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Water Splitting: Recent scientific and technological advances

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Abstract:

Hydrogen is the future of the world but to use it certainly, needed raw hydrogen from the environment to process it or split it up from the water. Water is available in abundance on the earth; thus, water will serve as excellent raw material for hydrogen generation. Water splitting is not a spontaneous process as it requires much energy. Depending upon the energy sources used for this highly energy extensive reaction to happen, methods for water splitting are classified. It is observed that catalysts play a vital role in facilitating water splitting. Extensive research is going into this field to develop cost-friendly and stable catalysts. Nanostructured materials also help significantly to boost the hydrogen production from water. This review briefly analyses various approaches in developing the conventional water-splitting method.

Keywords: Graphene, Electrocatalyst, Metal oxide, Semiconductors, Hydrogen

1. Introduction

Hydrogen is an ultraclean as it does not release destructive gases such as CO_2 that can cause global warming because only water does generate as the product. Hydrogen energy carriers have a large energy density (122 KJ/g), considered one of the most desirable alternatives to fossil fuels. Moreover, the energy yield of H_2 power is reportedly 2.75 folds greater in comparison to hydrocarbon fuels [4]. Hydrogen generation depends mainly on thermochemical water splitting and steam reforming of hydrocarbons. These processes are relatively cheaper. Industrially are well-tuned. However, the disadvantage with the thermochemical method is that it requires high-temperature high pressure. The steam reforming process uses hydrocarbon as the hydrogen source, which is nothing but the fuel that gets from fossil fuel. Statistical data from 2018 indicates global hydrogen production to be 63 million tons, which consumed $\sim 2.2\times10^8$ kWh of electricity while simultaneously emitting $\sim 6.3\times10^8$ tons of CO_2 [3].

Classification of water splitting processes:

Energy	***Process***
Light	Photocatalytic
Electrical	Electrocatalytic
Heat	Thermochemical

Production of hydrogen from water splitting is because at least resources used which are readily available. Since hydrogen energy is clean energy, various catalysts do use for this process, some of which are either platinum or graphene-based. However, as we know, platinum is expensive for everyday purposes. Research is building to find such metal with the same or somewhat better properties than platinum, which is widely available, thus solving the issue of cost.

According to recent research, the most used catalysts are metal-nonmetal complexes, including metal oxides, sulfides, phosphides, carbides, and nitrides. Carbon-based materials exhibit superior photocatalysis and electrocatalysis due to the concerned effects between doped metal atoms and carbon support. Carbon supports can provide solid anchor sites for metal atoms and regulate the coordination environment of metal atoms to have more favorable binding energy towards reactants [35]. These cost-effective metals will help the extensive formation of the hydrogen fuel cell.

Generally, oxygen vacancies are known to facilitate the adsorption of O on a metal surface and can thus induce Ni to oxidize high-valent species. The adsorption of OH^- on the catalyst surface was found to stimulate by oxygen vacancies, resulting in a lower Gibbs free energy for the formation of oxide species, which is considered the rate-determining step of the OER [2]. TiO_2, ZnO, and ZnS have been comprehensively investigated in the past. Still, their large bandgap (~3.2 eV) is now replaced by other types of photocatalysts, including metal-free catalysts as carbon-based nanomaterials [4].

In the Thermochemical water splitting process, an electrochemical reactor system, including the thermal process, shows relatively high efficiency for hydrogen production from water decomposition. Nanostructured carbon materials are helpful for hydrogen production from photocatalytic water splitting because of their high conductivity and large surface area as active reaction sites. In addition, because the photocatalytic activity showed significant differences according to the geometrical characteristics of photo-active materials, various nanosized materials have been fabricated for the photodecomposition of water [5].

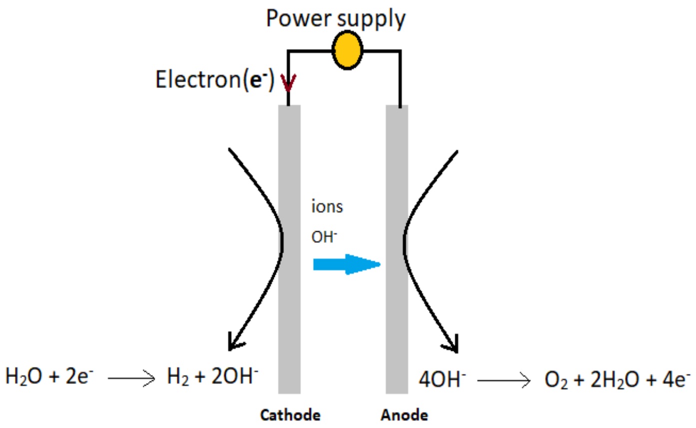

Fig 1: Electyrocatalytic water splitting

2. Discussion

2.1 Energy analysis of water splitting

Based on the water-splitting Equation (1), the changes of enthalpy ($\Delta H^0{}_1$) And entropy ($\Delta S^0{}_1$) Of that reaction can calculate by Eqs. (2) and (3).

