

Recent Innovations in Bismuth-Based Photocatalysts for Water Splitting and Green Hydrogen Production

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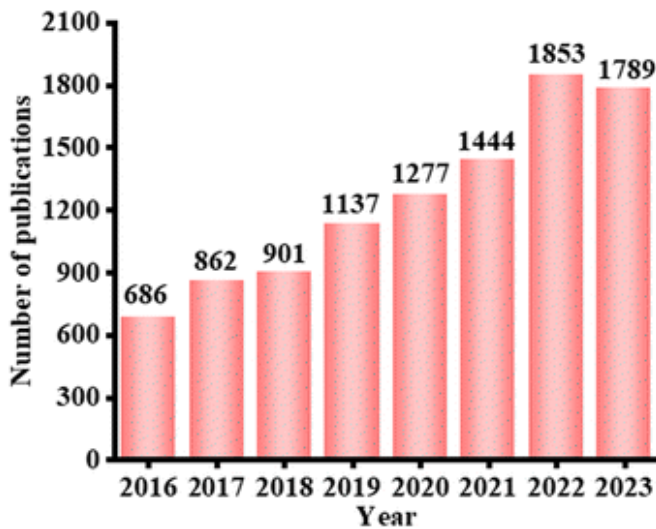
Abstract.

In the current scenario there is a great demand for energy for various needs which comes primarily from fossil fuels and these are dwindling day by day and also causes pollution by emitting toxic gases. There is an urgent need to switch on to the alternate energy sources which could meet present day demand. This necessitated the search for clean and sustainable energy alternatives. Hydrogen is considered to be an alternative form of clean energy for the future prospects. In recent years attention has been drawn for bismuth based nanomaterials for generation of hydrogen by photoelectrochemical water splitting. Bismuth based materials gained more importance due to its low cost, nontoxicity and narrow band gap. This review addresses the photocatalytic mechanism, role of bismuth based materials for hydrogen production heading towards greener and sustainable future.

1. Introduction

Due to the rapid advancements in Science and technology there are many problems with regard to the energy crisis, environmental pollution and medical field due to which there is an urgent need to develop new technologies to achieve long term sustainable society. Photocatalysis is one such mechanism which would contribute to the clean and green environment. Hydrogen alternative energy source considered to be future clean energy finding many applications in domestic, automobile and industries[1]. The most promising way of photocatalytic H₂ production from water due to three reasons 1) This methodology makes use of solar energy which is renewable source 2) Ecofriendly technology as it leads to the generation of harmless by-products and 3) Process converts solar to Hydrogen, a storable energy form. Often it is difficult to get an ideal photocatalyst which would meet all the requirements necessary for hydrogen production an alternative form of energy source. Nanotechnology is a promising field for the development of new class of materials that boosted the modification of existing photocatalyst.[2]

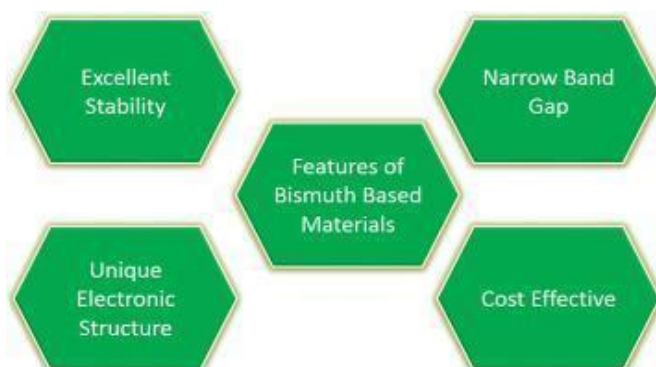
As illustrated in fig(1) which shows a rapid increase in the number of scientific findings which clearly constitutes bibliography related to the current topic. As mentioned in the fig(1) from 2004 there is great increase in the number of publications in the field of production of hydrogen by nanocatalysts by a factor of 1.5 times per year. This clearly depicts the impact studied in different papers on nanomaterials for their energy conversion efficiency by nanoscale properties[3].



Fig(1) From 2016 to 2023 -Number of papers published on Bismuth -based photocatalysts

Much importance has been to bismuth based materials (nano) due to their electronic structure which is unique to itself as it shows well dispersed v.b which comprises of 6s orbital of Bi and 2p orbital of O with a suitable band gap for sunlight to harvest. This article provides important advancements to exploit bi nanomaterials for PEC water splitting. Overall view of various strategies to improve the photocatalytic activity of Bi materials are addressed. Control of morphology, heterojunction, co-catalyst and doping are several approaches to improve the efficiency of photocatalytic water splitting. [4-8]

Hydrogen production via water splitting photocatalytic mechanism with nanomaterials (Bi) is discussed in this review, which highlights its sustainability as a solar-driven and strong renewable energy source. It inarguably aims to provide an all-around understanding of the synthesis [9-12] and mechanistic underpinnings of bismuth-based photocatalysts for hydrogen production. The review also highlights recent research on the topic and identifies key challenges that limit the large-scale implementation of this technology.



