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Hydrogen Production from Water Splitting Through Photocatalytic Activity of Carbon-Based Materials

Hydrogen is a free, limitless, and environmentally friendly resource. To enhance the production performance of hydrogen by photocatalytic water splitting, its preparation and application was investigated using carbon-based materials (graphene, graphite, carbon nanotubes, activated carbon). Photocatalytic hydrogen processing is among the most promising strategies for ensuring long-term energy stability and preventing further environmental degradation. The selection of co-catalysts and sacrificial agents to support the main catalyst is crucial for increasing hydrogen production. Several analyses were conducted to examine the characteristics as well as the use of various parameters to determine how carbonaceous materials would improve hydrogen production..

Keywords: Carbon-based materials, Graphene, Hydrogen Production, Photocatalysis, Water Splitting

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1 Introduction

All domains require steady and sufficient energy to accommodate the need for the fast-growing global population and industry; however, most populations depend on non-renewable oil and natural gas for their economic security and production of electricity. The energy demand is always rising [1]. Despite the needs, current sources were declining and foretold to deplete faster than anticipated. Therefore, researchers and many other environmental activists are currently turning their concerns towards sustainable energy to resolve this subject. Sustainable energy systems are being established to meet rising global energy demands and reduce reliance on fossil fuels, which are often correlated with environmental degradation [2]. To find a substitution for our reliance on fossil fuels for everyday use, the energy efficiency of the substitutes must be higher,

and their ecological effect, especially in terms of carbon emissions, must be lower than the fractionation of combusting fossil fuels [3].

Hydrogen is a clean source of energy for many purposes, such as for automobile power, heating, fuel cells, and many others with lower environmental impact [4–7]. Furthermore, the use of hydrogen as an alternative fuel is a long-standing substitute to decrease carbon dioxide generation globally through hydrogenation [8,9]. Photocatalytic hydrogen production through water splitting is one of the most promising techniques for long-term energy security, as it is resilient to more environmental problems. Moreover, water has no limitations in ensuring energy stability by nature for future generations [10,11]. Cost savings, quality and availability of materials, environmentally friendly production, and no hazardous waste generation, are all key elements of hydrogen-powered clean energy systems [12].

This review investigated the performance of hydrogen production using the photocatalytic water splitting method using graphene as an addition to the main catalyst. This major execution was done using the design liquid phase catalytic system. The selection of co-catalyst and sacrificial agent to help the main catalyst is critical for increasing hydrogen production. Several types of researches were performed to analyze and use various samples to assess how many concentrations of carbon-based materials improved the output. All procedures were documented accordingly and presented as scheduled.

2 Overview on Hydrogen Production and Photocatalyst

2.1 Hydrogen Production

All countries need consistent adequate energy to accommodate the need for rapid population growth globally, but most of the populations rely on oil and natural gas for its economic stability and generation of electricity. The consumption of non-renewable energy resources rate increases rapidly over the years [13]. The demand for energy increases as the rapid human population and industrialization increase. Furthermore, current resources were declining [14] and predicted to deplete faster than expected. For this reason, researchers and many other environmental activists are currently shifting their interest towards sustainable energy to resolve this matter [15]. Sustainable energy systems are implemented to support the rising global energy demands to lower dependence on fossil fuels, which are often associated with environmental degradation. Green power and sustainable energy systems are expected to address the growing demand of the world for energy with reduced reliance on fossil fuels, resulting in environmental degradation.

Renewable energy systems can be classified as beneficial in support of economic, environmental, and social advances. Critical aspects of renewable energy systems utilizing hydrogen include better cost productivity, efficient utilization and abundance of resources, efficient design and development, uncomplicated long-distance transportation, strengthening energy security, and improving the current state of the ecosystem. Hydrogen and electricity can be used as renewable and sustainable energy mediums. To resolve current and potential environmental, financial and technological issues, hydrogen and electricity should be generated using environmentally friendly energy and material resources [16].

Hydrogen is the cleanest source of energy obtained from water [17], with various possible implementations to many applications comprising vehicle power, household heating, fuel cell, and many others with minimal ecological impact [18–20]. Furthermore, the application of hydrogen as an energy resource is a long-standing alternative to minimize carbon dioxide, CO₂ production globally to value-added chemicals by hydrogenation. Hydrogen energy has already been brought into existence to the marketplace. However, it is much more costly than traditional fossil fuel due

to inefficient manufacturing methods such as steam and plasma transforming oxidation and electrolysis [21]. Photocatalytic hydrogen production transpires by the splitting of water is, therefore, one of the most promising approaches for sustainable energy security and environmental problems [22]. Water has no limitation by nature, giving generations to come energy stability.

Hydrogen processing methods for commercial processes such as thermochemical, photocatalytic, and electrochemical have been studied extensively in the literature and are still being improvised to achieve better performance. Following the primary discovery of water-dependent photo-electrolysis in 1972, researchers have concentrated on the production of hydrogen by photocatalytic water splitting utilizing a variation modification of semiconductors, for example, graphitic-carbon nitride [23], titanium dioxide [24], and cadmium sulfide [25]. Photocatalysis technology requires sunlight to break the bond between hydrogen and oxygen atoms found in water. Photocatalysis provides a solution associated with the nature of sunlight which is considered a sustainable and ultimate form of energy to power life on earth activities [26]. Numerous comprehensive studies have been concentrating on the band energy gap, pH value, surface area, choosing of sacrificial agent and co-catalyst, the temperature which influences the photocatalytic water-splitting outcome [17].

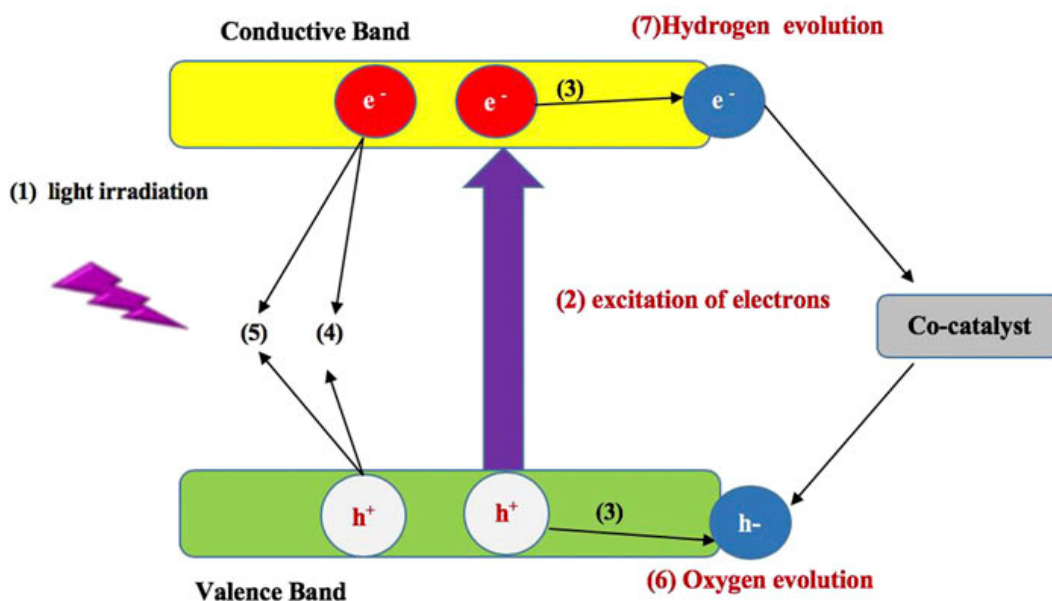


Figure 1. Schematic diagram of water splitting through the photocatalytic process [27].

Hydrogen-carrying compound produces hydrogen with the cooperation of a photocatalyst through solar energy conversion to chemical energy (Figure 1). The procedure requires placing a co-catalyst onto a semiconductor photocatalyst that is needed to reduce the overvoltage for the hydrogen and oxygen development schemes. In addition, the co-catalyst serves to overcome the recombination of photo-generated charges in the photocatalyst by effective expulsion of photoelectrons from charging positions and formulates catalytic positions for H^+ reduction [28].

2.2 Mechanism of the Photocatalytic Reaction

Photocatalysts are photo-active catalysts that act as a requisite part in the alteration of the rate flows of photochemical effects. Thermodynamically, the water-splitting chemical process is an energetically ascending and endothermic reaction with the standardized energy transition, Gibbs free energy. The photocatalytic process commonly includes the generation of electrons and holes through activating atoms or molecules of a substance, giving excitation by consuming energy.

Both electrons and holes are split and transmitted to the surface of the photocatalyst. In addition, the photo generated electrons and holes are obtained by the oxidation-reduction co-catalyst reactants and absorbed by catalytic water reduction and oxidation reactions, collectively [22]. The holes oxidize the water molecules to protons, H^+ and oxygen, O_2 . Meanwhile, the electrons are reduced to H_2 (Equation 1 to 3).