$$H_2O \qquad \frac{1}{2}O_2\uparrow + H_2\uparrow \qquad (1)$$

$$\Delta H^0{}_1 = (\frac{1}{2}\Delta H°_{O2} + \Delta H°_{H2}) - \Delta H°_{H20} \qquad (2)$$

$$\Delta S°_1 = (\frac{1}{2}\Delta S°_{O2} + \Delta S°_{H2}) - \Delta S°_{H20} \qquad (3)$$

Where $\Delta H^0{}_{O2}$ and $\Delta S^0{}_{O2}$ are standard formations of enthalpy and Entropy of oxygen, 0 $kJ\cdot mol^{-1}$ and 205.29 $J\cdot K^{1}\cdot mol^{-1}$, respectively; $\Delta H^0{}_{H2}$ and $\Delta S^0{}_{H2}$ are the standard formations of enthalpy and entropy of hydrogen gas, 0 $kJ\cdot mol^{-1}$ and 130.59 $J\cdot K^{-1}\cdot mol^{-1}$, respectively. $\Delta H^0{}_{H2O}$ and $\Delta S^0{}_{H2O}$ are the standard formations of enthalpy and entropy of water, −285.85 $kJ\cdot mol^{-1}$ and +69.96.4 $J\cdot K^{-1}\cdot mol^{-1}$, respectively [6].

2.2 Electrocatalysis Water splitting

Splitting Hydrogen and Oxygen into their gaseous phase use electricity. Water is a poor conductor of electricity. Therefore, to improve the conductivity, acid or base is used. In this process, because water splitting is not a spontaneous reaction, a highly positive free energy change applies the potential. So have to use the possibility to happen as water splitting needs energy. As shown in fig 1, in water splitting, applying an electric potential between anode and cathode and split the water molecule into oxygen and hydrogen in which protons get discharged by taking electrons to evolve hydrogen at the cathode, which is known as Hydrogen Evolution Reaction (HER) and Hydroxide if it is in alkali. Hydroxide ion gets split into oxygen and electron with the evolution of water molecule, known as Oxygen Evolution Reaction (OER), which occurs at the anode. Free energy associated with this particular process is highly positive.

The major problem of conventional electrolyzers like alkaline electrolysis polymer/proton electrolyte membrane electrolysis (PEM) is their high electricity consumption. The recent innovation of Steam Electrolysis technology reaches higher total energy efficiency than alkaline and PEM. At high temperatures, H2 reduces H2O vapor. The ionic conductivity of electrolyte and rates of electrochemical reactions at the electrode surfaces increases at high temperature. It is a high-pressure operation, thus increasing efficiency. But still, much research is needed to bring this process into actual practice due to high heat.

2.2.1 Graphene and Its uses

Among the successful 2d materials, graphene had unique physical and chemical properties like high conductivity and high stability. But the fact that graphene has in-plane sp2 hybridization and out of plane π bonding made it inert for the water reaction, so the researcher started to dope the graphene material to make it react by modifying its characteristics. Usually, transition metal atoms are often doped into graphene to form a single-atom catalyst. Furthermore, upon research researcher found out that by increasing the adsorption rate, we can improve the hydrogen adsorption free energy. They also found that hybridized graphene with SO4 had excellent Oxygen Evolution Reaction (OER) 7.

2.2.2 Sugar Bagasse for water splitting

The researchers have much faith in Carbon Nanofibers (CNFs) because of their large specific surface area, desirable mechanical properties, good electrical conductivity, high thermal stability, chemical stability, and mechanical stability. But we know that CNFs are polymers made from petroleum, which destroys our very purpose to do water splitting. Therefore, it is essential to design porous and free-standing CNFs based on renewable resources, such as agricultural residues (straw, cornstalk, bagasse) and forestry residues (bamboo and woods), as a catalyst carrier for overall water splitting. Herein, using the carbonization of electrospun nanofiber precursors derived from acetyl sugarcane Bagasse (ASCB) to produce CoP/Co_2P heterostructure encapsulated in porous carbon nanofiber. The addition of ASCB introduces the porous structure into the carbon nanofiber catalyst, which results in the exposure of great active sites.

According to the results obtained by the researchers after performing the XRD analysis, observed the formation of porous structure, which was probably due to the activation of oxygen during the annealing treatment process and the different Pyrolysis curves and yield of ASCB and Poly Acrylo Nitrile (PAN). Meanwhile, the researchers' observations on disordered carbon structure indicated that this could be beneficial to the exposure of the active catalytic site. The large Specific surface area with porous structure promotes the charge Transport and Mass transport during the electrocatalysis process, and therefore it facilitates the catalytic efficiency [8].

