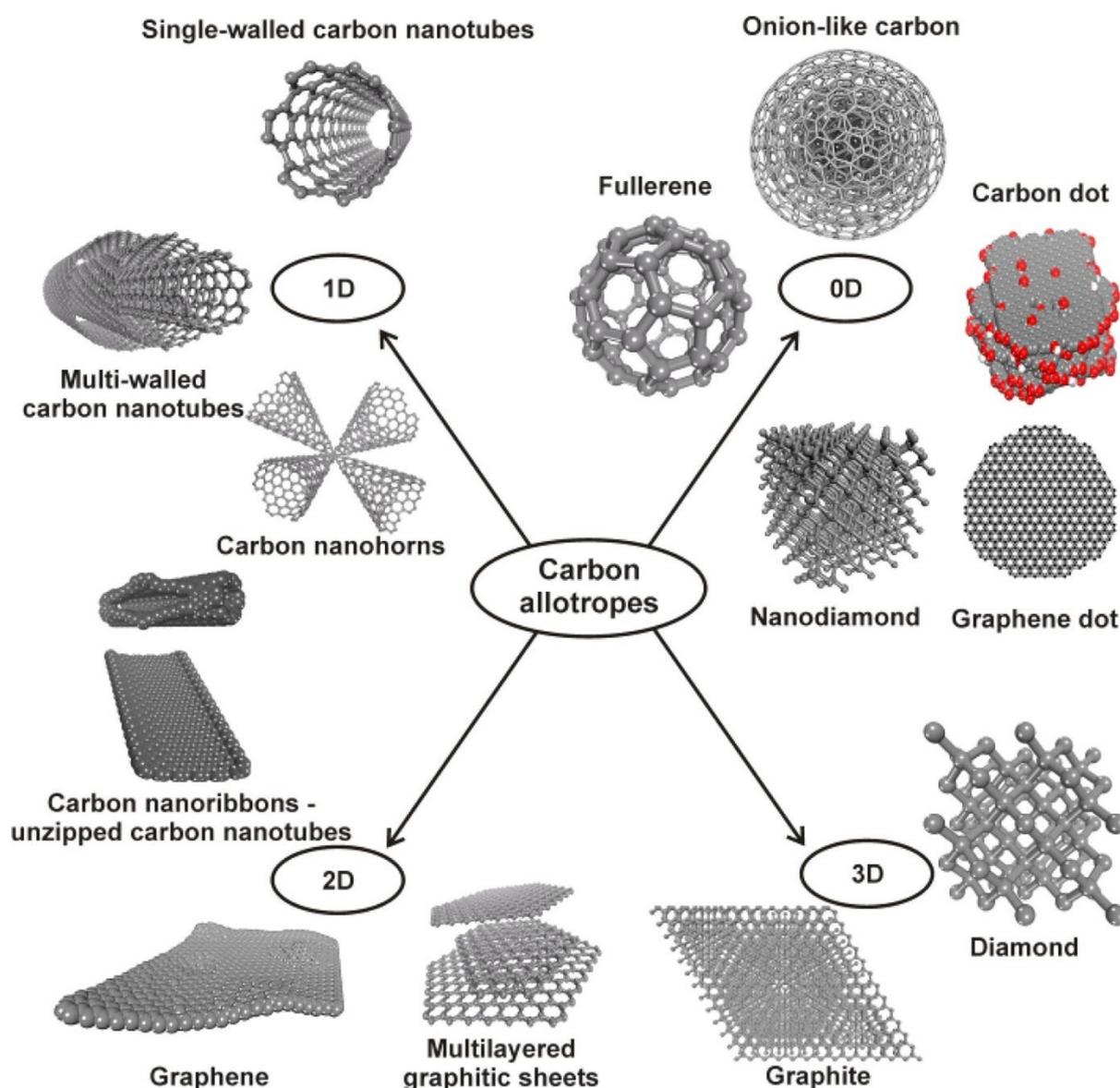


Figure 1: Different carbon allotropes. Reprinted from the reference [4] under ACS Author Choice.

From the economic and environment point of view, it is interesting to utilize wastes as sources of carbon (nano)materials [8] which can be used for several applications [9,10]. In this regard, biochar is today's emerging important carbonaceous material, and synthesized via thermochemical process (in the absence (pyrolysis) or presence of limited O₂) using biomass derived from *e.g.* plants and animals wastes [11,12]. It is a representative of a "trash to treasure" [13] or "waste to wealth" and/ or "waste to fuels" [14] concept. It is also an excellent example of accomplishing a "circular bioeconomy" [15,16]. Biochar shows unique chemical (high pH, carbon sequestration, cation exchange capacity, nutrient exchange site, and surface

functionalities: C=O, -COOH, -R-OH, and OH), physical (high porosity, water holding capacity, surface area, and surface charge), and agronomic (nutrients, salinity, etc.) properties [11,17–24]. Biochars were utilized in many fields including the green hydrogen generation [25].

Figure 2 plots the number of publications on carbon materials with particular emphasis on biochar for hydrogen production. Whilst hydrogen production using carbon is known for decades, the takeoff of research on biochar for hydrogen production dates back to 2005. According to the web of science, 4.47% of papers on hydrogen production using carbon allotropes in 2021 were dedicated to biochar, that is about ten-fold the 0.49% in 2011. In one-decade, remarkable interest has been expressed by materials scientists in the domain of hydrogen production using biochar.

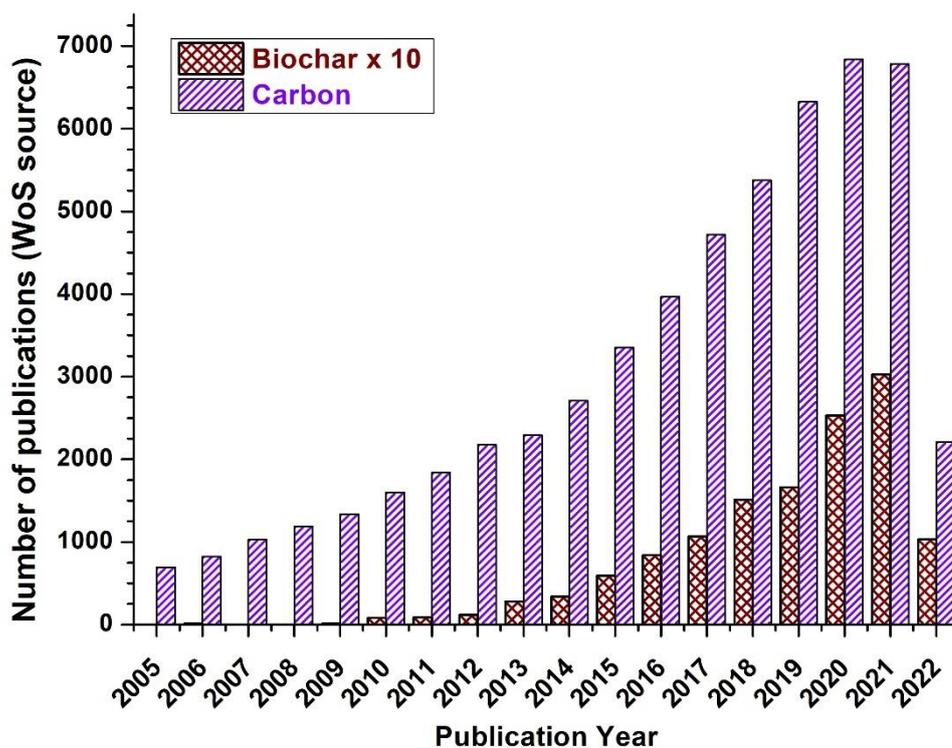


Figure 2: Plot of publication year of papers published in the field of biochar and carbon materials for hydrogen production vs number of publication. For biochar data, it is multiplied by ten times.

A thorough literature survey has been carried out to explore the recent findings related to biochar and carbon allotropes for hydrogen production. We have first screened the literature and hand-picked available reviews, gathered in Table 1. It features the variety of carbon materials and their hybrids utilized for H₂ evolution. Some articles deal with only one type of allotropes such as graphene and related materials, whereas some focus on a few carbon allotropes. They lack detailed information on the recent update in which biochar, nanocarbon, nanoparticles and their hybrids are discussed together in the single article specifically to hydrogen production. Some of them deal with several relevant applications, for example energy and the environment. There are also contributions describing the broad family of carbon nano-allotropes and their classifications; however, they do not tackle hydrogen production. As far as papers dedicated to hydrogen production are concerned, they deal with nanoparticles, but most are not focused exclusively on the broad series of carbon nano-allotropes. This created a literature gap in this field.

Table 1. Hand-picked published reviews having the concept of biochar and carbon nanomaterials for energy storage and production.