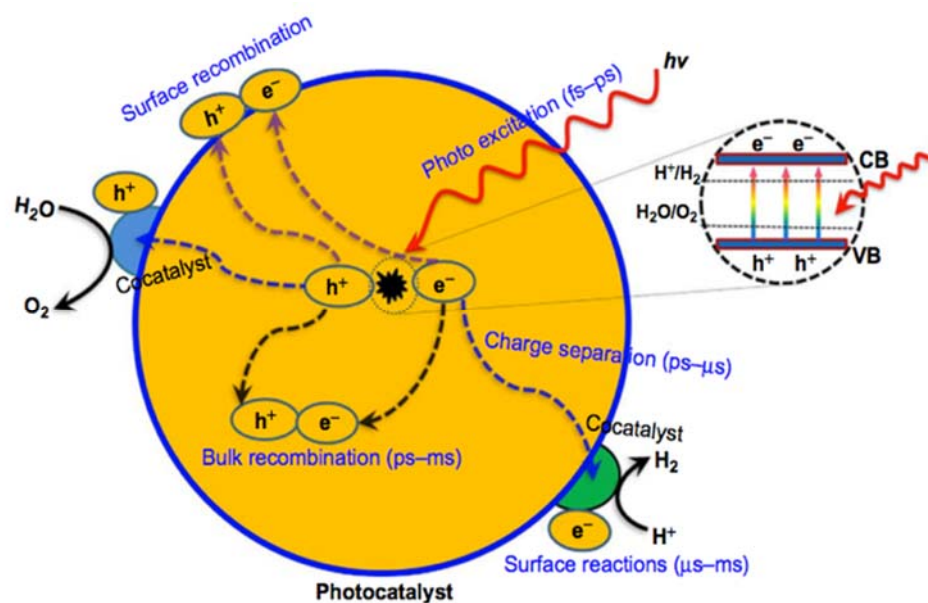
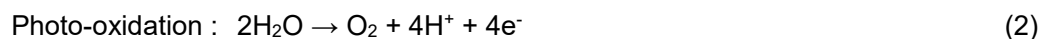


Figure 2. Photocatalytic water splitting mechanism on semiconductor-based photocatalyst [29].

This photocatalytic method converts the photonic energy from the visible light and UV spectrum to hydrogen in terms of chemical energy. Theoretically, the energy of the photon, E , is directly proportional to the radiation frequency, f where $E = hf$; given that h is the Planck's constant, which is equivalent to 6.626×10^{-34} Js. Semiconductors and metal oxides are extensively investigated as photocatalysts in previous literature [16]. For a photocatalyst to separate the covalent bond in water and produce hydrogen, oxidation and reduction reactions must have an adequate bandgap and properly positioned conduction bands and valence bands (Table 2). In most cases, semiconductors have complex band structures within the energy range 0.2 eV to 4.0 eV of the band gap.

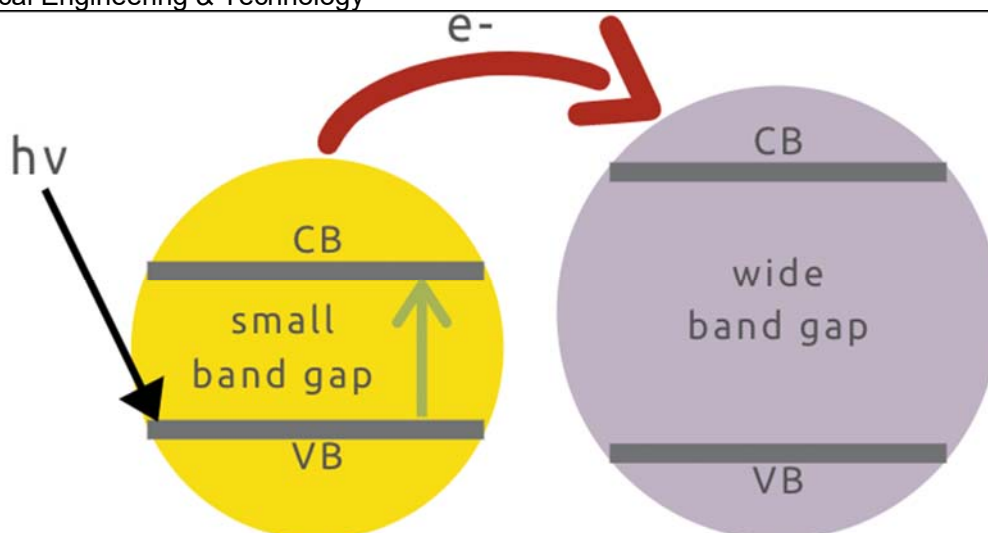


Figure 3. Electron migration [27].

For when the situation where the incident light from the photon energy is greater or equal to the bandgap, the valence electrons get photoexcited and leave the valence shell; the photon from a specific wavelength gets consumed by the electrons that live on the valence band, providing excitation to the conduction band. Therefore, the electrons become energetic, transmitting the valence band, composing a hole in the valence band. The excited electrons will then convey to the catalyst surface to begin the reduction process. Meantime, the holes of the valence band will proceed to the catalyst surface to inaugurate the oxidation process [30]. The reduction and oxidation reactions for the development of H_2 and O_2 are identical to the water electrolysis process [22]. Figure 3 describes the electron migration process.

3. Photocatalyst

3.1 Carbonaceous Photocatalyst

3.1.1 Graphene

Graphene combination with semiconductors offers a simplistic framework to enhance the behaviors and stability. Moreover, graphene is ordinarily inactive if disclosed to normal ambient at room temperature [31]. Graphene is a single atom layer made up of hybridized carbon sp^2 [32] with a distinctive 2D wafer lattice structure; moreover, it not only renders it the thinnest, strongest, and low-cost substance in existence (Figure 4), it empowers with many exemplary physical and chemical characteristics such as high thermal conductivity up to $5000 \text{ Wm}^{-1}\text{K}^{-1}$, outstanding carrier mobility at room temperature to approximately $20 \text{ m}^2\text{V}^{-1}\text{s}^{-1}$, decent electrical conductivity at 2000 Sm^{-1} , excellent environmental stability with exceptionally high theoretical specific surface area, high strength up to 1 TPa Young Modulus and certainly has a high potential of organic and inorganic molecule adsorption [33]. For composite materials based on graphene, graphene behaves as either a functional part or a substratum for inactivating the other elements. Reinforcing metal oxides on graphene can influence the productivity of different catalytic and storage reactions in systems for energy conversion [34]. In graphene, the close carbon-carbon gap influences the electronic bands to overlap intensively [35].

In recent advances, graphene is used in different areas, including hydrogen production, water splitting, carbon reduction, environmental management, organic synthesis, and bacterial decontamination.

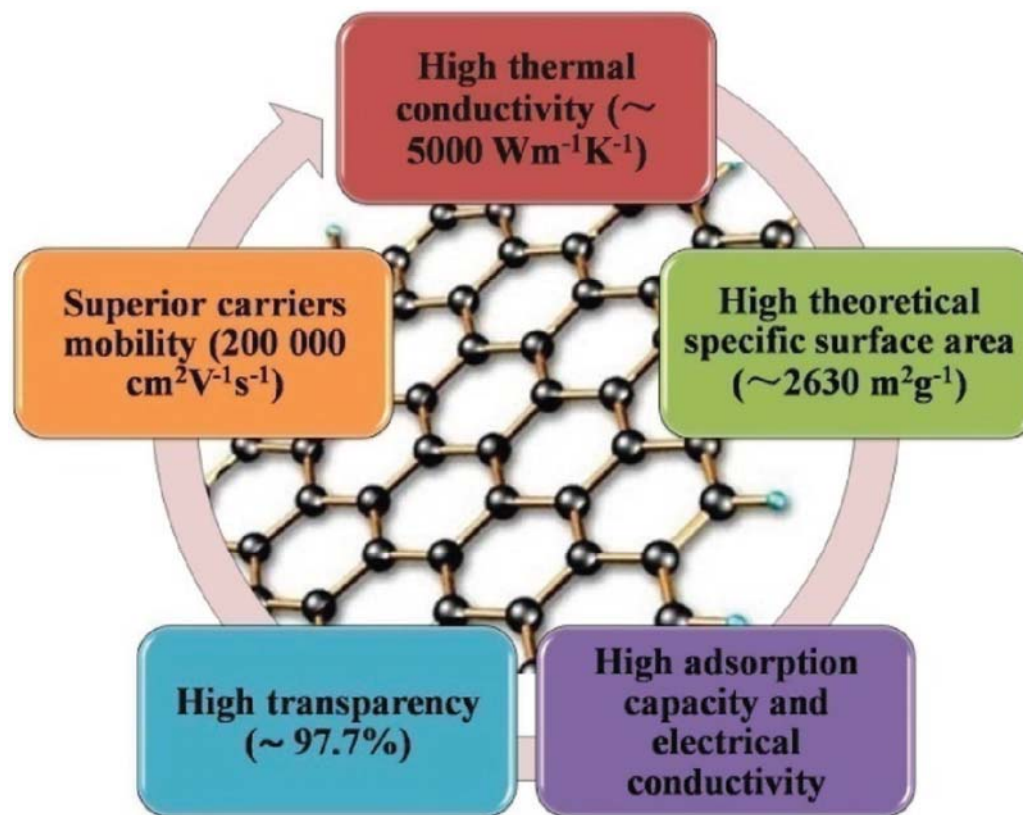


Figure 4. Graphene properties [33].