The researchers performed the electrocatalytic stability test. It showed some favorable attributes, namely (i) The annealing treatment in the air combined With P doping tuned the electronic structures of metallic Co in the Unique CoP/Co_2P heterostructure. In this case, the Co and P act as the hydride-acceptor and proton-acceptor centers, respectively, enhancing the hydrogen proton absorption and the H_2 desorption, therefore facilitating the HER activity. (ii) Due to the electrospinning Method, the Co metal particles are uniformly distributed on the CNF, and the possible agglomeration is also reduced. Meanwhile, the nanofiber structure provides a channel of rapid transfer of Electrons during the catalytic reaction process and then enhances the HER and OER performance. The carbon nanofiber provides the Protection layer for active sites, making the catalyst Stable. Considering the advantages of ASCB based CNF and the CoP/Co_2P heterostructure, the CoP/Co_2P@ACNF(Activated carbon nanofiber)-800 can regard as a superior and promising electrocatalyst for overall water Splitting [8].

2.2.3 Electrocatalysts

Electrocatalysts are materials that ease electrochemical processes. Researchers have been searching for electrocatalysts that can support water electrolysis, and some of the best catalysts are noble metals, non-noble metals, non-metals.

2.2.3.1 Noble metal catalysts

For hydrogen production, because of the high electroconductivity of noble metals, solid noble metal or noble metal-doped transition metal oxides have been used as electrocatalysts. Electrode materials' conductivity and electron mobility are essential for improving electrochemical water splitting to generate hydrogen. Mainstream water splitting electrocatalysts use noble metals such as Pt, Ir, and Ru for their high intrinsic activity and satisfactory stability. Their high cost and low abundance restrict their further applications. To increase utilization of noble metal catalysts, nanoparticles of particular noble metal dispersed evenly in some type of carbon-based materials. This process increases the conductivity of electrolytes, leading to improved efficiency with a low overpotential and low Tafel slope for hydrogen or oxygen evolution [5]. However, due to excess surface free energy, noble metals with small sizes (single atoms or nanoparticles) tend to aggregate into larger particles during pyrolysis. Aggregation can lead to extreme degradation or even deactivation of the catalyst, which can have a fatal effect on the utilization rate of noble metals. But can overcome this high surface energy by forming strong metal support interactions to stabilize tiny metal atoms thermodynamically. Also, confining the metal atoms within microporous solids can kinetically prevent the collision and coalescence of noble metal atoms or nanoparticles [32].

Compared with the pyrolysis method, the electrochemical process is mild and controllable. Unlike pyrolytic materials, it does not have to overcome the high surface free energy of highly dispersed noble metal atoms dispersed among the surface of carbon-based materials. It does not require complex and expensive noble metal salt electrolytes, too. Only a noble metal electrode needs to use as the counter electrode (CE), and the surface of the working electrode (WE) coated the carbon-based material precursor. The electrochemical workstation can modify at room temperature and normal pressure [1].

The nitrogen-doped multicomponent noble metal catalysts are an efficient substitute of noble metals used as electrodes for pollutants containing hybrid-water splitting [5].

2.2.3.2 Non-Noble Metal Catalysts

The efficiency of non-noble metal catalysts for hydrogen evolution from electrochemical water splitting in terms of electron transfer and overpotential are not superior to those of Pt and Ru-based catalysts. For water splitting by the electrochemical process using the Ni/NiO catalyst, kinetically as the first step, the atomic hydrogen adsorption would occur more favorably on the NiO sites. In contrast, hydrogen production, the second step, could occur faster on Ni sites. The composition ratio of Ni/NiO to exhibit playing an essential role in electrochemical water splitting can adjust in line with the nanoparticle size of the catalyst [5].

This unique metal-nitrogen-carbon (M−N−C) structure can regulate the coordination environment of the central metal atom so that it has an ideal electronic structure and adsorption energy towards reactants. The M−N−C structure can provide a robust metal-carbon-based interaction through chemical bonds, which can ensure the stability of the metal atom in the catalytic process [33]. To avoid the shortcomings of non-noble metal carbon-based materials in unsatisfactory performance and poor stability introduces two methods. One is to improve the innate catalytic activity of non-noble metal-carbon materials by regulating the coordination environment of non-noble metal in the carbon substrate. It has moderate adsorption energy comparable to that of noble metal towards reaction intermediate of electrochemical water splitting. Another way is to form a robust conductive carbon layer on the catalyst surface through other auxiliary substances such as surfactants to enhance the durability of non-noble metal materials greatly.

Cobalt Nitride catalysts are excellent ones with near-identical efficiency to platinum but less cost.

Surfactant-assisted confinement pyrolysis strategy can not only enable controlled synthesis of atomically dispersed Co_4N sites with increased density, therefore leading to significantly enhanced catalytic activity. This carbon shell derived from the surfactant layer can effectively retain dominant micropores and high N content in the carbon matrix and protect the active sites inside the carbon layer from acidic or alkaline solution, thus preventing aggregation leaching out of single atomic Co sites. The surfactant-assisted confinement strategy provides a new approach to synthesizing non-noble metal catalysts with significantly increased stability for widespread electrochemical energy conversion applications [34].