Running title	Scope and main lines of the review	Year [ref.]
Recent advancement on the sustainable biochar	Photocatalytic applications of biochar based semiconducting materials.	2022 [26]
Hydrogen production from water splitting	Carbonaceous photocatalyst (graphene, graphite, carbon nanotubes, activated carbon), non-carbonaceous photocatalyst, co-catalyst, sacrificial agents, and the factors affecting photocatalytic reactivity.	2022 [27]
Electrochemical energy storage electrodes	Rice biomass waste valorization (biochar) for electrochemical energy storage.	2022 [28]
Graphdiyne based catalysts for energy	GDY electronic structures and fundamental lattice. Graphdiyne-based energy storage materials and electrocatalyst.	2021 [29]
Biochar-based composites as electrode	Chemically and physically treated biochar-based hybrids and comparison of their electrochemical performance specifically in the energy storage system.	2020 [30]
Recent advances in electrocatalytic hydrogen evolution	Metal (noble metals, non-noble metals & alloys), non-noble metal compounds (transition metal oxides, nitrides, dichalcogenides, phosphides, carbides, and borides), and metal-free hydrogen evolution reaction electrocatalyst.	2020 [31]
Low dimensional carbon-based catalysts	Graphene, GO/rGO, graphitic carbon nitride, and graphene quantum sheets or dots for H ₂ O splitting through photo/electrochemical and photo-catalytically.	2020 [32]
Emerging applications of biochar-based materials	Energy conversion and storage (fuel cell, batteries, H ₂ generation and storage, supercapacitors, and oxygen electrocatalysts.) in biochar related materials.	2019 [33]
Carbon-based nanomaterials/allotropes:	Synthesis, properties, and application (biomedical and electrochemical energy storage) of different carbon materials. It includes the discussion about carbon derived from biomass also.	2018 [34]

Nasir *et al.* [34] focused on carbon allotropes and carbon-based materials for biomedical and energy storage applications. The authors consider the topic of biomass-derived carbon. Here, more focus is on the historical chemical background, synthesis, and properties, but the application (energy storage) is described briefly. To the best of our knowledge, no review has summarized the recent advancements in applying both biochar and the broad family of nanocarbons for H₂ production via different processes, hence the motivation for this contribution. It is significant to indicate that a recent review by Reza *et al.* [27] has taken into account nanocarbon and activated carbon, but it focused on a few carbon allotropes (graphene, graphite, CNTs, and activated carbon). Bhavani *et al.* [26] have discussed the role of biochar in photo-catalytic applications.

Herein, we discuss recent progress on biochar, different carbon forms like 0D (fullerene), 1D (CNTs), 2D (graphene, and graphdiyne) and 3D (nanodiamonds) and their hybrids for hydrogen (H₂) production. The cited literature is mostly from 2018-2022. For the sake of simplicity, detailed production methods of carbon nano-allotropes are not discussed in this review article.

The scope of this review article is the carbon-based materials for hydrogen generation using different techniques with a particular emphasis placed on the biochar production, structure, and its application in the hydrogen generation.

We aim at fulfilling the gap using both carbon nano-allotropes and biochar in the energy production sector, more specifically hydrogen (green fuel) synthesis. In addition, a comparative study has been carried out between biochar and other carbon allotropes in terms of hydrogen production efficiency. Finally, the future of using biochar is highlighted. We will finish by future perspectives and conclusions.

2. Different Methods of Hydrogen Production

Hydrogen is considered the third most plentiful element on Earth. Due to its unavailability in pure form, it is not an energy source but an energy carrier synthesized from other sources. Fascinatingly, it is denoted by several colors depending on its production methodology such as grey (or brown/black), blue, turquoise, green, and yellow (or purple) hydrogen. Further, hydrogen is also termed renewable hydrogen / clean hydrogen/ low-carbon hydrogen [35]. H₂ can be generated from fossil fuels, H₂O, and waste [36,37]. Solar water splitting [38] can be an

efficient method for a vast quantity of hydrogen production [39]. The process involving H₂O dissociation into H₂ (HER) and O₂ (OER), electrocatalytically is called electrolysis. The following equation describes this process [40]:



Reaction at cathode (HER):



Reaction at anode (OER):



The scheme indicating photocatalytic water splitting is shown in [41]. Regarding the green hydrogen (*i.e.* hydrogen produced without the use of fossil fuels), the solar water splitting, the photo-reforming or the photo-electrocatalysis can be fascinating routes to obtain hydrogen in a sustainable way. In particular, with the photo-catalytic solar water splitting, a crucial renewable source such as the solar energy is valorized and the use of semiconductors efficiently designed for the solar light harvesting allowed a promising H₂ yields [42,43]. The photo-reforming reaction is another valuable strategy that provides the addition into the water of a little amount of an organic compound that acts as holes scavenger avoiding in this way the photoelectrons/holes recombination (generated during the photocatalytic process on the surface of the photocatalyst) that is a common reason of the photo-catalyst deactivation [44,45]. With the photo-reforming process it is possible to increase the sustainability of the process with the use of different green scavengers as bio-alcohols, the glycerol or, also carbohydrates such as glucose [46–48].

Finally, the photo-electrocatalysis (PEC) process, similarly to photocatalysis, provides the use of 2 photo-active semiconductor electrodes such as: *n*-type (photo-anode) and *p*-type (photo-cathode). It is possible to excite it by photons (energy levels \geq band gaps). A constant bias potential / a appropriate constant current supplied to a semiconductor anode are applied in solar / UV-vis facilitated electrocatalysis. This is to facilitate photo-induced e⁻s movement towards an external electrical circuit continuously. The external potential enhances the charge carrier separation on the electrodes surface via photogenerated enabled charge-transfer reactions on

the semiconductor surface. Compared to the bare photocatalysis a higher H₂ yield was detected with this multi catalytic approach [49,50].

When compared to various methods of hydrogen production (gasification, steam reforming, dark-fermentation, pyrolysis, and photo-biolysis), water electrolysis has a definite advantage of using H₂O (feedstock) which is clean and readily available. As a matter of fact, the product of electrolysis is pollution-free which is very important for sustainable development [51].

It is with no surprise that even just biomass is involved in hydrogen production through microalgae as shown in reference [52]. **Nanocarbon** derived from biomass is a potential candidate for futuristic energy devices (energy storage and conversion) [53,54]. For example, human hair waste biomass is a source of activated-carbon nano-bundles (partially graphitized) for HER [55]. It is also possible to produce nanocarbon and hydrogen from the common **plastic waste** [56].

Physical and chemical modifications of carbon allotropes were shown to be important when it comes to hydrogen production. This can be well understood by the example of graphene. Pristine graphene (flat **material**) is catalytically inactive for **HER** and their curvature strongly affects the HER performances positively [57]. It is to note that their modifications, provide them with some unusual properties [58,59]. Also, modifications are considered for unbundling carbon nanotubes [60], exfoliating graphene [61] or dispersing nanodiamonds, 0D carbons such as fullerenes [62].

3. Application of **Carbon Allotropes for Hydrogen Production**

In this work, we have mainly focused on the photo-catalytic hydrogen production, **with emphasis on biochar**. It is clear from the literature that **biochar could serve as a catalyst to produce hydrogen**. However, the **biochar catalytic performances increase upon activation that could be achieved via simple methods**. For example, Liu *et al.* [63] have demonstrated that **activation of biochar in H₂O (15 vol%) under Ar, increases the o-containing functional groups, mostly aromatic C-O groups, with a result of enhanced catalytic steam reforming of tar**. It is also interesting to note that **biochar incorporation in composite materials improves its thermal, mechanical and electrical properties** [64]. The presence of nitrogen and phosphorus in the biomass is reflected in the biochar composition (self-doping) as these important elements impart photocatalytic properties to the biochar in HER [65].

3.1. Fullerene

Fullerene [66] or C₆₀ resembles a soccer ball in structure. The rate of hydrogen synthesis over pristine g-C₃N₄ photocatalyst has been increased by four times after making a hybrid with C₆₀ molecule (hydrogen production rate = 266 μmol h⁻¹ g⁻¹) [67]. Water and urea splitting has been successfully carried out at fullerene quantum dot in association with sheet of CoNi layered double hydroxides present on nickel foam (porous material) [68]. In the recent years, significant advancements in the field of photocatalysis using fullerene and their derivatives for hydrogen production have been noticed [69]. In this context, there are reports on WO₃/fullerene@Ni₃B/Ni(OH)₂ [70], MoS₂ “inorganic fullerene”/TiO₂[71], fullerene-WO₃ composites [72], C₆₀/graphene/g-C₃N₄ hybrid photocatalyst [73], etc. A composite between boron carbon nitride and C₆₀ has proven outstanding performance in the electrocatalytic reduction of H⁺ ion [74], where metal-free 10% C₆₀/BCN nanohybrid synergized that the intermolecular e⁻ transfer.