Many theoretical hypotheses and experimental discoveries of the utilization of graphene in heterogeneous catalysis have been made; the roles of graphene in catalysis may either be part of the system, acting as a support mechanism, or functioning as the catalytic core [36]. With its high electrical conductivity and electronic structure with zero bandgaps, graphene has drawn significant attention in electronics. Over the years, however, this ultra-stable and inert substance gradually became a desirable catalyst. Many theoretical hypotheses and experimental discoveries of the utilization of graphene in heterogeneous catalysis have been made; the roles of graphene in catalysis may either be part of the system, acting as a support mechanism, or functioning as the catalytic core [36]. In recent advances, graphene has been used in different areas, including hydrogen production, water splitting, carbon reduction, environmental management, organic synthesis, and bacterial decontamination.

When graphene acts as a support mechanism, it is defined into four different divisions, which depends on the external atom introduced where graphene limits metallic nanoclusters or nanoparticles (M_x/G), solitary atom for metallic and non-metallic (M_1/G), solitary atoms (N_x) moiety with graphene medium (M_1N_x/G) and solitary atoms or group reinforced via functionalized graphene catalyst; for instance, graphene oxide or graphene oxide that has been reduced. In any type of active catalyst used, graphene is out to secure the species effectively while operating as abet. Having an atom lies on graphene on the surface vacancy is able to alter the graphene electronic structure [37]. Adatom is basically a term used to call an atom that sits on the surface, and researchers have discovered that metallic adatoms formulate reliable agents for graphene electron-doping as the interactions of the charge transmissions from adatoms to graphene can be controlled through the ionic bonds without affecting the electronic components of the graphene.

Alternatively, when graphene involves adatom elements from either transition, noble, or group 14 on the periodic table, it forms a characteristic covalent bonding as a result of the strong electronic hybridization due to the subject of the adsorption [38]. In any case of which type of bonding occurs, the interlinkage between metal and graphene is said to be frail, which leads to the introduction and further research on the accumulation of nanoclusters on metal atoms as the experimental calculations of the adsorption energies of particular metallic atoms. The foremost debatable matter to propose graphene as catalyst support is the adjustment to the chemical reactivity and stability of the relationship between active adsorbate and graphene in order to enhance photocatalytic performance [36].

Theoretically, studies mention that zero bandgap due to low-density conditions and the wide-ranging conjugation of p-electrons spin have instigated structural steadiness and inert chemical reaction of graphene. Early findings upon catalytic characteristics of nanocavities in zeolitic structures, zero dimension metal-organic frameworks, and one-dimensional carbon nanotubes show that the adsorption of nanoparticles is influenced by the impact of nesting as well as the effect of quantum confinement. Nevertheless, by nature, zero-dimensional and one-dimensional frameworks are not fundamentally well developed in comparison with the two-dimensional enclosed framework causing complications to be properly analyzed theoretically or practically studied with advanced characterization techniques [36].

In research where multiple structure layers of carbon oxide comprising graphene cover the platinum surface, weaker adsorption of carbon oxides were examined with graphene than whilst platinum is unbound from any cover. Furthermore, carbon oxides reverse their adsorption at low temperatures with the manifestation of graphene cover. Introducing heteroatoms to graphene will tune the electronic characteristics, which prolong the photocatalysis applications. As an instance, covering with oxygen atoms will attune the electronic characteristics of graphene; oxygen adsorption eliminates the equality of the carbon-carbon sublattices in graphene by forming carbon-oxygen covalent bonds after splitting the initial orbitals [35].

Table 1. Examples of graphene-based photocatalysts for hydrogen production through water splitting.

Photocatalyst	Graphene (wt%)	Preparation Method	Source	H ₂ generation (μmolh^{-1})	Ref
P25/RGO	0.17	Hydrothermal	UV-visible	74	[39]
ZnCdS/RGO	0.25	Coprecipitation-hydrothermal	UV-visible	1824	[40]
TiO ₂ /RGO	0.7	Solution-mixing	UV	50	[41]
CdS/RGO	1	Solvothermal	Visible	1120	[42]
CdS/ZnO/RGO	1	Solid state	Visible	751	[43]
TiO ₂ /RGO	2	Hydrothermal	UV-visible	5.4	[44]
CdS/N-RGO	2	Solution-mixing	Visible	210	[45]
TiO ₂ /MoS ₂ /RGO	5	Hydrothermal	UV-visible	165.3	[46]
TiO ₂ /RGO	5	Sol-gel	UV-visible	8.6	[47]

Table 1 illustrates the hydrogen production through water splitting for different graphene-based photocatalysts. Generally, graphene is a single layer of atomic structure that can perform as the core catalyst. Charge sharing befalls naturally when different atoms adjoin graphene catalysts. One primary benefit is that graphene can indeed be developed on a suitable substrate, and the substrate can be designed for catalytic applications pre or post-development, preventing the need for exfoliation and transfer of graphene, which preserves the quality product of graphene. The simplistic catalytic activation of graphene without changing the quality assures artificial progression specifying suitability for engineering implementation [36].

3.1.2 Graphite

Consequently, chemical or heat reduction will substantially enhance the heat conductivity of graphite oxide, primarily due to the regeneration of a graphic chain of sp² bonds [33]. The traditional method to synthesize graphite oxide is by oxidizing graphite with strong chemical oxidants, for example, nitric acid HNO₃ and sulfuric acid H₂SO₄, to formulate graphite oxide [34]. In addition, graphite oxide can also be reduced to graphene by means of thermal, chemical, electrochemical, photothermal, photocatalytic, and microwave reduction methods, with partial restoration of the sp²-hybridized system. The graphite-based photocatalysts for hydrogen production through water splitting are described in Table 2.

Table 2. Examples of graphite-based photocatalysts for hydrogen production through water splitting.

Photocatalyst	Preparation Method	Source	H ₂ generation ($\mu\text{mol g}^{-1} \text{ h}^{-1}$)	Ref
g-C ₃ N ₄ /ZnIn ₂ S ₄	Hydrothermal	Visible	2780	[48]
g-C ₃ N ₄ / α -Fe ₂ O ₃	Thermal annealing	Visible	31400	[49]
TiO ₂ /g-C ₃ N ₄	Hydrothermal	UV	18200	[50]
N-La ₂ Ti ₂ O ₇ /g-C ₃ N ₄	Sonication	UV	430	[51]
O-g-C ₃ N ₄	Thermal oxidation	Visible	8874	[52]
g-C ₃ N ₄ /CaIn ₂ S ₄	Hydrothermal	UV	102	[53]
g-C ₃ N ₄ /Graphene	Impregnation/ thermal annealing	Visible	451	[54]

3.1.3 Carbon Nanotube

More recent research has centered on the use of carbonaceous nanomaterials such as carbon nanotubes, CNT and fullerenes, C₆₀ in combination with semiconductor photocatalysts to develop high-performance composite materials [55,56]. That is because the delocalized conjugated system found in the carbon allotropes will act as electron reservoirs for prompt transfer and splitting of photo generated electrons. They also help to improve the adsorptive properties of photocatalysts and lead to catalytically active sites [57]. Another interesting approach to expanding TiO₂ photocatalytic behavior to electromagnetic radiation regions is to dope this substance with carbon. For reference, doping TiO₂ with carbon nanotube, CNT has drawn the attention of the researchers for its synergistic effect improving the overall photocatalytic efficiency of TiO₂ and suggested a combination of several mechanisms through its justification remains uncertain [58]. Regardless of the ambiguity, the improved photocatalysis of carbon nanotubes with titanium dioxide, CNT-TiO₂ materials have degraded organic impurities in wastewater and air. Furthermore, the carbon nanotubes mechanism is capable of serving as an electron pool to split electron-hole pairs effectively, and also, other mechanism advocates that carbon nanotubes may perform as a photosensitizer to directly pump electrons into the TiO₂ conductive band [59].