2.2.3.3 Non-Metal Catalysts

In general, obtaining hydrogen water splitting using non-metal compounds containing transition metal electrocatalysts has been performed. In particular, in phosphorus or sulfur combined with transition metal electrodes, the d orbitals of phosphorous or sulfur can interact with transition metals for electron transfer during water splitting. Therefore, transition metal phosphides or sulfides can lower the energy barrier and stabilize the intermediates produced from the anode and cathode.

Bimetal phosphides, Fe-doped Ni2P nanosheets, were used as the anode and cathode electrodes for water splitting and showed improved efficiency by supplying an effective electron transfer platform. The redox reactions between Ni/Ni2+ and Fe/Fe3+ regarding the oxidation of water to generate oxygen can occur via the formation of metal phosphorus into phosphorus oxide. The metal Ni on Fe-doped Ni2P catalyst was oxidized to Ni2+ by Fe3+, but from the Ni-foam support generated Ni. The redox shuttle reactions between the metal phosphorus and phosphorus oxides can be conducive to electron transfer between Ni/Ni2+ and Fe/Fe3+ by forming P-O bonds from metal phosphine. The water electrolysis as an anode and cathode fabricated the Ru-doped NiFe bimetallic phosphide catalyst (Ru-NiFeP) supported by Ni foam. Ru-NiFe bonds transformed into Ru-O bonds while Ni2+ oxidized Ni in the oxygen evolution process. They explained that the electrons derived from metal phosphide would help stabilize the oxidized metal cations through the bond formation of P-O. These synthesized metal phosphorus electrode materials show significantly improved efficiency for water splitting 5.

Phosphate-based electrocatalyst $Fe_3Co(PO_4)_4$ at reduced graphene oxide (rGO) shows excellent results for OER than Ir-based catalysts. This electrocatalyst offers high current density, i.e., 100 mA $cm^{-2,}$ and high durability [29].

2.2.3.4 Bifunctional Electrode

The introduction of p orbitals or electrons available non-metal atoms, such as nitrogen, sulfur, and phosphorus, can make a significant change in the electronic states of electrocatalysts fabricated using transition metals, which may remarkably improve the oxygen evolution rate by the formation of oxides (–O) or hydroxide bonds (–OH) by the oxidation of p electrons in non-metal atoms. In the case of nonmetallic components with unpaired p orbitals, such as sulfides or phosphides, the empty or unpaired p orbitals can interact with the empty or unpaired d orbitals of metal components that are more available for water splitting by stabilizing the intermediates in the water-splitting reaction.

2.3 Photocatalytic water splitting

Natural photosynthesis: There are two kinds of photosystems(PS). In PS(II), the sunlight absorbs, and the electron gets excited and leaves the hole, which can not go alone. Hence, the system pulls the electron from what is known as water oxidation complex (WOC), and that is no longer a way positively charged that hole disappears, and now that WOC (inorganic unit inside the chlorophyll) shot out an electron that pulls out water electron, water will get oxidized and gives oxygen [8]. That oxygen human being breath.

Over a human being always excel nature. Researchers have found that this natural photosynthesis can split water. As shown in Fig 2, Artificial photosynthesis uses two systems like PS. For example, a diruthenium complex that gets excited when exposed to light and loses electrons becomes trivalent ruthenium from divalent and immediately pulls out an electron from the catalyst. That catalyst then pulls an electron from water. The main goal in the research of photocatalytic water splitting is to make that fantastic complex like WOC one nature has [30].

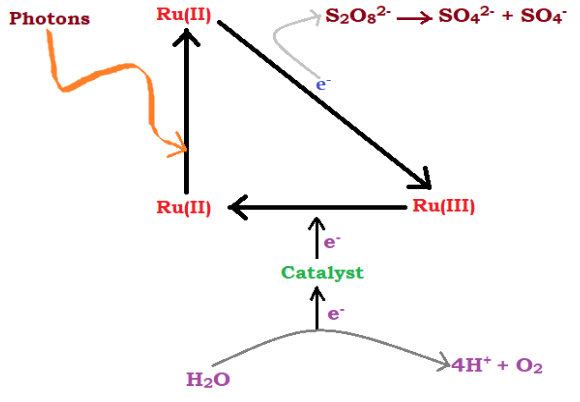

Fig 2: Mechanism of Artificial Photosynthesis

2.3.1 Semiconductor Photocatalyst

Using semiconductor photocatalysts, photochemical water splitting into hydrogen and oxygen has become a promising strategy for effectively capturing solar energy into clean H_2 fuel through a cost-effective, environmentally favorable route. Bandgap modification and coupling with narrow bandgap semiconductors, dye sensitization to enhance the visible light activity of semiconductors are the critical research points in the case of semiconductors photocatalysts. ZrO_2, $KTaO_3$, $SrTiO_3$, and TiO_2 possess appropriate water splitting bands among the different metal oxides. Different co-catalysts modify these materials with high bandgap energies active for water splitting when they are particularly modified [4,10,11]. The bandgap of a visible-light-driven photocatalyst should be narrower than 3.0 eV (λ>415 nm). To increase the activity of the photocatalysts under visible light considered several, such as the consolidation of transition metals and non-metals, creating oxygen vacancies. To enhance the adsorption of OH^- on the catalyst surface found Oxygen vacancies, resulting in a lower Gibbs free energy for the formation of oxide species, which is considered the rate-determining step of the OER [2].