3.2. Carbon Dots

Carbon dots [75,76] are considered one of the essential materials in the nanoscience world [77]. There is a debate about their specialty over fullerene. Carbon dots are remarkable e-acceptors and donors [78]. They are potential candidates for solar hydrogen production due to their excellent electrical, optoelectronic and photophysical properties [79]. It is well known that carbon dots are photoluminescent [80]. This property can be exploited to tune the wavelength to affect the hydrogen production. A case study was carried out using various modified carbon dots [81] as depicted in Figure 5. It is found that there is an enhancement in hydrogen evolution with the duration of irradiation. Maximum was found for the CD₂ sample (2g of BPEI is used in the synthesis procedure) (Figure 3a). Stability and retention of the photocatalytic efficiency is depicted through cyclic experiment (Figure 3b). Advantage of this method is that it is best suited at pH close to neutral (Figure 3c). The role of hole scavenger is shown in Figure 3d.

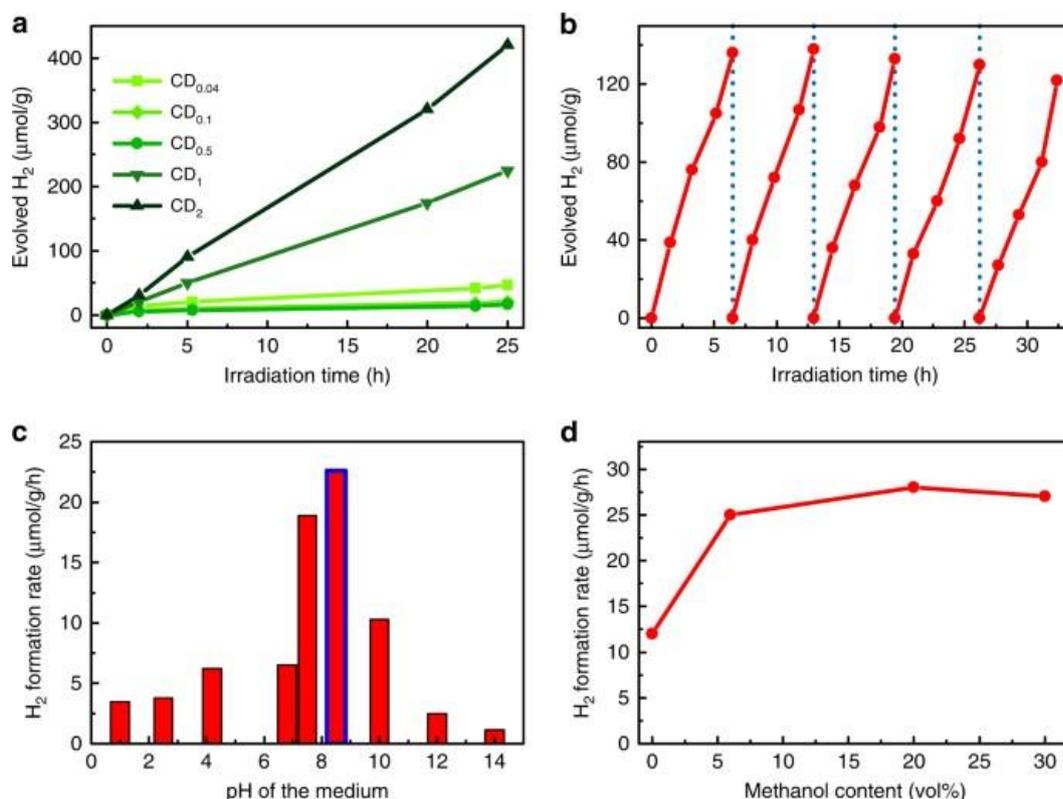


Figure 3. Photocatalytic H₂ production. (a) Xe lamp irradiated various carbon dots samples for H₂ generation, (b) 5 cycles of H₂ generation through CD₂, (c) effect of pH, and (d) effect of hole scavenger (CH₃OH). Reprinted from reference [81], © The Author(s) 2017, which is under a Creative Commons Attribution 4.0 International License.

3.3. Carbon Nanotubes

CNTs [82] are long hollow tubular cylindrical structures in shape. They possess a high surface-to-volume ratio. They have sp²-hybridized C-atom. They can be single-walled (SWCNTs), double-walled (DWCNTs), or multi-walled (MWCNTs). In the carbon materials family, CNTs continue to raise much hope worldwide, in the domain of *e.g.* electronic devices, biosensors, catalysis and nanocomposites [60,83].

SWCNT/fullerodendron/Pt(II) supramolecular nanocomposites based on a photosensitizer/co-catalyst interconnecting system have been developed, which can generate hydrogen (QY = 0.015) from H₂O in the presence of light ($\lambda = 600$ nm). In nano-coaxial photocatalysts, both chiral indices (*n*, *m*) and the individuality of these CNTs affect the photocatalytic efficiency [84]. Enhanced hydrogen synthesis was observed in the case of Mn_{0.5}Cd_{0.5}S/CNTs in which nanotubes serve as an e⁻ acceptor which inhibit the recombination

of charges and holes at this composite photocatalyst [85]. A study about the Ni/ α -Al₂O₃ catalyst for toluene reforming (for hydrogen production) has revealed that the occurrence of self-growth amorphous carbon on Ni surface decreases the activity of the catalyst by blocking the active site (reactant are not able to reach active site of the catalyst) while self-growth carbon nanotubes increase the stability and activity of the catalyst [86].

When five samples were compared for their hydrogen production efficiency, it was noticed that the combination of TiO₂, Pt, and functionalized CNTs have superior performance. Pt (noble metal) has played a significant role in separating photogenerated charged species (electron: e⁻ and hole: h⁺) resulting In high photocatalytic activity [87]. The mechanism of the reactions is shown in Figure 4A.

Interestingly, incorporation of MWCNTs in the ZnO composite resulted in **5-fold** improved PEC performance. Under solar light irradiation, this porous structure (Figure 4B) caused **458%** enhancement of the photocurrent density [88].