3.1.4 Activated Carbon

Activated carbon, AC is normally utilized as a source of aid for heterogeneous catalysts by a certain degree of surface correlating to the appearance of non-carbon atoms such as hydrogen, oxygen, sulfur, and nitrogen [60–63]. Scattering techniques are inscribed to many different methods, including hydrothermal [64], mechanical mixing, chemical vapor deposition, sol-gel, and low-temperature hydrolysis [65]. Previous investigation has shown that the fusion of activated

carbon-TiO₂ has a beneficial impact on photocatalytic activity. AC is basically desirable depending on the situation since it has a high surface area of around 900m²g⁻¹ to 1200m²g⁻¹ and can repress another catalyst like titanium dioxide particles during calcination procedures and counterwork agglomeration [66]. As a result, activated carbon contributes to the high degree distribution of titanium dioxide particles with smaller size and higher surface area, enhancing photocatalytic degradation [67]. Furthermore, researchers documented that AC quickens photocatalytic degradation due to its capability to adsorb high concentrations of organic composites [68], affecting the stability and nature of the different other nanocomposites such as titanium dioxide.

3.1.5 Other Carbonaceous Materials

In catalytic procedures utilizing carbon-containing reagents, carbon layers, for example, carbide carbon, and graphitic carbon, frequently form on transition metal coatings. [69]. As hydrogenation processes are added by carbonaceous species such as carbide, the participation credits to higher reaction activity, which contradicts when transition metals incorporate graphitic carbon deposition that chemically instigates material inertness and physically creates clogging on the surface active sites [70]. Typically, researchers assume that the composition of graphitic carbon on metal catalysts shall be prevented both before and during catalytic activity [71]. Even so, further comprehensive investigation works have been devoted for years to using surface carbon films built on metallic elements to comprehend their duties in catalytic activity, which unfortunately hinders the complexities of the poorly defined carbon compositions. Graphene has been growing on many transition metal surfaces as a simplified type of graphitic powder by catalytic cracking of carbon-containing gases [72]. Exterior experimental investigation of graphene and metal surface has continuously demonstrated that beneath the graphene overlayers contain gaseous molecules including carbon oxide, oxygen, and water [73]. Nevertheless, the island borders [74], domain limits [75], and wrinkles [76] are the beneficial shortcomings in graphene as it allows a passage for particle diffusion to penetrate the graphene or any metallic edges [77].

3.2 Non-Carbonaceous Photocatalyst

Titanium dioxide, TiO₂ and cadmium sulfite, CdS are frequently examined photocatalysts for hydrogen generation by water splitting, according to [78]. In addition to the co-catalyst and sacrificial agents, numerous researchers have presented review papers addressing distinctive aspects that correspond to the photocatalytic water splitting mechanism behind its fundamental theory, philosophical philosophy, characteristics, and properties of the photocatalyst. However, in terms of the essence of a photocatalyst, there are still not many published studies to define specific and effective catalyst, co-catalyst, and sacrificial reagent. There are a variety of experiments using TiO₂-based photocatalytic activity to counteract the hazardous greenhouse gas emissions to the ecosystem [79]. Chemical stability, simple accessibility, non-toxicity, and the capability to oxidize under the presence of light radiation encourage photocatalysts based on TiO₂ to resolve the significant global environmental issues and the need for renewable power [80].

TiO₂ is a broad-bandgap semiconductor typically found in three distinct crystalline structures in a natural state: rutile, anatase, and brookite [81]. The most popular photocatalyst for the production of hydrogen is TiO₂ in anatase form. It cannot be used in the visible light spectrum, nevertheless, as TiO₂ bandgap is within the UV range for various crystalline phases, where anatase-3.2 eV, rutile-3.0 eV, and brookite-3.3 eV [13]. Furthermore, with the energy band gap, the effectiveness of photocatalysis relies on several other variables. This process includes a photocatalyst (TiO₂), water, sunlight, or ultraviolet radiation during the entire process. The capability of TiO₂-based photocatalysts to discolor and fully disintegrate organic dyes found in water is another valuable feature [82].

TiO₂ is currently manufactured commercially in powder form as a photocatalyst, and the findings of spectroscopic studies show that the time intervals between redox reactions or recombination involving charge carriers are significantly lesser, leading to a substantial reduction

in the TiO_2 photocatalytic process [82]. Other examples of non-carbonaceous photocatalysts are doped non-metals such as oxygen, sulfur, nitrogen, boron, and phosphorus with metal oxides such as zinc oxide and zirconium dioxide.

TiO_2 / EG, TiO_2 / GLY, TiO_2 / Na_2S / Na_2SO_3 , TiO_2 / GLU, TiO_2 / Na_2S of hydrogen generation efficiencies were observed to be 190.2 μmol , 130.8 μmol , 126 μmol , 120 μmol , and 120 μmol as shown on Figure 5. Although the energy gap continues to show full efficiency for TiO_2 , according to Figure 5, the most suitable agents for any kind of oxide photocatalyst are glycerol and glucose. This is attributable to their quantity, less toxic effects, low price, and the ability to undergo dehydrogenation conveniently compared to others [83]. Table 3 represents the non-carbon-based photocatalysts for hydrogen production through water splitting

It is further suggested that materials with layered perovskite-type comprising TaO_6 in octahedra formation are suitable candidates that fit the hydrogen generation process through water splitting [84]. For example, $\text{Sr}_2\text{Ta}_2\text{O}_7$ is a layered perovskite-type semiconductor, so when it is coupled with nitrogen and graphene sheets, it has been proclaimed to be effective for water-splitting photocatalysts with the presence of ultraviolet radiation [85]. The typical current photocatalyst elements such as the well-known P-25 titanium dioxide, TiO_2 , including the above-mentioned $\text{Sr}_2\text{Ta}_2\text{O}_7$, are active under the presence of UV light radiation due to their wide bandgap property, ranging from 3.0 eV to 4.0 eV [86]. Since the past decade, researchers have been concentrating on investigating photocatalyst materials that can be used efficiently under visible light with the deliberation of the cumulative solar spectrum incident reflecting on Earth which is about less than 5%. A suitable photocatalyst should perform in the visible light range $420\text{nm} < \lambda < 800\text{ nm}$ with a bandgap no more than 3 eV [85].

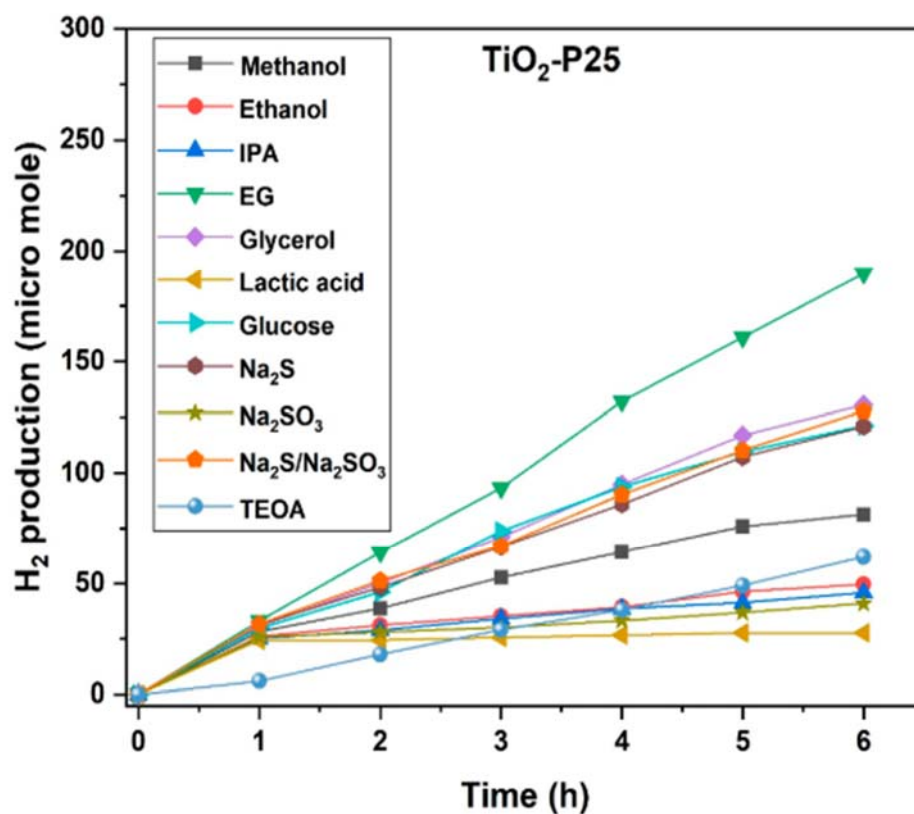


Figure 5. The efficiency of using TiO_2 for hydrogen generation using different sacrificial agents [87].