Fig(2). Key Characteristics of Bismuth-Based Photocatalytic Materials for Hydrogen Generation.

Photocatalytic mechanism of water splitting relies on the utility of semiconductors acting as photocatalysts, and a variety of them have been extensively studied and developed for this purpose. Narrowband gaps give the right

energy levels for producing electron-hole pairs required in redox reactions and enhance the capacity to absorb solar energy.

2.Literature Survey:

Yao Y, et al. [1] studied about the hydrogen as the future energy carrier due to its low carbon emission and a sustainable energy resource .

Davis KA, et al.[2] studied about the generation of hydrogen from biomass and biomass derived substances for industrial usage.

Shi J, Guo L. [3] studied about production of clean energy in the form of Hydrogen by making use of semiconductor photocatalysis mechanism.

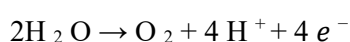
Joy J, Mathew J, George SC [4] studied regarding the different strategies for the improvement of properties of photocatalyst for evolution of hydrogen.

The literature survey strongly recommends the new methodologies which would help in generation of clean and sustainable energy source as Hydrogen from PEC due to its low cost, harmless products and storable form .

3.Mechanism of photocatalytic Water Splitting

Water splitting is the dissociation of water into—hydrogen and oxygen its elemental components—using an energy source. For the sustainable generation of hydrogen, especially by photocatalysis and electrolysis, this reaction is crucial. Designing effective catalysts and increasing the efficiency of hydrogen production require an understanding of the thermodynamics and underlying mechanism of water splitting.[13-15]

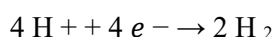
Oxygen Evolution Reaction (OER): This anodic process releases protons and electrons when water oxidises to oxygen gas.



Because there are several electron transfers and bond-breaking processes involved, this reaction is difficult to understand both thermodynamically and kinetically. It necessitates a high overpotential and an effective catalyst, like metal oxides (BiVO_4 , TiO_2 , etc.).

The Evolution of Hydrogen Reaction (HER)

Protons are converted to molecular hydrogen in this cathodic reaction:



Even though this reaction happens more readily than OER, the reaction rate still has to be increased by an effective catalyst, such as Pt, MoS_2 , or Bi-based materials.

Total Water Splitting Reaction $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

For this process to happen, an external energy source is needed, either electrical energy for electrolysis or solar energy for photocatalysis.

The utilization of solar energy for hydrogen production is considered the most straightforward, economical, clean, and efficient method of photocatalytic water splitting. It does not produce byproducts, making it a promising process for the production of hydrogen. A study by Dincer et al. revealed that the process of photocatalytic water-splitting is the most economical and abides by an environment-friendly approach. For efficiency elevation, it is necessary to develop materials specifically designed for photocatalytic water splitting.

In photocatalysis, light is absorbed and electron-hole pairs are created for the process using semiconductor materials (such as BiVO_4 , Bi_2WO_6) [16-18].

Electrolysis: The process is fuelled by an external voltage, usually derived from renewable sources.

PEC, or photoelectrochemical Water splitting is a more effective method of producing hydrogen from solar energy by combining photocatalysis with electrolysis.

Properties of Photocatalysts for photocatalytic water splitting

A photocatalyst for water splitting should possess specific physicochemical properties to efficiently drive the hydrogen and oxygen evolution reactions (HER & OER) under light irradiation. These properties influence the light absorption, charge separation, surface reactivity, and overall stability of the photocatalyst [19-21]

Other characteristics required to bring out photocatalytic water splitting's efficient method to produce hydrogen are listed in Fig(3).