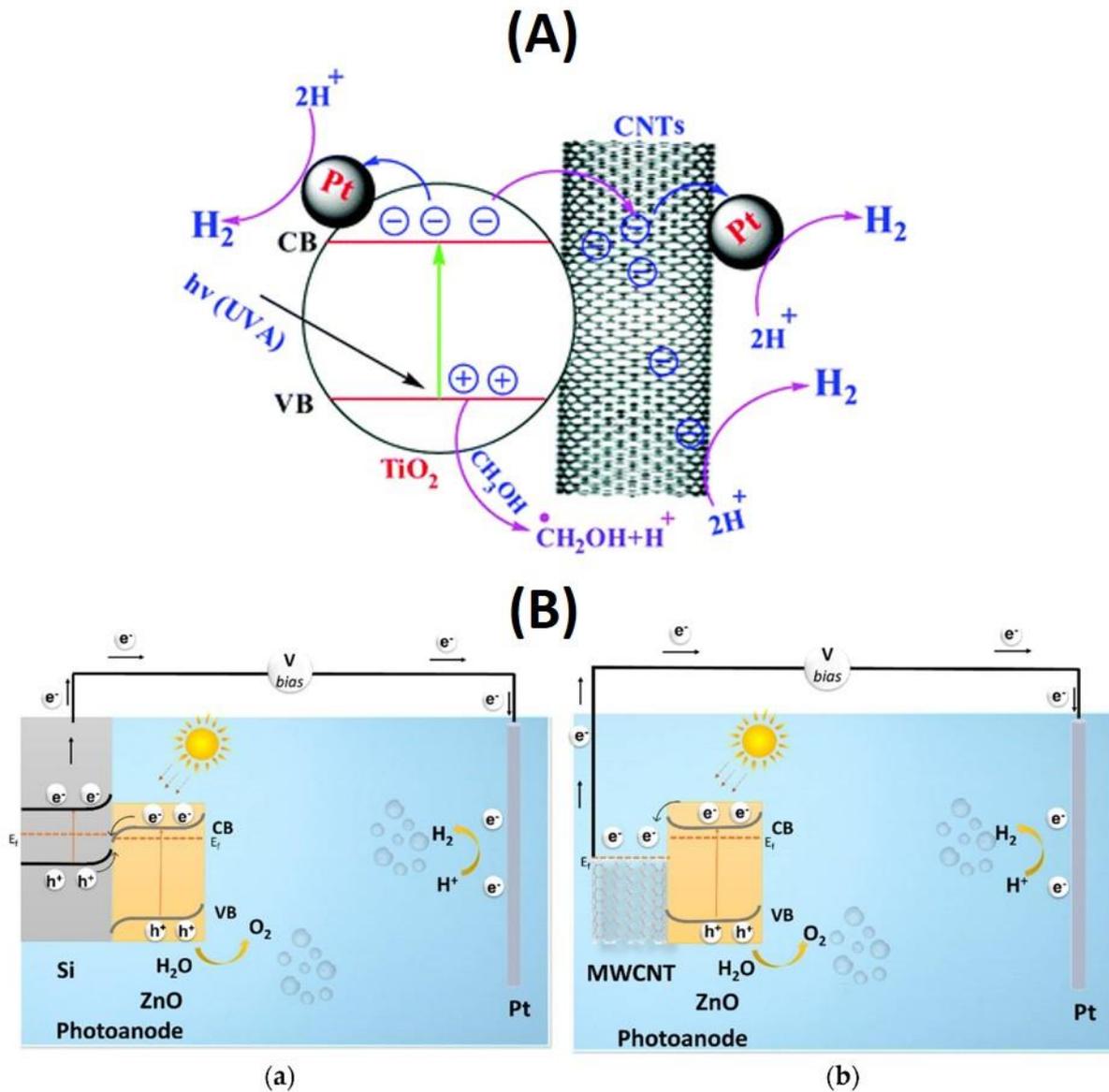


Figure 4(A). Ternary composite (Pt–TiO₂/fCNTs) reaction mechanism, reprinted from reference [87], under a Creative Commons Attribution-Non Commercial 3.0 Unported Licence and Figure 4(B) Si-ZnO and (b) CNT-ZnO photoanodes in PEC water splitting, reprinted from reference [88], under Creative Commons Attribution License.

3.4. Graphene

Graphene [89] is a one atom thick planar structure in which C-atom is in an sp^2 hybridized state. For the past decades, graphene has dominated the carbon family for many applications, including clean fuel [90]. There are numerous reports on hydrogen production utilizing graphene and its composites, such as CdS@hexagonal boron nitride on reduced graphene oxide (rGO) [91], and CuO/rGO [92]. A computational study has been carried out on nitrogen-doped graphene [93] in order to understand the characteristics responsible for efficient HER. **Density functional theory (DFT) calculations suggested** that effective H_2O splitting is due to the more conductive system. This is happening because of **the Fermi level movement towards conduction band and the intrinsic electronegativity of 'N' moiety.**

In an experiment, GO was reduced to RGO and simultaneous impregnation with $Zn_{0.8}Cd_{0.2}S$ NPs. Figure 6c has the sample **labelled as GS** followed by **some numbers**. **These numbers** are indicative of GO to $Zn_{0.8}Cd_{0.2}S$ weight percentage ratio. The maximum rate of H_2 production **was** obtained at GS0.25. **Indeed, as noted from Figures 5a-b,** after solar irradiation, sp^3 VB electrons get excited to the conduction band. Further, these electrons in CB of $Zn_{0.8}Cd_{0.2}S$ are transferred to RGO, avoiding or lengthening the recombination step of the photogenerated charges (electrons and holes). RGO also acts as co-catalyst where H^+ is reduced to H_2 [94].

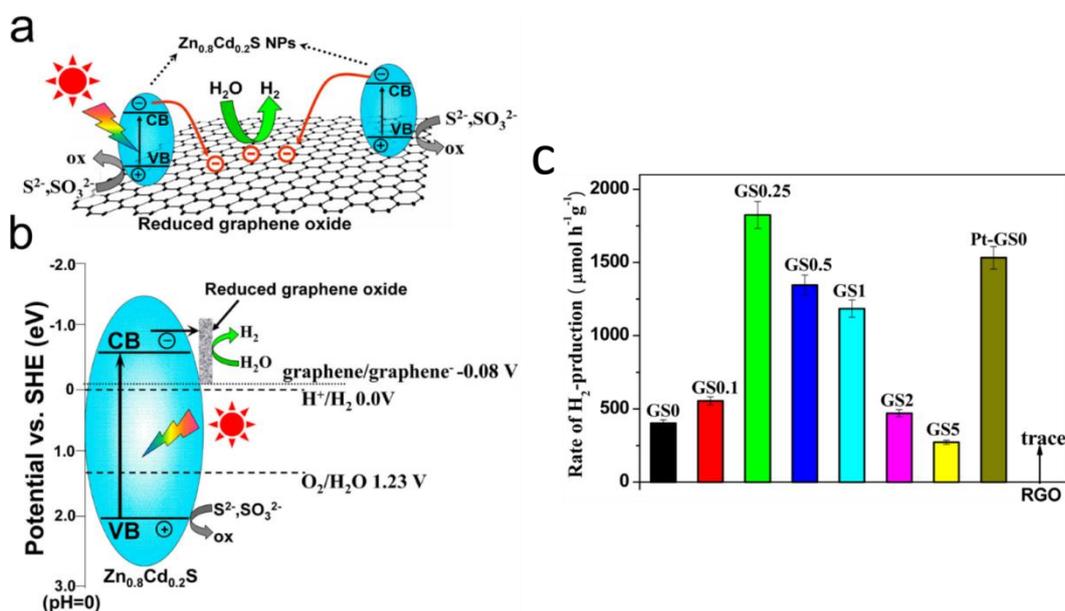


Figure 5. (a) Charge transfer and separation in RGO- $Zn_{0.8}Cd_{0.2}S$ system, (b) Mechanism of hydrogen generation, and (c) Comparison of photocatalytic activity of different samples.

Reprinted from reference [94], with permission of the American Chemical Society.

3.5. Graphdiyne

Graphdiyne [95] comprises an sp and sp^2 co-hybridized C network [96]. It has a porous structure (rapid mass transfer and uncover active sites) with a direct band-gap and elevated carrier mobility (better for light absorption) [97–99]. Interestingly, GDY also exhibits antibacterial properties [100]. GDY itself plays a crucial role in photo-electrocatalysis or act as a support for catalyst [101]. Each unit cell in GDY consists of two acetylenic linkages. It is comparatively softer than graphene or graphyne [102].

Cu atoms anchored on GDY act as an efficient catalyst for HER with selectivity and activity greater than commercial one (20wt.% Pt/C), 18 times higher turnover frequency (30.52 s^{-1}) was found [103]. H_2 generation using CuI (156.5 $\mu\text{mol}/5\text{ h}$) and GDY (29.4 $\mu\text{mol}/5\text{ h}$) is less than the In-situ photocatalytic H_2 generation over GDY-CuI (465.9 $\mu\text{mol}/5\text{ h}$) composite photocatalyst, viz. 3 and 15.8 times of pure CuI and GDY, respectively. This is an indication of a synergistic effect [104].

Thus, GDY and related structures are increasingly raising interest in the field of energy. For example: GDY ultrathin nanosheets [105], GDY@ $\text{NiO}_x(\text{OH})_y$ heterostructure [106], GDY-nickel boron oxide hybrid [107], self-active metal-free GDY [108], porphyrin-based GDY [109], and so on for hydrogen production.

Integrated PEC cells are shown that after irradiation with a Xe lamp, it shows photocurrent with applied potential, and H_2 generation is observed simultaneously. Gas chromatography (GC) studies have revealed that H_2 production is directly proportional to the time at CdSe QDs/GDY photocathode (0.1M Na_2SO_4 , -0.20 V vs NHE). Also, stable photoelectrochemical activity is observed during 12h test [110].

In another work, graphdiyne was impregnated with CdS. A schematic depiction of the materials synthesis and their photocatalytic mechanism is shown in Figure 6c. The effect of graphdiyne composition on CdS photocatalytic activity is clearly seen in Figure 6b. Another experiment set was carried out with just graphdiyne and a physical mixture of CdS and graphdiyne. Graphdiyne shows no hydrogen production (Figure 6a), indicating its inactivity towards visible light reaction in the current circumstances. The physical mixture (Figure 7b) does not boost the photo-catalytic activity of CdS, indicating the need for compositing rather than physical contact [111].