Table 3. Examples of non-carbon-based photocatalysts for hydrogen production through water splitting.

Photocatalyst	Preparation Method	Source	H ₂ generation ($\mu\text{molg}^{-1} \text{h}^{-1}$)	Ref
Black TiO ₂	Solvothermal	UV	0.4	[88]
2HMoS ₂	Exfoliation/Thermal annealing	Visible	300	[89]
CdS	Sonication	Visible	41100	[90]
Black BiOCl	Hydrothermal	Visible	0.00251	[91]
Fe-BiOCl	Hydrothermal	Visible	0.00354	[92]
O doped-ZnIn ₂ S ₄	Hydrothermal	Visible	2120	[93]

3.3 Co-catalyst

Generally, a co-catalyst is necessary for proton reduction and water oxidation in the water-splitting process. Apart from intensifying the speed of reaction, a suitable co-catalyst increases the efficiency of the reaction process. The speed of photocatalytic reactions can be accelerated by the suitable preparation of co-catalysts on the surface. Besides, co-catalysts operate as the base of reaction to act as an agent on surface reactions and are often considered to facilitate the separation of charge regulated by the co-catalyst and semiconductor interfacial electric field. As the co-catalyst is included in the process, the depletion layer develops at the layer between co-catalyst and semiconductor, causing the induction of an electric field that offers dynamic force to separate the electrons and holes during the photocatalytic water splitting reactions [22].

Table 4. Examples of co-catalyst used in previous research.

Co-Catalyst	Source	Reference
CuO-Cr ₂ O ₃	Direct solar light	[94]
Cu ₂ MoSO ₄	Visible light irradiation	[95]
Pt	Visible light	[96] [97]
Ni ₃ C	Visible light irradiation	[98]
NiS	Visible light	[99]
NiS ₂	Visible light	[100]
Pt and RuO ₂ (dual co-catalysts)	Visible light irradiation	[101]
Au/TiO ₂	UV light	[102]

Table 4 illustrates the different co-catalysts was used for various research in the water splitting process. Over the decade, the interests of many researchers who concentrate on co-catalysts from the field of catalysis have captivated and drawn to a single atom or single-site catalyst as it allows new advances remarkably in heterogeneous catalysis [103] while improving the active sites and concurrently supporting metal interfaces with high-quality composition and chemical regulation [104] through reducing the metal consumption and allows unprecedented manipulation on the atomic effect. It is recognized that pinning on structural defects combined with coordinated unsaturated sites for support upholds isolated metal atoms. Notwithstanding the several ranges of supporting features, it is still difficult to create a high density of thermally stable support sites [105]. Therefore, the advancement and control of high single-atom catalytic activity is still a challenging issue [104].

3.4 Sacrificial Agents

Considering that hydrogen is essentially a zero-emissions greenhouse gas, a great deal of work has indeed been put into splitting water, facilitated by a variety of photocatalysts, including inputting sacrificial agents into the processing system. Although a catalyst may help accelerate reactions with the support of sacrificial electron donors and acceptors [106], this may not suffice for the complete separation of water. Nevertheless, the reactions where sacrificial reagents are applied in the development of hydrogen reactions mainly aim to upgrade the hydrogen and oxygen yield under such conditions. The effectiveness is dependent on the catalyst as well as the sacrificial electron donors employed [107].

In the process, abundant electron-hole pairs are generated through photon absorption. These charged particles subsequently travel to the catalyst surface to interact with active sites on the surface, causing the water to reduce, forming hydrogen, H_2 , and oxidizing water to produce oxygen, O_2 [58]. There are divided reviews on the usage of sacrificial agents beneficially. Thereby, making TiO_2 based catalysts as an example in true water splitting to evaluate in H_2 photogeneration with the assist of sacrificial electron donors, the overarching hypothesis seems to be that the information gained in one is not transferable to another, thus restoring any perception that sacrificial donors can also be used to learn about hydrogen production. The argument of the sacrificial electron donors methodology is less relevant when declining in water pollutants plays with this function. The information gained through the SED technique with a spectrum of substrates is essential for such strategies, demonstrated in many reviews utilizing methanol, CH_3OH , and formic acid, $HCOOH$ leads to the exceptional performance of the H_2 generation. Figure 6 describes the Earlier version of an experimental system for water splitting by photocatalytic [108].

Despite the questionable benefit of using sacrificial agents leads to practical and functional after-products, Hainer et al. [107] had also indicated the organic substances in the river water can act as the sacrificial electron donors through photocatalytic solar emissions while eliminating the pollutants. Although it is assumed that data gathered and published on water-splitting catalysts will be helpful for future researches, there are many uncertain subjects that require extensive queries, such as if the performance of the specific catalyst used to speed up the reaction during the water-splitting process is correlated when acts with the presence of sacrificial agent [107].

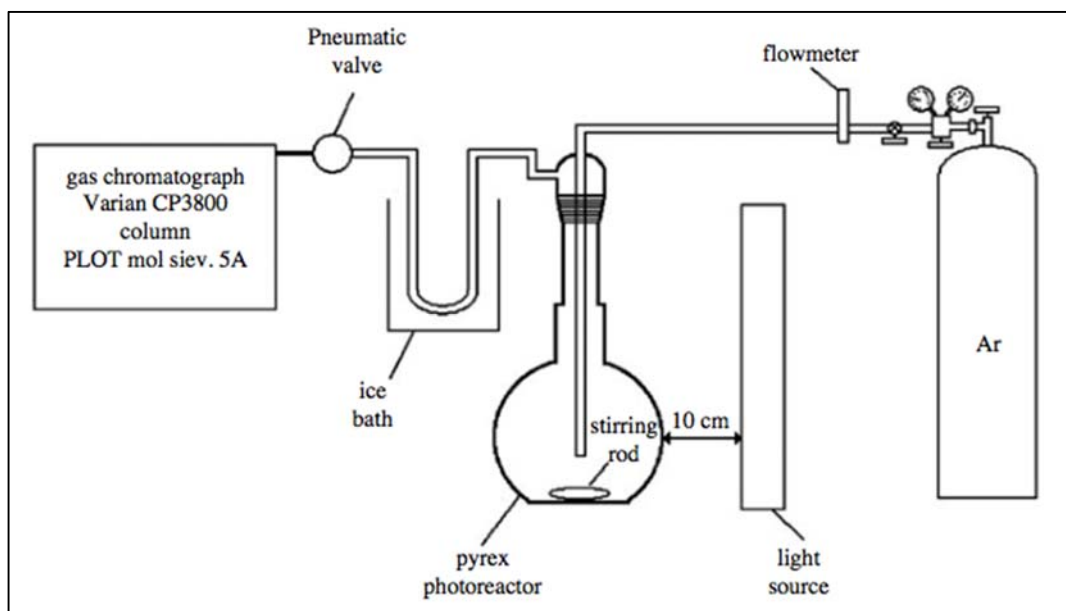


Figure 6. Earlier version of an experimental system for water splitting by photocatalytic [108].

Sacrificial agents can be divided into organic and inorganic types (Table 5). These agents can either be photodegradable or non-photodegradable. Generally, photodegradable industrial contaminants such as methanoic acid CH_2O_2 and oxalic acid $\text{C}_2\text{H}_2\text{O}_4$ are commonly used and more favored to protect the atmosphere when processing hydrogen [109].

In the organic sacrificial agent range, methanol CH_3OH is one the most common agent apart from propanol $\text{C}_3\text{H}_8\text{O}$, ethanoic acid CH_3COOH and the simplest carboxylic acid-- methanoic acid, CH_2O_2 that yields noticeable intensification of hydrogen generation under UV lights [110]. The enhancement was significantly improving with the presence of 0-20% methanol as the sacrificial agent; however, when more than 20% methanol is added, the performance degrades gradually [111]. The debasement is induced by the action of methanol functioning as a hole scavenger and recombination blocker, but not a hydrogen origin [112].

Table 5. List of sacrificial agents used for hydrogen generation [106].

Sacrificial agents	Source	Reference
Organic	CH_2O_2	UV light [109] [110] [113]
	CH_3OH	UV light [113] [112] [111]
	CH_3COOH	UV light [110] [113] [114]
	$\text{C}_3\text{H}_8\text{O}$	UV light [113]
	$\text{C}_2\text{H}_2\text{O}_4$	UV light [109]
	Inorganic	NaNO_2
NaOH		UV light [116] [114]
H_2SO_4		UV light [117] [116] [114]
KOH		UV light [114]
Na_2SO_4		UV light [114]

Comparisons were concluded during various testing of strontium titanate, SrTiO_3 with methanol CH_3OH , propanol $\text{C}_3\text{H}_8\text{O}$, methanoic acid CH_2O_2 , and ethanoic acid CH_3COOH ; it was revealed that methanoic acid CH_2O_2 had the most reliable performance [113]. The response transpired in a single step found that average hydrogen generation progresses with methanoic acid CH_2O_2 concentration. The benefit of using mentioned chemicals working as sacrificial agents is also that they can be adopted to refine the environment [118].