In semiconductors, the chemical reaction occurs due to the transfer of Electrons from the valance band (VB) to the conduction band (CB). As the number of orbitals (N) in the HOMO (highest occupied molecular orbital (valance band)) and LUMO (lowest unoccupied molecular orbital (conduction Band)) increases, there will be a decrease in the energy while shifting the electrons from the valence band (VB) to Conduction Band (CB). Reports on the photocatalysis mechanism indicate that the recombination of photogenerated electrons and holes occurs in the catalyst samples' bulk. This recombination process of the electrons and holes can reduce substantially if these charge-carrier species are separated by adding a suitable Scavenger or incorporating some of the trap sites on the surface due to Producing defects, surface adsorbents, or other sites. Suppose we provide sufficient time to the holes and electrons before they recombine. In that case, these produced charge carriers migrate to the catalyst's surface and can Undergo the charge transfer to initiate the redox reactions with the pollutants Adsorbed on its surface. A valence band hole, H^+, contains a strong oxidation power by having a redox Potential ranging from +1.0 to +3.5 V (measured vs. normal hydrogen electrode (NHE) at room temperature), depending on the semiconductor and pH. Thus, the hole's presence plays a vital role in the photocatalytic degradation of the Pollutants present on the catalyst's surface. Oxidation can occur either due to indirect oxidation through reaction with the surface-bound hydroxyl radical or directly via H^+ attached on the metal surfaces Before it is trapped within the particle or at its surface. All the Mn and Co oxides in the +3 oxidation state show good catalytic activity irrespective of their crystal structure. Trivalent ensures easy electron transfer from metal ions [10].

2.3.2 TiO2 as photocatalyst

Titanium oxide (TiO2) is mechanically, thermally, and chemically stable. It has a substantially high melting point of 1855 °C and is insoluble in water, HNO3, HCl, and dilute H2SO4. In hot concentrated H2SO4 and HF can dissolve it. Back in 1921, On TiO2 as Photocatalyst found reports. Titanium is supposed to be an excellent photocatalyst Due to its enormous properties such as high activity, low cost, photostability, nontoxicity [31].

2.3.2.1 Graphene modified TiO2

The photon flux of TiO_2 in the photoreaction process is elementary to reach Saturation under the weak light irradiation, which will significantly reduce the energy efficiency of the whole process during wastewater purification. The most prominent limitation of TiO_2 application is that it can only absorb UV light less Than 387 nm. In other words, TiO_2 can only effectively utilize less than 6% Of the energy derived from the sunlight, which suggests its low potential of sustainable development in photocatalysis.

Since the researchers discovered TiO_2/graphene composite, Different methods could synthesize the 2D-structured TiO_2/graphene with various morphologies, such as hydrothermal, mechanical mixing, pyrolysis, sol-gel, CVD, UV light irradiation, microwave, vacuum activation, and so on. Hence, the reported articles introduce several vital methods for synthesizing the TiO_2/graphene composites. In 2012, the TiO_2 spheres were combined with graphene by a hydrothermal method to prepare core–shell-like TiO_2/graphene composites. They successfully synthesized the graphene–anatase TiO_2 hybrid NPs(nanoparticles) by wrapping amorphous TiO_2 NPs with rGO (reduced Graphene Oxide), during which APTMS(3-Aminopropyltrimethoxysilane)-modified TiO_2 spheres chose as the precursor, followed by a one-step rGO reduction and TiO_2 crystallization via hydrothermal treatment. In addition to 2D-structured composites, the 3D-structured TiO_2/graphene composites also attracted intense attention in recent years. Compared to the 2D-structured graphene, 3D graphene such as hydrogel or aerogel has unique properties. For example, it has ultra-low density, a three-dimensional network structure, controllable morphology, mechanical strength, excellent electrical conductivity, and strong gasoline and other organic compounds [16]. In many photocatalysts studied, the Most potential one due to its merits of low cost, good stability, nontoxicity have widely recognized TiO_2. Heterojunction catalyst is one of the hot spots in the catalytic field in recent years, which usually consists of two different semiconductors contacting each other to form the structure of heterojunction. The heterojunction structure can elevate the transfer of the photogenerated electrons and holes in the opposite direction, significantly Improving the effective utilization rate of the excitons. Therefore, a heterojunction catalyst possesses a better catalytic effect than a single-component catalyst. Many materials can modify TiO_2 by forming the heterojunction structure, such as ZnO, SnO_2, g-C_3N_4. Among them, g-C_3N_4 as a stable non-metal semiconductor has attracted much attention in the catalytic field. Due to its particular triazine structure, g-C_3N_4 exhibits many remarkable properties, including low density, high chemical stability, enhanced biological compatibility, good abrasion resistance. In addition, the relatively narrow bandgap of g-C_3N_4 (about 2.7 eV) extends its light response to the visible region (about 450 nm). The g-C_3N_4 exhibited high photocatalytic performance for water splitting under visible light irradiation [16].