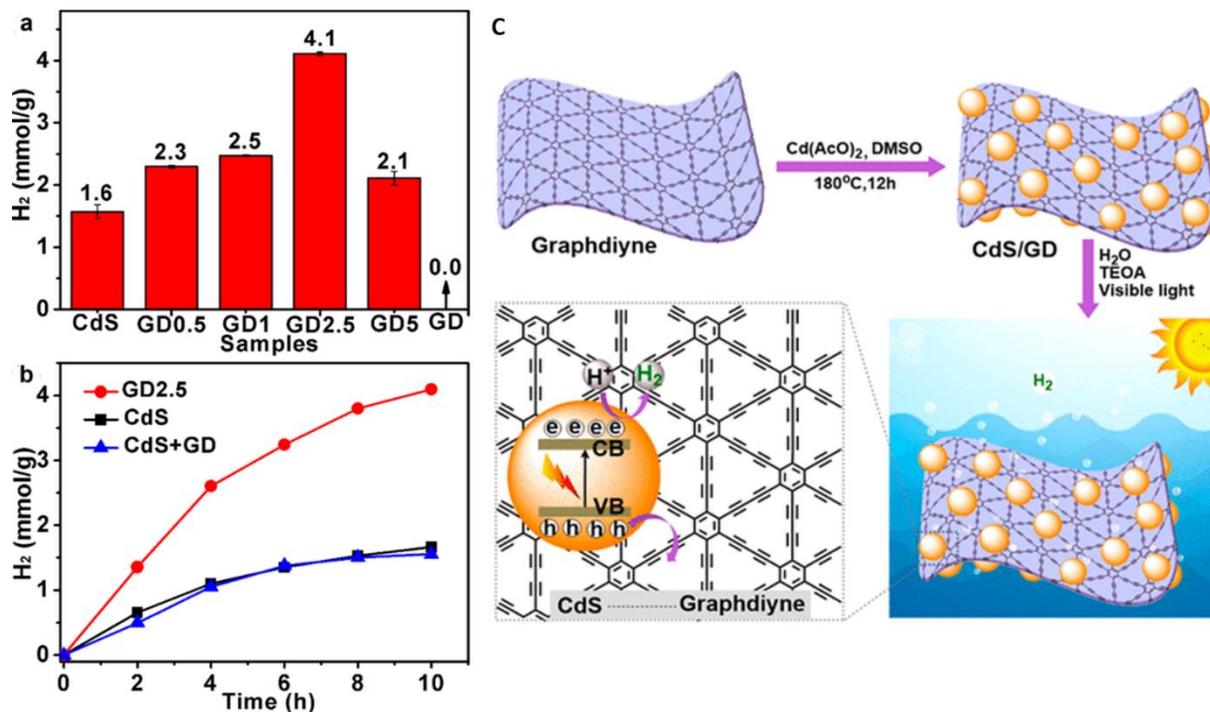


Figure 6. (a) hydrogen production using CdS, GD and different CdS/GD samples, (b) dependence on time, and (c) mechanism of photocatalytic process at CdS/GD composite. Reprinted from reference [111], with permission of the American Chemical Society.

3.6. Nanodiamond

Nanodiamonds (NDs) are well-known for their chemical stability, easy modifications, hardness, low toxicity, thermal conductivity, narrow band-gap (broad absorption-extension to near-infrared region), high surface area, high refraction, extraordinary resistance to photobleaching, fluorescence, biocompatibility, bulk preparations, unique optical and chemical properties [112–114].

Rh NPs impregnated NDs have been utilized for renewable green energy production (H₂ generation) via ammonia-borane hydrolysis (a model reaction to evaluate Rh NPs/NDs catalytic efficiency). Low activation energy ($E_a = 25.6 \text{ kJ mol}^{-1}$) and high turnover frequency (TOF = 729.4 min^{-1}) are observed. The high activity is due to the hydrophilicity nature (presence of oxygen-containing moieties) of NDs, which promotes well dispersion of Rh NPs on its surface. Thus, exposing more active sites for the catalysis [115]. Rh NPs are the main catalytic active sites, and NDs act as support. More information can be extracted from Figure

12. Hydrogen generation rate (GHT) relies on Rh content: 0.29-1.16 mM, substrate concentration: 150-300 mM and temperature: 25-40 °C with respect to reaction time.

Generally, photocatalysis is increased by high light absorption and charge transfer [116]. The large surface area, inhibits recombination of charge carriers (photo-generated), and increased charge transfer can enhance the H₂ synthesis by 50% [117].

3.7. Biochar

3.7.1. Production of Biochar

Biochar is manufactured via thermal treatment (gasification, torrefaction, vacuum, flash, intermediate, hydro, slow or fast pyrolysis) [118]. Numerous parameters [119] govern their properties, namely: (a) type of thermal treatment [120], (b) residence time [121], (c) atmosphere (air, N₂, H₂, Ar, their mixture, etc.), (d) temperature [120–123], (e) biomass (feedstock choice) [120,123] and their mineral composition [124], and (f) heating rate [121]. Biomass pyrolysis can also be carried out in the presence of a catalyst [125]. The feedstock can be obtained from the forest, aquatic, industry, agriculture, human, and animal waste [118]. There have been plenty of precursors-used for biochars synthesis: such as cornstalk [126], seaweed [127], cow dung [128], herbal medicine residues [129], brewer's spent grain (BSG) [130], freshwater macroalga [131], plastics (PVC, PET, and PE) [132], orange peel and albedo [133], tobacco stalk [134], oyster shell [135], cinnamon and cannabis [136], olive pit [137], date stone [138], pig bone [139], to cite but a few.

Fan et al. [140] have reported that sewage sludge was subjected to pyrolysis in a muffle furnace at several temperatures such as 200, 300, 500, and 700 °C for four hours maintained in a nitrogen atmosphere. In another methodology, biochar precursors (lignocellulosic: canola straw, wheat straw, sawdust of white spruce, and non-lignocellulosic: manure pellet) were placed in a quartz reactor enclosed within a microwave-oven maintained in a nitrogen gas environment, where pyrolyzed at low (300 °C), medium (400 °C) and high temperature (500 °C) [123]. *Ayala-Cortés et al.* [141] have reported a pyrolysis experiment utilizing a horizontal solar furnace. Dried agave leaves fibres, and tomato pruning were kept on an alumina crucible. In order to maintain non-stop exposure to concentrated solar energy, precursors were positioned inside the solar reactor, which has a continuous flow of argon gas and coupled temperature monitoring equipment (optical pyrometer and thermocouples).

Synthesis was carried out at various temperatures for agave (450, 600, 800, 900, 1100, 1400, and 1550 °C) and tomato pruning (450, 600, and 900 °C). Biochar preparation via concentrated solar thermal energy is exciting and can be applied to other wastes such as date palm waste [142]. Feng *et al.* [143] have worked on a top-down approach where grape pomace, walnut shell, and Brewer's spent grain have been utilized as complex carbon sources. They have played with the components of raw biomass. Non-lignocellulosic components (minerals, proteins, soluble extractives, and fats), hemicellulose, and cellulose were removed at different steps before carbonization, leaving behind just lignin. Manolikaki *et al.* [20] have shown interesting biochar prepared out of Brewery by-products (BSG and surplus yeast). The experiment was carried out in a muffle furnace having a nitrogen supply, and the temperature was allowed to reach 300 °C.

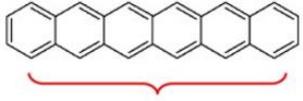
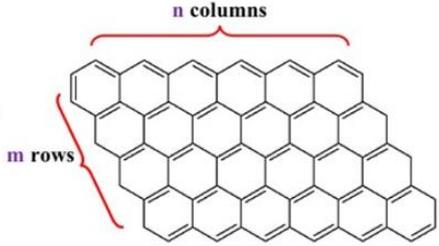
3.7.2. Structure of Biochar and Biochar Cycle

The biochar structure can be described using the formulae:

$$C_{(2m+2n+2m)}H_{(2+2m+2n)} \quad (5)$$

where m denotes "m" rows in the biochar structure, and n denotes "n" columns (Figure 7a) [144]. Besides the aromatic chemical structure, it is also essential to consider the H/C atomic ratio resulting from the pyrolysis temperature. Figure 7b displays a plot of H/C versus T obtained by Xiao *et al.* [144] for several biomass sources. An empirical correlation is shown in the inset; it permits confidently estimating the H/C ratio expected from the pyrolysis temperature (heating rate - 5°C/min and holding time 6h).

a

Formula	Structure	H/C
One rows $C_{(2+4n)}H_{(4+2n)}$		$\frac{4 + 2n}{2 + 4n}$
m rows $C_{(2mn+2n+2m)}H_{(2+2m+2n)}$		$\frac{2 + 2m + 2n}{2mn + 2m + 2n}$

b

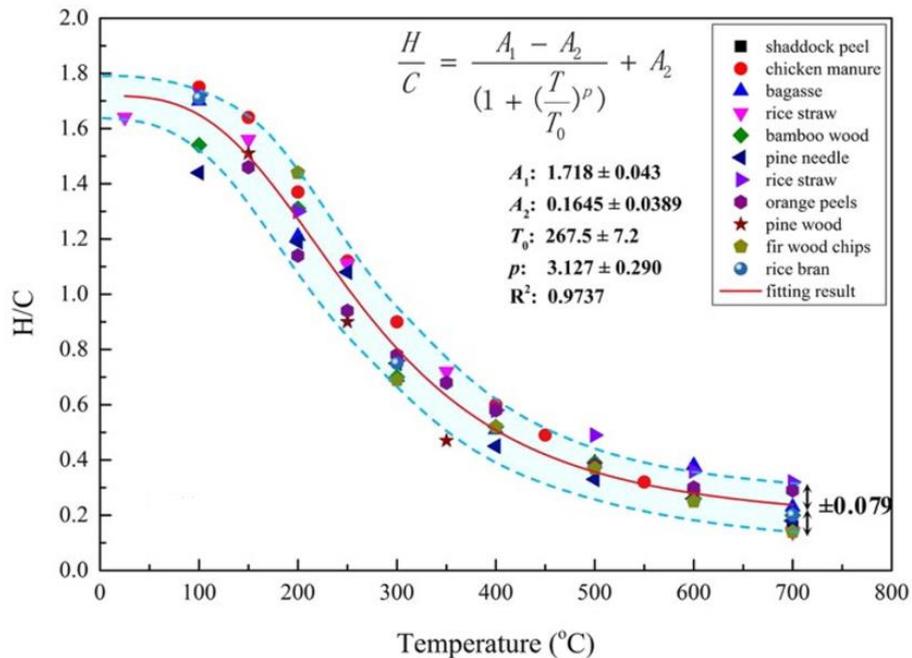


Figure 7. Chemical composition of biochar: (a) aromatic clusters and their expected H/C ratios; (b) experimental H/C ratio versus pyrolysis temperature. Empirical formulae to determine H/C versus temperature is shown in the inset. Reproduced from [144], licensed under commons attribution 4.0 International License.