Furthermore, inorganic compounds were also often applied as sacrificial agents acting as additives or as cutting-off filters from UV lights or even just to attune the pH of solution used [106], such as sodium nitrite, NaNO_2 [115].

4. Factors Affecting Photo Catalytic Reactivity

Factors that influence photocatalytic activity reactivity vary, including bandgap energy, light intensity, temperature, sacrificial agent, pH levels, and surface area [14].

4.1 Band Gap Energy

The energy bands or bandgap characteristics usually represent the electronic properties of the semiconducting electrodes and can be considered a spectrum of energy levels attributed to the variations in energy between the conduction band and the valence band. Thermodynamically, the covalent band has to exceed higher than the relative acceptor potential level [119]. Concerning thermodynamics, the H^+ from the water is consumed by the active side and undergoes reduction via photoelectron usage to form H_2 [120]. The peak of the valence band for TiO_2 is at $+2.7\text{eV}$ with a pH value of 7, which is more positive in comparison to the O_2/H_2O redox pair. Figure 7 (b) represents a schematic image of different types of photocatalyst band energy gap [14]. Meanwhile, referring to the same Figure 7 (a), the covalent band of the H_2/H_2O redox pair has a higher value than the covalent band of TiO_2 [102]. Table 6 represents the photocatalyst bandgap values determined by valence band x-ray photoelectron spectroscopy.

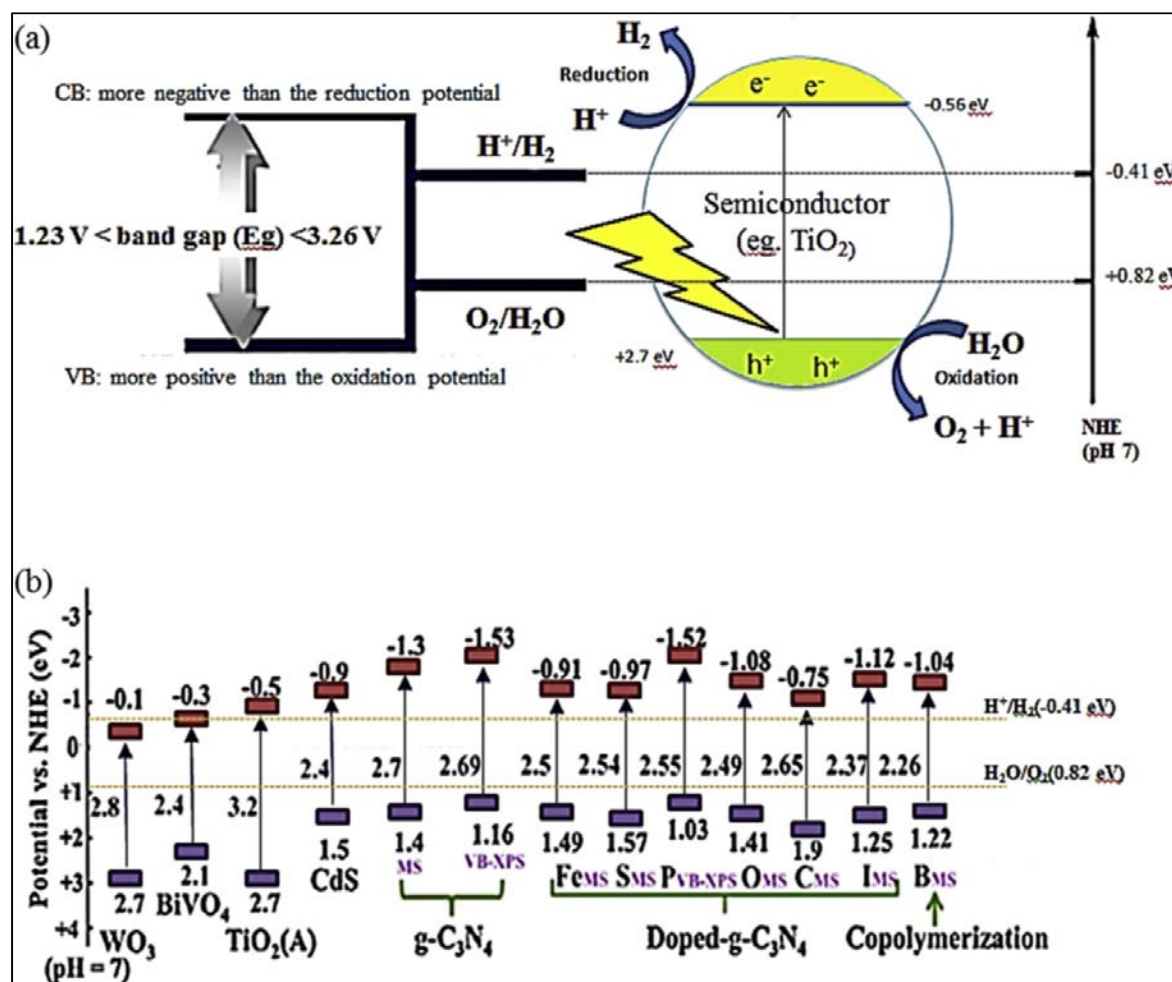


Figure 7. (a) The basic principle of hydrogen generation using photocatalytic water splitting method, (b) An schematic image of different types of photocatalyst band energy gap [121].

Table 6. Photocatalyst bandgap values determined by valence band x-ray photoelectron spectroscopy [17].

Semiconductor Compound	Conduction Band	Valence Band	Energy Gap (eV)
TiO ₂	-0.5	2.7	3.20
SrTiO ₃	-0.61	2.59	3.20
SiC	-0.46	2.34	2.80
WO ₃	-0.1	2.7	2.80
g-C ₃ N ₄	-1.3	1.4	2.70
CdS	-0.9	1.5	2.40
Cu ₂ O	-1.16	0.85	2.10

The circumstance is that TiO₂ has a bandgap of 3.2 eV; hence, TiO₂ is unfitting for visible light irradiation unless if TiO₂ undertakes doping procedures with metals, non-metals, coupling semiconductors, and utilizing other practicable schemes to promote bandgap diminution. As compared to BiVO₄ and WO₃, the g-C₃N₄ band gap is reasonable at 2.7 eV with the most negative CB level at 1.3 V to foster its extensive applicability in photocatalytic activity of visible light spectrum [122], leading to a recommendation on benefitting TiO₂ to dope with g-C₃N₄ for intensifying semiconductor visible light absorption reactions and maximizing the performance of the photocatalyst. Co-catalysts may also perform an essential role in enhancing the stability and conceivably segregating the charge of semiconductors to accelerate the growth on hydrogen generation level [122].

4.2 The Light Intensity

The performance efficiency of a photocatalytic water-splitting can be optimized by increasing the light intensity amidst energy higher than the activation limit [123]. In accordance with UV-photon flux, there are two framework schemes relating to the photocatalytic activity; the first order normally uses electron-hole couples and 25 mWcm⁻² flux, causing faster chemical reaction consumption rate than by recombination reactions, and the other half order involves the recombination of a higher intensity which influencing less on the activity rate. Fundamentally, the adsorption range of the catalyst with a threshold corresponds to the band energy diversifies depending on the functional wavelength [14]. The lighting intensification from 900 to 1000Wm⁻² when using ZnS as a catalyst advances the production of hydrogen by up to 20 percent [124]. Hence, hydrogen generation increases as light intensity increases [125].

4.3 Temperature

The photocatalytic reaction does not induce the presence of temperature as it is not a creation factor of both electrons and holes. Regardless, the increase in the rate of releasing an adsorbed substance from a surface will be greatly influenced by the temperature [14]. Generally, temperature factors under different catalyst types will increase the pace of the reaction rate in any photocatalytic process. Hence, this aspect shall be put into consideration during the experimental stage. Zhang & Maggard, 2007 claimed that the ideal temperature range in the photocatalytic analysis is stated to be within 60 and 80 [126]. Fundamentally, electrons on the valence shell will receive higher energy transfers to the greater energy level at a high temperature which directs the electron-hole to oxidize and reduce accordingly [127].

Alternatively, temperature reduction will decelerate the flow of hydrogen generation as a result due to the interference caused by the desorption. The development of hydrogen generation upsurges at 30 °C, 40 °C, and 50 °C, producing 59 mol/g.s, 92 mol/g.s and 370mol/g.s of hydrogen correspondingly [128]. In another experimental procedure where pt/TiO₂ were used in a photocatalytic reaction, hydrogen generation increases its performance with temperature

change from 45 °C to 55 °C giving 4.71mmol g^{-1} to 15.18mmol g^{-1} after four hours [129]. This evaluation of studies has shown us that degree of temperature influences the efficacy of any photocatalytic action.