2.3.3 Use of CdS

One outstanding innovation is that CdS nanorod attached with CdSe nanorod, platinum particle added here. As soon as the electron got excited in CdS, the whole went towards CdSe. The electron went to platinum, which reduced the proton to hydrogen [12]. But this process is very complex.

Another system is CdS nanoparticle and ZnO nanoparticle and platinum and used CdS to excite the electron. The whole system cannot be left alone. Otherwise, electron and hole pairs might combine. So immediately scavenger takes away the hole, gets oxidized. Any scavenger can use, but preferably organic molecule which can oxidize to be beneficial chemicals like benzene or benzaldehyde and get rid of their hole so this electron is available for reduction of the proton. A simple solution process prepared the ZnO/Pt/CdS nanostructures. ZnO/Pt/CdS nanostructures exhibited good H_2 evolution properties. The use of organic molecules such as benzyl alcohol shows excellent results in H_2 evolution and products such as benzaldehyde. ZnO/Pt/CdS and ZnO(N, F)/Pt/CdS both catalysts showed excellent H2 evolution with a rate of 35 mmol/h/g and an apparent quantum yield of 30% in the presence of benzyl alcohol as a scavenger under visible light irradiation. Effect of substitution of Zn as in $ZnO_{1-x}(N, F)_x/Pt/Cd_{1-y}Zn_yS$ - substitution of Zn is CdS has further improved the hydrogen evolution with an evolution rate of 43 mmol/h/g with a quantum yield of 44% [13].

2.3.4 Use of NiO as a co-catalyst in ZnO/NiO/CdS type heterostructure

Of course, one of the problems was platinum in all the results. To eliminate platinum cells, which are very simple chemicals CdS, ZnO, NiO because nickel oxide has a favorable conduction band, it can use even though it is an insulator to form a heterostructure gives outstanding results [14].

2.3.5 Use of molybdenum sulfide (MoS2)

Earlier studies show the use of MoS2 does in photocatalytic water splitting. Usually, dye excites the light electron and uses the electron to reduce protons to give hydrogen. A small particle of MoS2 got a small amount of H2.

Same as the previous method, when composite made with MoS2 and graphene combination. Slightly better results got than the previous one. Here reduced form of graphene is used as graphene is a good conductor 14.

Dye is excited to a triplet state, but it picks up an electron from an amine to become negative in charge, which is unstable. Immediately it gives an electron to MoS2. Graphene is used as a medium to send the electron, and the proton gets reduced in MoS2. A comparative study shows that only MoS2 gives a minimal number of moles of hydrogen. RGO- MoS2, i.e., composite of graphene and MoS2, gives slightly better yield but lightly nitrogen inside graphene makes it a bit more conducting, which was even slightly better. Now, NRGO- MoS2 highly nitrogenated nearly 15% nitrogen in graphene unbelievable increase in hydrogen yield 15.

Recent studies turned the perspective of the use of MoS2. Instead, nitrogenating graphene makes it significantly conducting, making MoS2 itself conducting. Lithium into MoS2, exfoliate it, and sheets that come out after exfoliation is lithium intercalated and dumped in the water. The lithium interacts with water gives hydrogen, and all the single sheets of MoS2 start floating in the water. That floating sheets are no longer original MoS2. Previously it was semiconducting MoS2 direct bandgap semiconductor, but the new floating MoS2 is 1T MoS2 which is metallic. This chemically exfoliated MoS_2 gives a 50 mmol/h/g H_2 generation rate.

Recent advancement in MoS_2 is that instead of MoS_2 use 1T $MoSe_2$. 1T $MoSe_2$ got the result of 75 mmol/h/g. It is the highest record of hydrogen evolution by semiconductor method using dye-sensitized process [15].

N-doping of graphene improved the electron-donating ability of graphene and created a p-n junction that suppresses charge recombination.

2.3.6 Borocarbon Nitride

Borocarbon nitride has proved an excellent catalyst for the photocatalysis of water. Graphene is highly conducting, whereas boron nitride is highly insulating. BC_xN_Y, this composition can tune the bandgap in this material depending on the composition and how it makes.