When biochar is in the 2D form, it becomes even more interesting as it acts as a sheet-shaped substrate for varieties of structures. For example, Zhao *et al.* [145] have used this surface as a platform to grow NiPS₃ nanoparticles. It is found that high-temperature pyrolysis

is usually required to make graphitized biochar structure [146]. In recent years, there has been increased attention toward 3D interconnected biochar due to its superiority over 2D in terms of short ion diffusion paths and continuous e⁻ pathways. This topic has been comprehensively discussed by Norouzi et al. [30].

3.7.3. Modification of Biochar

Usually, biochar contains limited functionalities, small surface area as well as small pore volume. Pores developed in the course of carbonization get blocked by tarred materials during dry pyrolysis. This creates strong need for chemical/physical treatment for better specific surface area, pore structure and volume, in order to exploit its real properties [147–149]. Biological [150] (digestion), physical (magnetic, steam/gas/CO₂, grinding/ball mill, and microwave) and chemical (composite, surfactant, oxidizing agents, alkali and acid) processes are three currently investigated ways of biochar modifications [151,152]. For example-micropores formation occurs when pretreated with H₃PO₄, leading to an increase in biochar specific surface area [153], carbon retention and sorption ability [154]. **However, we have also noted development of biochar porous structure upon maceration of the initial biomass in water-alcohol medium [155], or when catalyst precursors are impregnated on the biomass powder prior to pyrolysis [156]. These routes should further be exploited in future developments.**

3.7.4. Application of Biochar in Hydrogen Production

Literature has revealed that biochar itself is catalytically active [157]. Currently, the field of biochar has progressed at a remarkable pace for the purpose of hydrogen evolution. Norouzi *et al.* [158] have made sewage sludge biochar and shown hydrogen production from H₂O under artificial solar-light irradiation (visible light) driven. This metal-free photocatalyst has exhibited remarkable photoactivity of 3845 μmol/g of hydrogen yield. This value is more significant than their traditional carbon nanoallotropes such as CNTs and graphene, and carbon nitride. This superior activity is due to the high surface area, electron-conductive nature, inorganic materials, hydrophilic surface functional groups, and aromatic carbon structure. This work is an excellent example of a stable, eco-friendly, low-cost, and sustainable technique [158,159] contributing toward sustainable development goals 7:affordable and clean energy (SDG 7) [160]. Biochar manifests excellent potential as an alternative to commercial active materials in energy storage systems: supercapacitors and Li-ion batteries[161].

Catalytic decomposition of methane over biochar can also produce hydrogen. This concept can be well understood by the reaction given below [162,163]:



A comparative study of 12 varieties of biochar manufactured at three temperatures (300, 500, and 700 °C) and obtained from 4 sources (sawdust, wheat bran, peanut shell, and sewage sludge.) was carried out. Experiments with **biochar** produced at higher temperatures have shown increased hydrogen production **compared to the biochar** formed at low temperatures [164].

3.7.4.1 Minerals Containing Biochar

In the case of anaerobic digestion (mesophilic) of food waste to increase hydrogen generation, the incorporation of biochar has enhanced the Y_H (cumulative hydrogen yield) and R_H (max. H_2 generation rate) by 107 % and 54 %, respectively. Incidentally, Fe, K, and Ca are the key component in biochar which have played a significant role in hydrogen-generating bacteria *Clostridium butyricum* by enhancing their butyric acid, acetic acid, and prevalence. In this regard, comparatively leached biochar was less productive [165].

Biochar from pig bone powder (prepared by thermal treatment at 700, 800, and 900 °C), in situ co-doped with N, P, and Ca was utilized for electrocatalytic HER. The factors such as better conductivity = $0.053 \pm 0.004 \text{ Scm}^{-1}$, **low** charge-transfer resistance = 23.9 Ω , **high** electrochemically active surface area (EASA = $18.9 \text{ m}^2\text{g}^{-1}$), presence of minerals (N, P, and Ca), and **high** specific area ($\sim 280 \text{ m}^2\text{g}^{-1}$) are responsible for remarkable activity [139].

The doping of nitrogen in biochar directly affects its specific surface area and electrical conductivity. For example, **N-doping** in biochar derived from corncob has decreased specific surface area and increased electrical conductivity by ~ 14 times. The value of specific surface area before and after doping are 944 and 831 m^2g^{-1} , respectively [166].

3.7.4.2. Biomass-derived carbide

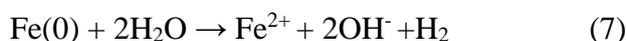
With 1 M KOH electrolyte, HER electrocatalyst was manufactured from treating watermelon rinds powder with hexaammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and

fumaric acid (C₄H₄O₄). Pyrolysis was conducted at 800, 850 and 900 °C under nitrogen gas and the resulting biochars exhibited Tafel slope 71, 75 and 78 mVdec⁻¹ with electrocatalytic performance ($\eta/10\text{mAcm}^{-2}$) 133, 147, and 177mV, respectively. The remarkable HER performance is due to the facile mass transfer of electrons, unique pore size, and large surface area [167].

Another study reported that N, K Co-activated biochar (feedstock-pomelo peel) was exploited as a source for molybdenum carbide. Effective HER is due to populated active sites, **large** specific surface area (611 m² g⁻¹), facile e⁻ transfer, and enhanced intrinsic activity [168].

3.7.4.3. Metallic Catalysts Loaded on Biochar

The combination of iron nanoparticles in the metallic state (zero valent) and biochar has synergistically improved grass fermentation induced by bacteria, therefore, leading to biohydrogen generation (89.8% increment) [169]. As a matter of fact, biochar constitutes a nutrient for microbial growth whilst Fe(0) removes oxygen from the medium of fermentation medium (Equation (6)) thus improving the activity of oxygen-sensitive hydrogenase. In addition, the production of Fe²⁺ from Fe(0) by electrolysis produces H₂ and harnesses hydrogenase activity in the system (Equation (7)).



In the case of steam reforming of CH₃COOH, metals like Ni, when supported on biochar activated with alkali KOH and HNO₃, give liquid hourly space velocity (LHSV)=10h⁻¹ at 700 °C with a H₂ yield of 71.2% [170].

3.7.4.4. Metal Oxide Catalysts Loaded on Biochar

A microwave hydrothermal technique was employed to prepare mesoporous biochar/ZnFe₂O₄ composite. Biochar plays a key role as an e⁻ mediator, which has promoted vis-light photocatalytic H₂ production [171]. Figure 10 compares the hydrogen evolution rate using photocatalyst and biochar-supported catalyst (Figure 8b) with the highest performance for BFZ-5 (biochar/ZnFe₂O₄ mass ratio=5/1). The photocatalyst could be employed at least three times without significant hydrogen evolution loss. Figure 8c depicts possible mechanisms of photocatalyzed dihydrogen production.