4.4 pH Levels

The pH level in the hydrogen creation process has been considered as a key factor that modifies the reactivity level with an increase in pH from low to moderate alkaline values. As stated by [130], the bandgap energy shift towards dependent on the variation in pH and yield of hydrogen production improves in basic solution, particularly in a weak base. The extraction of hydrogen from water splitting can be deemed to depend on the proton concentration of the pH values considering proton reduction is induced during the splitting of the water molecules [14]. In the context of photo-reformation, this contextual aspect is particularly crucial because the existence of a sacrificial organic substance is necessary.

In a testification by [131], examining the performance between pH2 to pH12 and noticed using an alkaline medium with pH10 and a strongly acidic medium with pH2 exhibits a notable difference. In accession to the usage of CuO $_x$ /TiO $_2$ as the catalyst with different types of mediums, the base medium assists in generating the maximum hydrogen outcome, and the result appears to contradict whilst employing the acidic medium. The outcome is attributable to the low adherence of copper, Cu on the titanium dioxide, TiO $_2$ surface in pH2 medium. Moreover, due to weakened stability in higher concentrated acid or base solution, the performance of hydrogen generation using titanium dioxide/platinum/silicon/cadmium sulfide catalyst ought to have the lowest efficiency [132].

Meanwhile, an examination for four hours using Pt/r-TiO $_2$ generated maximum hydrogen at pH5.5 then followed by a strongly basic medium of pH12 and strong acidic medium pH2 [133]. However, another investigation was done using a photosensitized catalyst such as photosensitized TiO $_2$ /RuO $_2$ -MV $^{2+}$ in an acidic state produces more hydrogen [134]. According to [135], hydrogen production opposed the general conclusion and stated that evolution is more effective in acidic than in the basic state. The science behind this result is that more hydrogen ions can be easily adsorbed at acidic pH, hence, regulating the reduction of hydrogen ions to form hydrogen. Regardless, the general deduction from the earlier researches done is that the photocatalytic activity working in a basic approach presents more augmentation in hydrogen production.

4.5 Surface Area

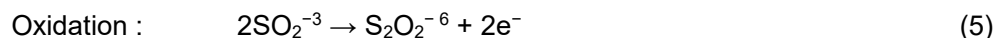
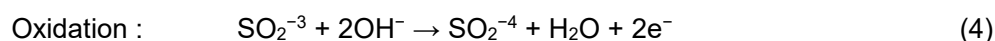
Considering the bandgap is one of the main variables impacting photocatalytic reactivity, surface area modulation is a strategic approach to narrowing the catalytic bandgap [136]. The photocatalytic development of hydrogen generation is also influenced by the composition of the catalyst. By having a wider surface region, the photocatalytic activity can progress better with more reactive sites [137]. According to an experimental journal by [67], the diffusion of titanium dioxide particles as a catalyst is greater with smaller size, and higher surface area will increase the photocatalytic reaction of the water-splitting process. This experimental declaration was theoretically supported by another researcher; remodeling titanium dioxide nanoparticles to a bigger size direct to a more vulnerable metal foundation synergy [138]. Smaller sizes crystalline photocatalysts provide a shorter distance for photo-generated electrons and holes to pass rapidly to active reaction sites on the catalytic surface, thereby reducing the possibility for recombination [139]. The composition of the photocatalyst frequently relies on the synthesis approach adopted for the preparation of the catalyst.

Analyzing the performance of treated g-C $_3$ N $_4$ with HNO $_3$ and untreated g-C $_3$ N $_4$ following the equivalent and controlled operation condition practically confirms that the treated g-C $_3$ N $_4$ with HNO $_3$ performs better photocatalytic activity [140]. The addition of h $^+$, hydronation to g-C $_3$ N $_4$ results in structure depilation, forming small pores that support higher feasibility for the electrons-

holes couple detachment and transfer efficiency of the photo-generated electrons and holes. The common general integration techniques applied are mechanical mixing, sol-gel method, solvothermal, hydrothermal process, and chemical vapor coating [141]. The size, shape, and structure of any catalyst nanomaterials can further be adjusted by implementing variation temperature during the catalyst preparation. Based on an experimental data by [142], the size of the catalyst increases when temperature increases from 6nm at 250 °C, 11nm at 380 °C, 30nm to 45nm at 550 °C, above 45nm at 650 °C and above 100 nm at 800 °C. Besides, a separate photocatalytic test whilst considering the surface area, it was found that TNT photocatalyst had a higher hydrogen generation output rate of 4.6 mmolh⁻¹gcat⁻¹ compared to TNR and TNS [143].

4.6 Sacrificial Agents

Improvement of highly efficient photocatalysts for the development of hydrogen generation through water-splitting has aroused interest from all researchers. For years, researchers have been investigating different aspects that may improve the outcome, including adding the sacrificial agents to the system. The sacrificial reagent is widely used for photocatalytic water splitting processes and the sacrificial agent used in recent times includes Na₂SO₃ [78]. The photochemical interactions of the Na₂SO₃ mixture of sacrificial agents and their breakdown products during H₂ generation are evaluated as follows (Equation 4 to 5):



A sacrificial agent is also named an electron donor who plays an important part in hydrogen generation. Additionally, the quality of photocatalyst performance can be enhanced by the addition of organic forms that function as sacrificial agents or in other words, hole collectors; for instance, CH₃OH, C₂H₅OH, C₆H₆O and C₃H₈O₃ [144]. The utilization of alcohol permits semiconductors to oxidize organic particles and reduce H⁺ to H₂ by gaining electrons, hence, raising the hydrogen output. This methodology is termed 'photo-reforming'. The photo-reforming of alcohols in the reaction mechanism as a sacrificial agent can be interpreted as; C_xH_yO_z + (2x - z) H₂O → xCO₂ + (2x - z + (y/2)) H₂ [145]. As stated by [102], with the assist of silver/titanium dioxide as the co-catalyst, photocatalytic activity with glycerol produces the greatest amount of outcome and consequently with methanol than ethanol. Figure 8 illustrates the hydrogen production in mmolg⁻¹ under different sacrificial agents.

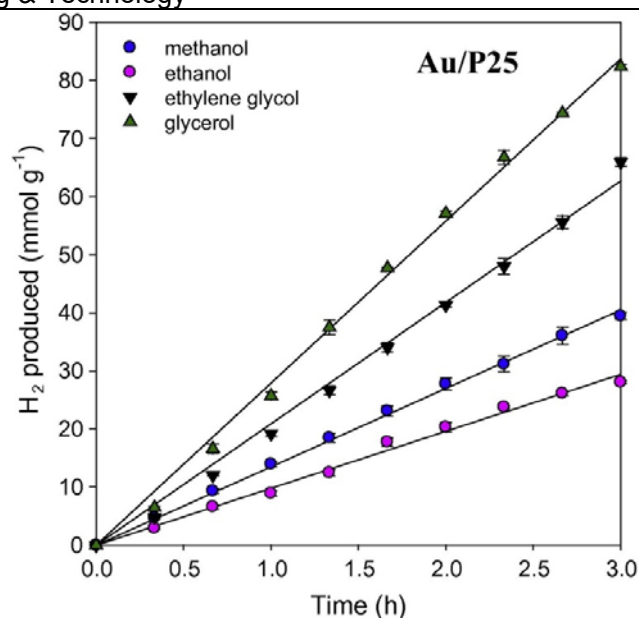


Figure 8. Hydrogen production in mmol g^{-1} under different sacrificial agents [146].

Based on the geometry reactivity group, the result was anticipated that the sacrificial hole collector would have an α -H adjacent to the OH-groups as seen in Figure 9: Configurations of the sacrificial agents with the other major by-products of alcohol photo-reforming just being relatively foreseeable based on the alcohol configuration [14].

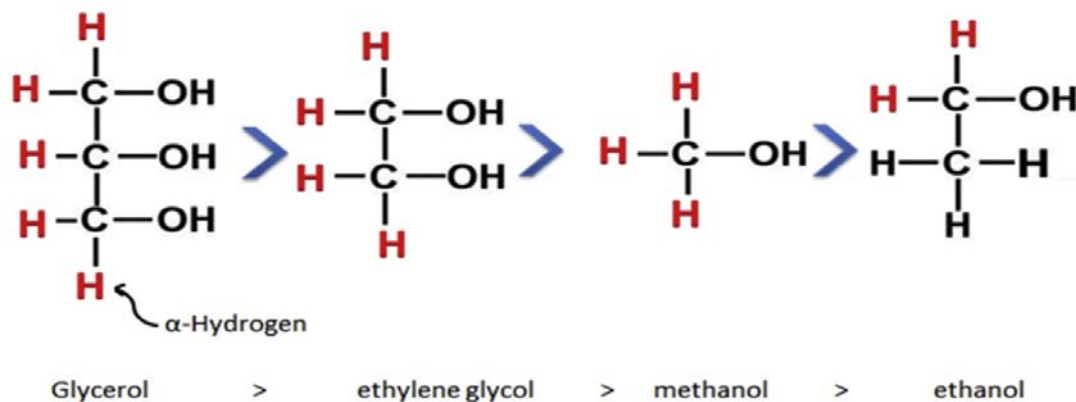


Figure 9. Configurations of the sacrificial agents [121].