Borocarbon nitride sheets are an excellent low-cost metal-free catalyst for hydrogen generation with remarkable efficacy. Carbon-rich BCN shows the best activity with performance superior to other non-precious metal electrocatalysts. Theoretically, studies show that substituting B and N in equal concentration opens up the gap with the valence band unfavorably located relative to the HER potential. Substitution of excess N results in a population of conduction bands with electrons, shifts the valence and conduction bands to lower energy and favors the alignment of bands to facilitate photocatalysis [17].

2.4 Photoelectrochemical Cell (PEC)

PEC technology uses a solid-liquid junction by immersing a semiconductor material (photoanode or photocathode) into an electrolyte. Semiconductors absorb solar energy to produce electron-hole pairs is observed. Electrons separate from holes via an external circuit and move towards the counter electrode & holes travel over the depletion layer to the semiconductor surface to effectively separate the two water splitting products of water splitting to yield high purity products.

The metal oxides facilitate PEC water-splitting reaction. However, the conventional metal oxides have VB edges that are much too low in energy concerning the water oxidation potential (1.23V versus normal hydrogen electrode (NHE), at pH 0), resulting in an enormous over potential (>1.7V). Consequently, metal oxides with VBs comprised predominantly of O (2p) orbital having the bandgap energy that is only responsive to UV light (<400nm).

A term called "solar-to-hydrogen" conversion efficiency (STH) is often used to describe the hydrogen production efficiency of a water-splitting reaction under sunlight. The definition of STH conversion efficiency is represented as

$STH = (Jsc \times 1.23 \times \eta F)/Ptotal$

where Ptotal represents the power density of the incident simulative sunlight (AM1.5G), Jsc is the short-circuit photocurrent density, the thermodynamic voltage required for water splitting is 1.23V, and ηF is the faradic efficiency. To become viable and meet the energy demand, a water-splitting system should be ∼10% STH efficient, stable over an extended period, and cost-effective to fossil fuels. The solar output in the visible spectrum is significantly higher (∼43%) than the UV (4%). As the PEC reaction relies on absorbing light, the greater the number of photons absorbed, the higher the theoretical efficiency of a system. The target goal of 10% STH efficiency also necessitates using a material that significantly absorbs the segment portion of the solar spectrum 11.

There will be a minimum number of defects for a highly crystalline semiconductor. The defects act as trapping and recombination sites between photogenerated charge carriers resulting in lowering of PEC activity. With the decrease in particle size, the distance traveled by the photogenerated carriers to the reaction sites becomes short, reducing the recombination probability.

2.4.1 Metal-organic frameworks (MOFs)

The basic structure of MOFs clearly defines it as a 3D porous network of organic-inorganic species wherein actinides, alkaline earth metals, and mixed metals work as a metal source. In contrast, organic species such as imidazole, aromatic carboxylic acid, cyanometallate reagents, and heterocyclic compounds use MOFs as organic linkers [3].

MOFs are not actual semiconductors like organic semiconductors due to their highly localized electrons and immobility of charge carriers, but they behave like semiconductors due to experimentally obtained calculations of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). MOFs have a high density of accessible sites and adjustable pores, providing a high charge transport rate through their skeletons.

The use of MOF as co-catalysts facilitates electron-hole separation have found. That avoids direct contact of semiconductor or metal oxide with electrolyte for reducing optical corrosion, consumes captured holes (for enhanced surface hole injection efficiency), lowers the onset potential, and improves spectral absorption efficiency (by delocalized p bond present in organic ligand) [3].

As stated by the principle of catalysis, only coordinatively unsaturated atoms can participate in the catalytic reaction.

2.4.2 InGaN Based Photoanode

TiO_2, ZnO, and InGaN were suitable for photoelectrochemical water splitting because of appropriate band gaps for light absorption. ZnO nanowires have been adapted to increase InGaN semiconductors' efficiency for water splitting. ZnO nanowires on InGaN-based photoanode surfaces effectively increase light trapping. Bare InGaN photoanode has less surface area, but ZnO nanowires have a larger surface area. Thus more active sites are involved in the reaction [23].

2.5 Thermochemical water splitting

Thermochemical water splitting uses high temperature from concentrated solar power or waste heat of nuclear power reaction. Conventionally temperature required for this process is around 500-2000°C. Chemicals used in this process are reused within each cycle, creating a closed-loop that consumes water only.

2.5.1 Two-Step solar thermochemical cycle

Based on metal oxide reactions, two-step solar thermochemical cycle. MxOy Thermally dissociated into metal or lower valence metal oxide M and oxygen. In the two-step process, one is endothermic, and the other is exothermic. In the second step, M reacts with water to hydrogen. The resulting metal oxide is then recycled back to the first step itself.

Sulfur Iodide thermochemical water splitting- With a suitable catalyst, high-temperature decomposition of sulfuric acid achieves 10% conversion at 510°C and 83% conversion at 850°C. Sulfuric acid decomposes at about 850°C, releasing oxygen and recycling the SO2. Then HI can be decomposed at about 400°C, releasing H2 and reclaiming the iodine. So, all reagents are recycled. There are no effluents. The S-I cycle has significant conversion at much lower temperatures.