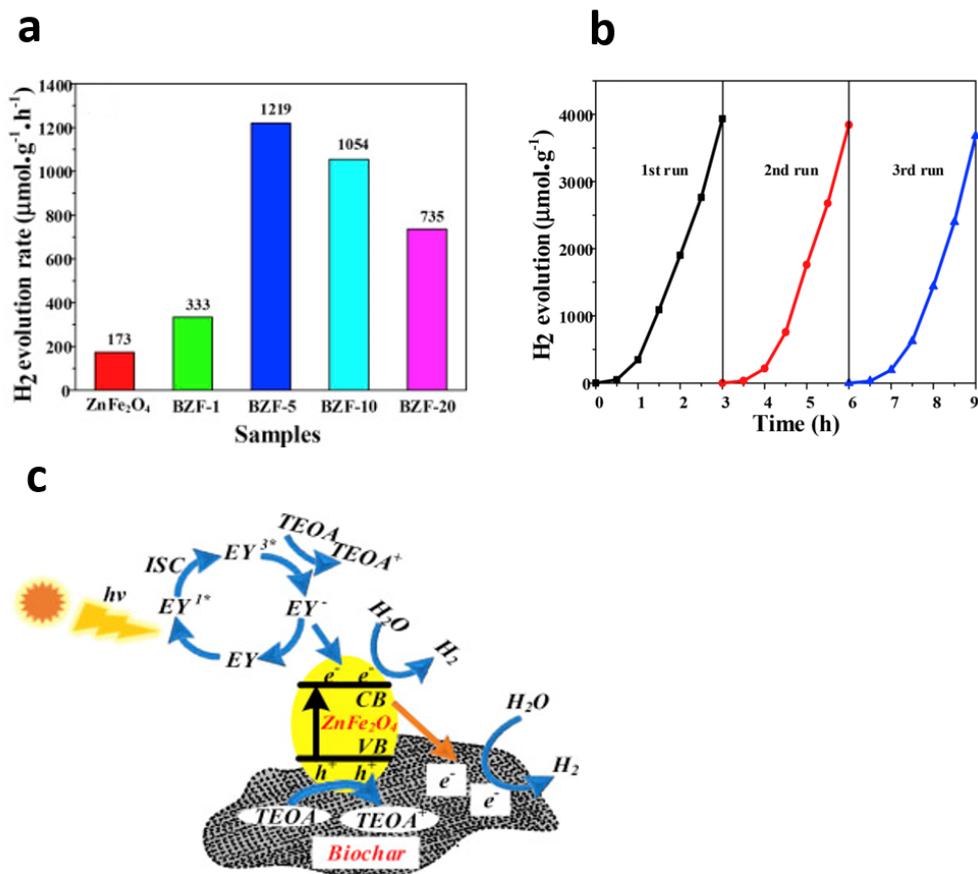


Figure 8. H₂ evolution rate for ZnFe₂O₄ reference sample and BZF composites (a), and for BZF-5 vs time and run number. The proposed mechanism of catalyzed H₂ production over BZF composite is shown in (c). Reproduced from ref. [171] with permission of Elsevier.

Liu *et al.* have reported that biochar can be a good substrate. Its surface can be utilized to create several morphological structures. They have demonstrated this by synthesizing biochar (elm-money feedstock) and using the one-pot solvothermal method to create a MnFe₂O₄ sphere (hollow and porous in characteristics). With current density = 10 mAcm⁻², little overpotential (156 mV) is observed. They claim that the current technology could be regarded as a potentially general approach for bifunctional electrocatalysts, as well as various other transition metal oxides that can be utilized in the field of water splitting with the concept of saving energy [172].

3.7.4.5. Biochar Composite with other Carbon Materials

Due to potentiality of biochar, currently there has been lots of efforts to make nanocomposite of biochar with other carbon materials such as growth of CNTs on biochar [173]. Another example: a study has been conducted by Zhou et al. [174] on a composite consisting of g-C₃N₄, biochar, WO₃ and Cu²⁺-doped carbon sphere (Figure 9) for visible light driven H₂ evolution, they demonstrated that biochar was acting as a platform on which stable Z-scheme heterojunction was made.

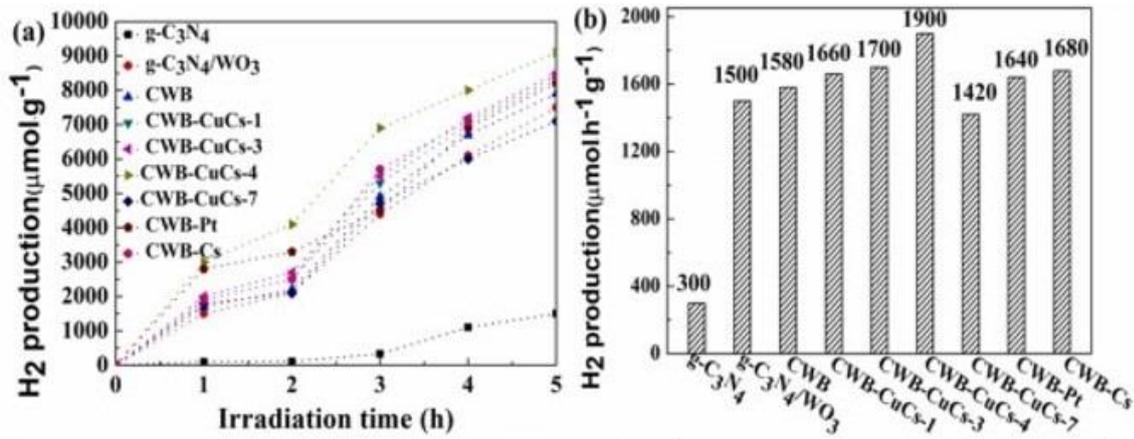
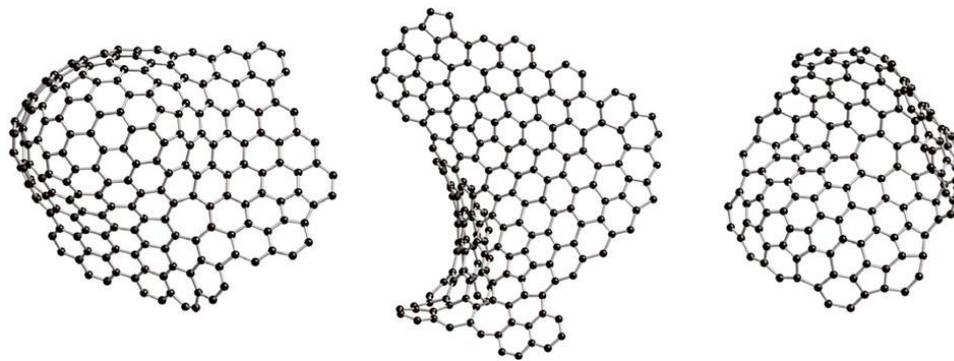


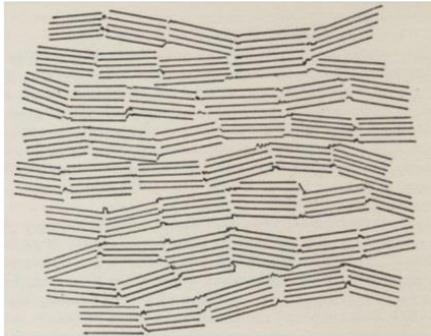
Figure 9. Hydrogen production efficiency of 3D g-C₃N₄/WO₃/biochar/Cu²⁺-doped carbon spheres (CWB-CuCs). Reprinted from the reference [174], with permission from Elsevier.

To conclude, biochar in supported photocatalytic systems, apart from playing an obvious role as support for nanoparticles [175], enhances the active sites and surface area by well-distributing nanoparticles on its surface. In addition, biochar acts as an electron reservoir, reduces band-gap energy, serves for shuttling electrons, and promotes charge separation [176]. No doubt that biochar and related materials help in overcoming the problem of high overpotential and small H₂ yield in water splitting, a green and efficient way to get hydrogen [177,178]. It is important to know that biochar, depending on their synthesis methodology, they mimic graphene [179,180]. So, it may be seen as an interesting surface, like graphene, to catalyze several reactions directly, or as a platform on which different photocatalysts could be immobilized and dispersed. There are different models reported in the literature to describe the structure of coal and activated carbon [181] as shown in Figure 10. According to Rosalind Franklin, carbon obtained by pyrolysis of organic materials can be categorized into two categories: graphitizing or non-graphitizing (small, randomly oriented graphene like sheets), as shown in Figure 10b and Figure 10c, respectively [182]. It is also interesting to discuss that

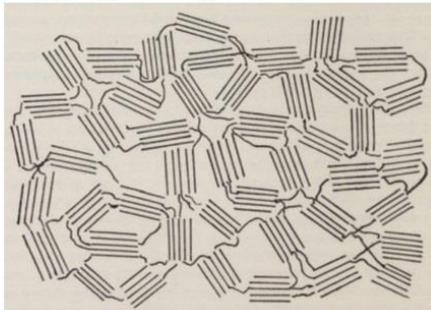
there is structural resemblance of non-graphitizing carbon with fullerene (presence of fullerene like sheets) as shown in Figure 10a [183]. It shows the curved nature of carbon fragments containing cyclopentane, cyclohexane and cycloheptane- ring systems. Figure 10d, showing the 2D coal structure, points to possible carbon matrix with defects and complex oxygenated groups [184]. These models are excellent proof of connection between biochar and other nanocarbon, more specifically, graphene and fullerene. These are the reason that makes scientist to also think about making composite of biochar with nanocarbons. For example, a report by Zhang *et al.* [185], have developed biochar-CNT-nickel oxide composite for energy applications.