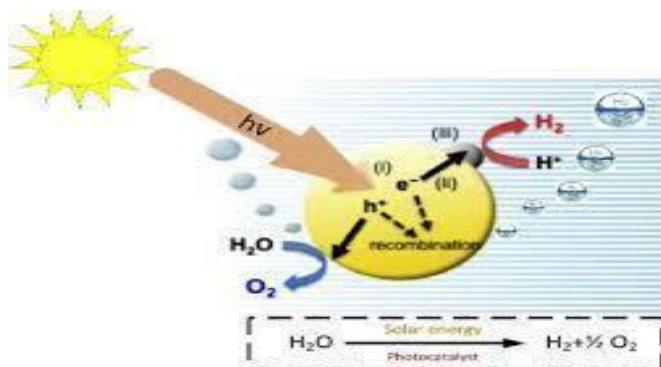
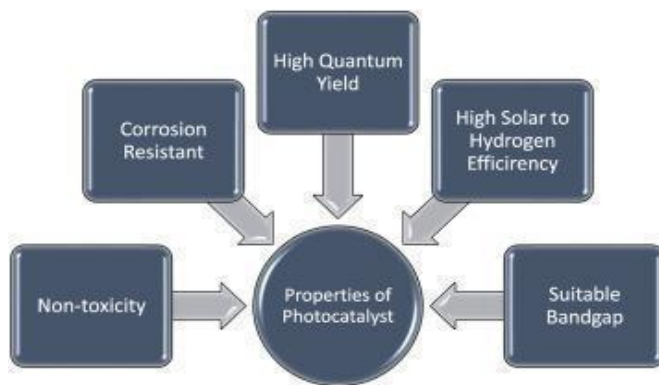


Fig (3) Depicts the photo-excitation mechanism in splitting of water.

The promise of bismuth-based materials in photocatalytic water splitting for the generation of hydrogen is highly considered due to its non-toxic nature, small band gap, unique electronic structure, economical, and strong reusability. Bismuth-based nanomaterials demonstrate exceptional photostability and water stability.



Fig(4)Desirable characteristics of the perfect photocatalyst for producing hydrogen from water

Bismuth-based materials - Water splitting

Materials based on bismuth have shown promise as water splitting photocatalysts because of their advantageous band structures, chemical stability, and absorption of visible light. BiOCl, BiOCl, BiOBr, BiOBr, BiOI, BiOI, bismuth tungstate, bismuth vanadate are some examples of these materials.[22-24]

Both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) and are supported by favorable band edge positions.

Good Chemical Stability: More photocorrosion-resistant than organic perovskites or metal sulphides. Tunable Electronic Properties: Doping, heterojunctions, and nanostructuring can change the band structure.

Bandgap: visible light active, about 2.4 eV. strong chemical resistance in watery solutions.

BiOCl, BiOCl, BiOBr, and BiOI are bismuth oxyhalides that have special 2D electron transport characteristics.

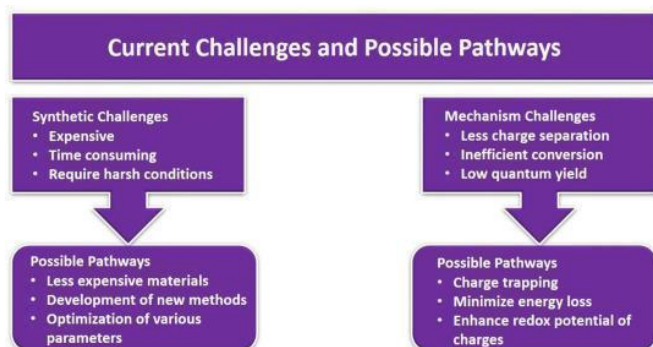
Because of their stability, tunability, and visible-light activity, materials based on bismuth show great promise for sustainable water splitting. Enhancing catalytic efficiency, stability, and charge transfer is still difficult, though. Their ability to produce green hydrogen will be further enhanced by developments in co-catalyst engineering, heterojunctions, and nanostructuring.

4.Present challenges and future recommendations

Currently, there are two primary obstacles to photocatalytic water splitting: the creation of photocatalysts and the photocatalytic process itself (Fig.5).

Additionally, the recombined version of photogenerated electron-hole pairs leads to a loss of energy.

However, these processes could be minimized by adding trap sites to the semiconductor photocatalyst, which would further prevent charge from recombining, thereby reducing energy loss and in turn increasing the production of hydrogen.



Fig(5): Current challenges and possible pathways -photocatalytic water splitting

5.Conclusion

This article reviews in detail the latest studies on hydrogen production through the photocatalytic method in the context of growing energy needs that are reportedly heading for an imminent energy crisis and discusses some potential alternatives of renewable and alternative fuels from those produced by hydrogen. They are intriguing options for solar-to-hydrogen conversion because of their advantageous band structures, absorption of visible light, and chemical stability.

The technical insights shared in this review are aimed at guiding experts in advancing photocatalytic hydrogen production. This work is expected to enormously encourage further research aimed at developing advanced photocatalysts with enhanced photocatalytic mechanisms

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