When metal oxide is heated at a specific temperature, it loses oxygen, an endothermal process. Absorbs heat, then at that time CO_2 is passed. Then this oxide which is deficient in oxygen pulls out oxygen from CO_2 gives CO. That oxide state goes back to the original oxide or puts that system in water steam, and it puts out oxygen from steam, gives hydrogen, and goes back to the original oxide.

Cerium oxide is heated at a specific temperature. It loses oxygen, passes some CO2 or H2O over it, and gets CO or H2 18.

Oxide on Mn4+ loses oxygen and becomes Mn3+. Then it goes back to Mn4+ after reaction with water or CO2 [19, 20].

Instead of manganese oxide, tried Lanthanum Manganesium oxide (La1-xCaxMnO3). Much more oxygen is given out then pass CO2/H2O, it goes back to its original state, so the amount of oxygen released or CO produced is enormous with Manganese oxides 21.

Some researchers also found that they can use rare earth metals instead of lanthanum. Oxygen evolution increases with decreasing the size of the rare-earth ions.

2.5.2 Multi-step solar thermochemical cycle

Temperature is too much for the thermal decomposition of the water process. High temperature created a need to produce a new thermochemical cycle for splitting water at relatively lower temperatures. Mn3O4 heated with Na2CO3 will get sodium manganate and CO2. Sodium manganate reacts further with water while heating, getting hydrogen eventually and CO2, and finally producing Mn3O4 and Na2CO3 again. At 850°C, this multi-step cycle can work, which is the very lowest temperature for the decomposition of water. It was always 1500°C to 2000°C, but now it is brought down by using multi-step chemical cycles to 700°C 22.

Conclusion

This review examines the various innovative methods and catalysts used in water splitting. For noble metal-based catalysts, even dispersion throughout the electrodes in electrocatalysis increases the utilization of noble metal, thus reducing the cost of catalyst. The noble metal-containing electrode improved efficiency for electrochemical water splitting to generate hydrogen, but it is too expensive to apply to large-scale production. Non-noble metal catalysts cannot survive under electrolyte conditions such as acidic and alkaline. So the introduction of a carbon layer protects the active sites of catalysts from such conditions. Recently, nonmetal-based phosphides and sulfides combined with transition metals have drawn attention due to the lower energy barrier and stabilization of the intermediates produced from the anode and cathode. Inexpensive Fe and Co hybrid with P and O shows good OER performance. However, specific metal-free catalysts have not been considered yet as many metal-free catalysts yield low H2 evolution from water splitting, limiting their application. Therefore future efforts in this direction are needed. Acetyl sugarcane bagasse (ASCB) based CNF, and the CoP/Co2P heterostructure can consider as promising electrocatalysts due to the introduction of the porous structure into the carbon nanofiber catalyst, which results in the exposure of great active sites. Doping of graphene material with transition metal can modulate the electronic structure of graphene, which makes it an electrocatalytically active material for water splitting.

Photochemical is the best water splitting process because sunlight is the only energy source needed. Photochemical cells are challenging to operate but can work. Photochemically the quantity of required product there is good but not enough to get large amounts. More research is needed to make catalysts like Water Oxidation Complex as it is in nature. By utilizing semiconductor photocatalysts, photochemical water splitting has become a promising strategy for capturing solar energy effectively. Various semiconductors such as oxides, nitrides, and their derivatives have developed. In many photocatalysts studied, TiO2 is the Most potential one due to its merits of low cost, good stability, nontoxicity. The heterojunction structure of TiO2 with g-C3N4 (graphitic Carbon nitride) has gained the majority of researchers' attention owing to its simple preparation method, abundant kinds of precursors, and the advantages of low cost, becoming the first choice to form a heterojunction with TiO2. MoS2 has become one of the critical emerging catalysts due to its high photocatalytic activity, strong absorptivity, and low cost. Borocarbon nitride sheets are an excellent low-cost metal-free catalyst for hydrogen generation with superior efficacy.

Photoelectrolysis research has configured different combinations of semiconductor materials and electrocatalysts in Photoelectrochemical cells. Researchers have reported that MOFs impart additional stability to the electrode system, making it more suitable in PEC applications.

The thermochemical water splitting process is explored because quantities produced are much work very fast. Efficiency is more. This system is also suitable for CO2 reduction to CO and H2O. At the same time tackled two problems.

The less expensive metals will facilitate a more exhaustive accumulation of hydrogen fuel cells. That will help us to overcome reliance on fossil fuels for energy. Hydrogen generation from water splitting is a great renewable substitution with only water and negligible heat as byproducts.

Author Contributions

Aditya Joshi contributed to the writing. Sahil Jadhav searched for the maximum resources, wrote the manuscript, and edited it. Both authors analyzed the resources and developed the draft. Both authors read and approved the final manuscript.

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