Furthermore, the appearance structure of α -H atoms and the concentration of the sacrificial agents also have an effect on the generation rate of hydrogen [147]. In consideration of the fact that $\text{C}_3\text{H}_8\text{O}_3$ has five α -H atoms, it can create more hydrogen than with $\text{C}_2\text{H}_6\text{O}$, CH_3OH , including $\text{C}_2\text{H}_5\text{OH}$. Table 7 describes the effect of several sacrificial agents used in the photocatalytic process of water-splitting for hydrogen generation.

Table 7. Brief summary and effect of several sacrificial agents used in photocatalytic water-splitting for hydrogen generation [14].

Feed	Catalyst	Hydrogen (H ₂) Production	Ref.
CH ₃ OH, C ₂ H ₅ OH, C ₂ H ₆ O ₂ & C ₃ H ₈ O ₃	75ml TiO ₂ 2.1wt% Pt/TiO ₂	1134 μmol h ⁻¹ CH ₃ OH (17.13M) > C ₂ H ₅ OH (7.34M) > C ₂ H ₆ O ₂ > C ₃ H ₈ O ₃ (27.9 mmol g ⁻¹ h ⁻¹)	[148]
10% volume of alcohol-H ₂ O, H ₂ O, CH ₃ OH, C ₂ H ₅ OH, C ₂ H ₆ O ₂ & C ₃ H ₈ O ₃	65mg 1.5wt% Au/TiO ₂	Au/P25 > Au/anatase SG ≈ Au/brookite > Au/anatase HT ≈ Au/rutile HT C ₃ H ₈ O ₃ > C ₂ H ₆ O ₂ > CH ₃ OH > C ₂ H ₅ OH	[102]
10% volume of alcohol- H ₂ O, CH ₃ OH, anhydrous C ₂ H ₅ OH, C ₂ H ₆ O ₂ & C ₃ H ₈ O ₃	450ml aqueous solution, 2.5 Cu ₂ O/TiO ₂	(2048.25 μmol g ⁻¹ h ⁻¹) CH ₃ OH > C ₂ H ₆ O ₂ ≈ C ₃ H ₈ O ₃ > anhydrous C ₂ H ₅ OH	[149]
10% volume of alcohol- H ₂ O, H ₂ O, CH ₃ OH and C ₂ H ₅ OH, 2-C ₃ H ₈ O, tertiary C ₄ H ₁₀ O, 1,2- C ₂ H ₆ O ₂ & 1,2- C ₃ H ₈ O ₂ & C ₃ H ₈ O ₃	0.0065g 1wt% Pd/TiO ₂	Pd > Pt ≈ Au C ₃ H ₈ O ₃ > 1,2- C ₂ H ₆ O ₂ > 1,2- C ₃ H ₈ O ₂ > CH ₃ OH > C ₂ H ₅ OH > 2-C ₃ H ₈ O > tert-C ₄ H ₁₀ O ≈ H ₂ O	[138]
25% volume of alcohol- H ₂ O, H ₂ O, -C ₄ H ₉ alcohol (t-C ₄ H ₁₀ O), n-C ₄ H ₁₀ O, n-C ₃ H ₈ O, C ₂ H ₅ OH & CH ₃ OH	50mg 0.5wt% RuO ₂ /TiO ₂ 1wt% Pt	(4200 mmol g ⁻¹ h ⁻¹) CH ₃ OH > C ₂ H ₅ OH > n-, C ₃ H ₈ O > n-C ₄ H ₁₀ O > t-C ₄ H ₁₀ O	[150]
10% volume of alcohol- H ₂ O, H ₂ O, C ₃ H ₈ O ₃ & Propan-2-ol	85mg 0.5wt% Pt/TiO ₂	(ca. 5.5 s ⁻¹) Pt > Pd > Au Propan-2-ol > C ₃ H ₈ O ₃	[151]
5% volume of alcohol- H ₂ O, H ₂ O, CH ₃ OH, C ₂ H ₅ OH, C ₃ H ₈ O, C ₂ H ₆ O ₂ & C ₃ H ₈ O ₃	0.05g MWCNTs/TiO ₂ /MMT	(1888 ppm h ⁻¹) C ₃ H ₈ O ₃ > C ₂ H ₆ O ₂ > CH ₃ OH > C ₂ H ₅ OH > C ₃ H ₈ O > H ₂ O	[152]

5. Recommendations

Future directions for more effective photocatalytic water splitting can be concentrated on other viewpoints, which cover;

- i. Apart from mentioned carbon-based catalysts, several non-carbonaceous photocatalysts can also be investigated for hydrogen generation through water splitting.
- ii. The mixture of Different carbonaceous materials can be investigated for hydrogen production as they contain the different crystalline structures of carbon.
- iii. Co-catalyst (carbonaceous to non-carbonaceous) shall be integrated into a photocatalyst framework to support the water splitting and optimize the production of hydrogen.
- iv. Noble metals like platinum or other potential chemicals shall be integrated into the system as the co-catalyst.
- v. Further research to comprehend more knowledge and achieve the target on photocatalytic water splitting for hydrogen generation with the resolution to design a better effective system such as using different reactors to maximize the performance efficiency from selecting different the photocatalyst, co-catalyst and sacrificial agents.

6. Conclusions

This study has exhibited numerous modification progress and advancement of carbonaceous photocatalysts for water splitting. The purpose of this capstone design project inquiries that it is feasible to formulate an effective photocatalyst that exhibits better efficiency to be marketed for reducing the dependency on natural gas and fossil fuels especially to supply energy for residential and industrial sectors. It is acknowledged that graphene combination with semiconductors offers an enhancement of behaviors and stability. Graphene does not only presents as the thinnest but also one of the strongest and low-cost substances in existence, enabling many excellent physical and chemical properties. However, to conclude that it is efficient 100% is still quite questionable and requires further research with many trials and errors. The overall performance of the carbon-based materials as a photocatalyst for hydrogen production from water splitting is promising for clean energy.

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Disclosure Statement

There are no conflicts of interest from the authors.

Symbols used

e^-	[-]	electron
h^+	[+]	positive electron hole
h^-	[-]	negative electron hole
H^+	[+]	hydrogen ion
OH^-	[-]	hydroxied ion
h	[Js]	Planck's constant
E	[J]	energy of a photon
f	[hz]	frequency

Greek letters

λ	[nm]	radiation wavelength
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Sub- and Superscripts

CO_2	carbon Dioxide
H_2O	water
H_2	hydrogen
O_2	oxygen
fs	femtosecond
ps	picosecond

μ s	microsecond
ms	millisecond
TiO ₂	titanium dioxide
ml	milliliters
Pt	platinum
Na ₂ SO ₃	Sodium sulfite
°C	degree celcius

Abbreviations

CB	Conductibe band
VB	Valance band
UV	Ultraviolate
TNT	titanium dioxide with nanotubes
TNR	titanium dioxide with nanorods
TNS	titanium dioxide with nanosquares

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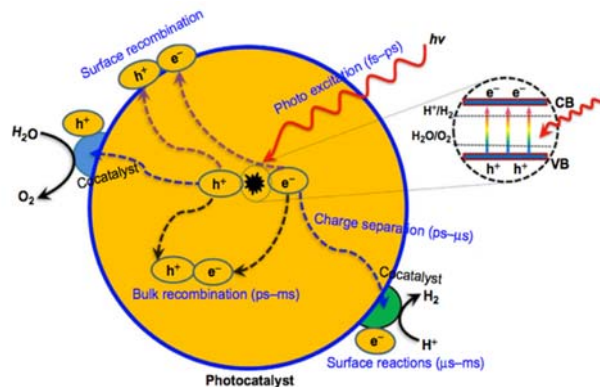
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Entry for the Table of Contents (Graphical abstract)



Carbonaceous materials (Graphene, Graphite, Carbon nanotubes, Activated carbon, etc.) has the potentiality for hydrogen production from water splitting through the photocatalytic process. The combination of graphene with semiconductors plays a significant role in this process for outstanding physical and chemical properties. The overall performance of the carbon-based materials as a photocatalyst for hydrogen production from water splitting is promising for clean energy production to enhance environmental sustainability.