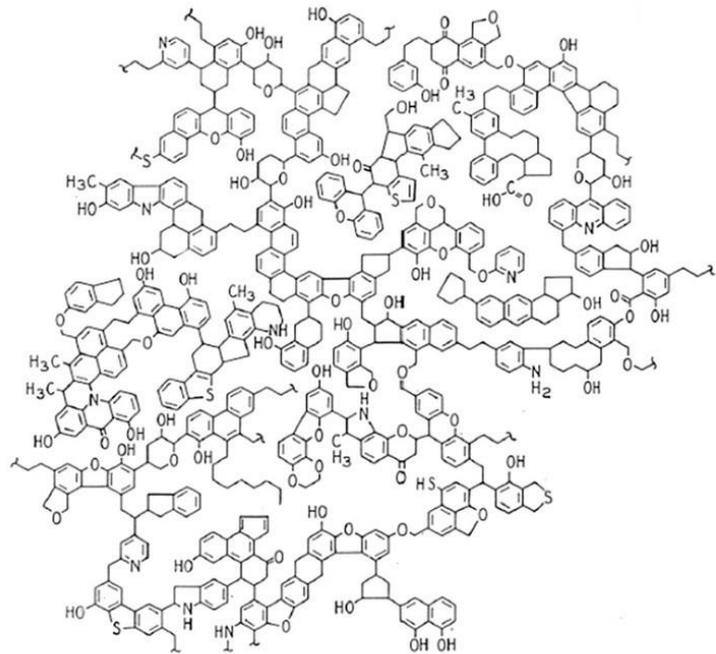
(a) Curved carbon fragments



(b) Graphitizing (but non-graphitic) carbon.



(c) non-graphitizing carbon



(d) Model of bituminous coal

Figure 10. Various models to explain the structure of coal and activated carbon [181]. (a) Shown by Harris et al. [183], reproduction permission obtained from IOP publishing, (b,c) Hypothesized by Franklin [182], reproduced with permission from Royal Society and (d) given by Shinn [184], reproduced with permission from Elsevier.

4. Comparison of hydrogen production efficiency of Biochar and other Carbon Allotropes

The hydrogen production efficiency of a catalyst is calculated based on three factors: the amount of hydrogen produced, the amount of catalyst taken, and the time duration. The efficiency of a cell can be shown using the following equation [186]:

$$STH = \left[\frac{\text{Output energy as H}_2}{\text{Energy of incident solar light}} \right] \quad (6)$$

$$\text{AQE or AQY} = \left[\frac{nR}{I} \right] \quad (7)$$

Where,

STH= Solar to hydrogen conversion efficiency,

AQE = Apparent quantum efficiency,

AQY = Apparent quantum yield,

n = no. of e⁻s required for the reaction (~2 for photocatalytic hydrogen generation),

I = rate of incident photons,

R = rate of hydrogen generation.

Table 2 compares the hydrogen production activity of different carbon-based catalysts (biochar and other allotropes of carbon). The values reported in the literature were given in different units; we have thus considered the time or the amount of catalyst used to compare the various activities. Surprisingly, biochar shows remarkable catalytic activity, up to 80% of the synthetic graphitized nanodiamond, but two-fold that of graphdiyne. The reason behind this peculiar hydrogen generation performance of biochar can be attributed to the inherent mix of mineral composition (in terms of mg/Kg dry wt, As (<0.72), Cd (12.36), Cr (292.72), Co (12.68), Cu (296.63), Pb (195.93), Hg (<0.23), Mo (4.67), Ni (66.25), Se (<1.40) and Zn (896.21)) [159]. Depending on the type of biomass used, biochar's inherent chemical composition varies. It should thus be stressed that the cost-effectiveness of biochar makes it highly interesting for its commercial use. In contrast, fullerene, MWCNTs, and graphene do not exhibit any hydrogen production activity; they are catalytically inactive toward hydrogen production reaction for that particular condition.

Table 2. Comparison of hydrogen production activity of biochar with other carbon nanoallotropes.

Materials	Reagent	Light source	Hydrogen production	Reference
Fullerene (C60)	Aqueous soln. with triethanolamine and eosin Y.	Visible light ($\lambda > 420$ nm), 300W Xe lamp.	0 μ mol/h/g	[67]
Pure MWCNTs	Aqueous soln. of 0.25 M Na ₂ SO ₃ and 0.35 M Na ₂ S	Visible light, ($\lambda \geq 420$ nm)	0 μ mol	[187]

	(sacrificial reagent).		(300 W Xe lamp		
Graphene	Aqueous soln. of 0.05M Na ₂ SO ₃ and 0.1M Na ₂ S		$\lambda \geq 420$ nm, 200 W Xe lamp	0 $\mu\text{mol/h}$	[188]
Graphdiyne	15% v/v triethanolamine solution (ph=9)		5-W light emitting diode lamp	29.4 $\mu\text{mol/5h}$ (588 $\mu\text{mol/h/g}$) ^a	[104]
Graphitized Nanodiamond	Water		532 nm, Nd:YAG lase pulse	32 $\mu\text{mol/h}$ (1600 $\mu\text{mol/h/g}$) ^a	[189]
Biochar	Water with 10vol% triethylamine		300W Xenon arc lamp, 420nm	3845 $\mu\text{mol/g}$ (1282 $\mu\text{mol/h/g}$) ^a	[158,159]

^acalculated considering the mass of catalyst and catalyzed reaction time.

5. Future Prospects

The future of carbon nanoallotropes is bright by taking advantage of the synergy between two or more nanocarbons. For example, when C₆₀ fullerene (high e⁻ attracting ability) and graphene (conductivity) collaborate, it enhances the hydrogen production ability of pure g-C₃N₄ by ~540 times. They enhance the photogenerated charge separation and increase the usage efficacy and migration ability of photogenerated electrons [73]. Focusing on this can enable the expansion of green energy areas for sustainable development. Carbon dots have the potential to dominate the zero-dimensional materials [78]. Interestingly, due to their response to light stimulation, they have high potential as photocathodes for hydrogen evolution reactions from water in a metal-free photo-electrochemical set-up [190]. Variation in the structure of graphene can create a novel carbon allotrope, such as a biphenylene network [191].

Also, enriching the biochar with nitrogen before doping with metal and/or non-metal catalysts are expected to improve biochar application in the green generation of hydrogen. In addition, compositing the biochar with metal and non-metal-doped carbon nitride can boost the application of the biochar in hydrogen generation due to the thermal and optical properties of g-C₃N₄ [192,193]. A new approach that will emerge soon is the biochar-based boron-carbon nitride compositing with fullerene. Boron carbon nitride (BCN)/C₆₀ has proven to have an outstanding electrocatalytic H₂ evolution/oxidation reactions and O₂ evolution or reduction

reactions [74]. Preparing BCN from biochar will be an additional application to change waste to fortune.

To the best of our knowledge, the chemical attachment of biochar-carbon nanomaterials for hydrogen generation is either absent or, if present, rarely reported in the literature. Despite its potentiality for different applications, availability, and simplicity, it has not been fully exploited, more **specifically** in the **field** of green energy. This gap can be a good boost for flourishing the biochar field in H₂ production. This field can be a unique area to work.

One of the advantages working in the field of biochar is the natural abundance of its sources. There are plenty of precursors that can be used which is not yet explored or rarely utilized for biochar production. Due to the constant increase in overall population growth in the upcoming era, the cost of materials can be a crucial factor for their commercialization. In this regard, biochar can be one of the first candidates on the materials list.

6. Conclusions

Biochar is a unique carbonaceous material that is a hot topic for research in the current world. To improve the circular economy, biochar is an ideal material. Various fascinating precursors can be used to synthesize biochar, **such as brewer's spent grain or sugarcane bagasse**. One of the exciting facts about biochar is that its extent of graphitization can be easily controlled by playing with temperature for their manufacturing. **Sometimes, biochar may mimic the structure of graphene can be very interesting for application involving low-cost ecofriendly biocarbon catalyst. It is interesting to say that carbon fragments in biochar may resemble fullerene. This resemblance with previously known nanocarbons brings an important outlook for biochar future.** Biochar composite is an extraordinary and promising alternative candidate to carbon nanoallotropes for the application of hydrogen production. It is also a material that can play a significant role in metal-free catalysis. Its properties are depended on several parameters, including the type of feedstock, pyrolysis process (temperature, methodology, residence time, atmosphere, heating rate, etc.), and mineral composition. Hitherto, much work was devoted to wastewater treatment, and, comparatively, energy applications were less investigated. From what has been stated above, one could expect dramatic progress in the coming years in the utilization of biochar for energy and particularly hydrogen production.

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