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STUDY ON THE HYDROGEN PRODUCTION AS A CLEAN ENERGY CARRIER THROUGH SEMICONDUCTORS

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ABSTRACT

Because technology is getting better and environmental problems are getting worse, the need for clean energy has grown a lot in recent years. In this way, hydrogen, which is a clean, sustainable energy carrier with a high energy density, is one of the best ways to deliver and store energy and can also be used to clean up the environment. Renewable hydrogen energy carriers can replace fossil fuels, cut down on carbon dioxide (CO2) emissions, and slow down global warming. Making hydrogen from renewable sources of solar energy and water is an environmentally friendly way to meet the world's growing energy needs. Among the many ways to get hydrogen from the sun, semiconductor-based photocatalysis looks like a good one. It is mostly done with two types of methods: homogeneous and heterogeneous. The latter is better. In semiconductor-based heterogeneous photocatalysis, light stimulates a solid material to make an electron-hole pair, which then takes part in redox reactions that lead to the production of hydrogen. This review paper tries to explain and talk in depth about the different semiconductor-based photocatalysis processes for cleaning up the environment. It focuses on heterojunction semiconductors in particular, with the hope that it will lead to new designs that are better at protecting the environment.

Keywords: ***Semiconductors, Photocatalysis, Hydrogen***

1. INTRODUCTION

As the world's population grows and the need for clean resources grows due to environmental limits, the search for clean and sustainable sources is becoming an increasingly important issue. Unfortunately, most of the energy needs are met by fossil fuels, which have limited supplies. When these fuels are burned, greenhouse gases are released, which change the climate and cause other major environmental problems. In this way, renewable or alternative energy sources like solar, wind, and biomass were put in place to reduce greenhouse gases, especially carbon dioxide. The amount of energy that can be made with traditional methods is ten times as much as what can be made with solar photovoltaic. Equipment can be developed quickly when it is made smaller because it costs less to invest and works better. Now, solar power is the cheapest way to get electricity in many parts of the world, and by 2023, the world should have a total capacity of more than 1 TW. Solar photovoltaics will play a big role not only in the power grid but in the whole energy system, thanks to current integration strategies and those that are being made. To decarbonize and reach the goals of the Paris Agreement, the world's energy system needs to change in important ways and be updated in a big way.

With this important change comes an urgent and complicated problem that needs system solutions and global efforts that work together. Hydrogen is one of these solutions. Hydrogen is an important part of making a low-carbon energy system happens. It has the potential to be a powerful accelerator for this system and solve a number of energy problems, such as making it easier to use a lot of renewable energy sources and reducing the amount of carbon dioxide in energy production. It could also help with energy transportation in a zero-carbon energy economy and the electrification of end users. Hydrogen is one of the most promising renewable energy sources that can replace fossil fuels. It has a high energy density of 120 to 142 MJ/kg, while gasoline only has 44.5 MJ/kg. Also, burning hydrogen is clean (it doesn't make $CO2$) and makes water ($2H2 + O2 = 2H2O$; $\Delta E = 286$ kJ/mole). But almost 96% of hydrogen production is very dependent on fossil fuels. This makes it very important to find renewable resources. Recently, there has been more interest and development in hydrogen than ever before. Soon, it will be a key part of the transition to a climate-neutral society.

It will replace coal, oil, and gas, making it a key energy vector and the other leg of the energy transition, along with renewable electricity, in many parts of the economy. As the demand for renewable energy sources grows in the electricity sector, the grid needs more technologies to keep it balanced. But electricity isn't easy to store, which is a chance for hydrogen to be used and for its technologies to be developed. Hydrogen technologies can have a big impact on how energy is distributed, making it easier to cut down on carbon use. Delivery plays a big role in how much energy is used, how much it costs, and how much pollution is made. These things are all closely related to the ways hydrogen can be delivered, such as through pipelines or on the road. This choice depends on the location, geography, and markets in the area. Using a mix of renewable resources is important for making sure that there is always power and that the electrical grid is stable. When other renewable sources of energy can't be used, hydrogen can be turned back into electricity.

Also, the extra can be sold and used for other things. Hydrogen can also be used as the main raw material for fertiliser, refining, and other chemical-based industries. It can also be a byproduct of other industrial processes, which makes it a strategically important commodity. It can be put into the natural gas grid at the same time to keep the gas clean and reduce emissions and other stranded assets. To keep electric grids stable, it is important to control the flow of electricity from power generators that use renewable energy. To get the most out of renewable energy and avoid output control, we need places to store electricity. Storage batteries are going to play a key role in this matter in the near future. With the growth of renewable energy, the need for output controls will also grow. However, large-scale and long-term power-to-gas systems will also use hydrogen. Renewable hydrogen has a lot of uses. It is used to make clean chemicals, fertilisers, and methane.

Hydrogen from Semiconductor-Based Photocatalysis

Photocatalysis based on semiconductors seems to be a good idea for making hydrogen in a clean way. Using semiconductors like TiO2, photocatalytic processes produce hydrogen in a way that is similar to how photovoltaic systems do it. Based on how the catalysts, reagents, and products are spread out, the catalysis process can be either homogeneous or heterogeneous. However, heterogeneous catalysis is preferred because it is easier to separate. Semiconductor-based photocatalysis is a type of heterogeneous catalysis that uses photon energy. In this type of catalysis, a solid material is stimulated by light and makes a pair of electrons and holes. After that, the species made by photosynthesis take part in redox reactions. Honda and Fujishima came up with the idea for the photo electrochemical cell in 1972.

They used ultraviolet (UV) light to split water into oxygen and hydrogen. Since then, many studies have focused on developing and improving the photocatalysis process. In these processes, the photogenerated carriers should move to the surface of the photocatalysts to take part in the necessary electrochemical reactions. One of the biggest problems is that the recombination of photogenerated charge carriers (electrons and holes) is, from a thermodynamic energy point of view, better. This hurts the performance of photocatalysis because a small number of photo generated species can move to the surface of the catalysts and join redox reactions. Several ways have been found to solve the problem of electron–hole recombination. These include adding noble-metal co-catalysts, doping with cations and anions, and making heterojunctions between different semiconductors, which is also called composite photocatalysis. The ability of hierarchically ordered macro-mesoporous TiO2-graphene composite films to quickly absorb organic dyes and break them down with light is increased. The assembly of interconnected macropores in mesoporous films has the following effects:

(1) It improves the flow of matter through the film;

(2) It increases the area of the thin film that can be reached;

(3) It makes the photocatalytic properties of the film much better; and

(4) It shortens the length of the mesopore channel.

These structures could be used to treat wastewater and clean the air by getting rid of organic pollutants. This could be a good opportunity for industrial applications. Photocatalytic processes have the potential to create renewable and environmentally friendly energy carriers like H_2 and O_2 by splitting water. They can also break down organic pollutants, convert energy, store materials by reducing CO_2 with photocatalysis, make organic substances, and even reduce iron ore with hydrogen. In this way, semiconductor-mediated photocatalysis can be used to treat both energy problems and environmental pollution in a cost-effective way. For example, photocatalytic reduction of protons by photoinduced electrons can be used to make hydrogen, which is an ideal green fuel. Toxic organic pollutants can be broken down by using multi-step photocatalytic oxidation reactions. Due to the high binding energy of excitons, it is not possible for a single semiconductor to lead to a quick recombination of photoinduced charge carriers. So, it is very important to make heterostructure photocatalysts, well-designed heterojunctions, and multi-component semiconductors to keep an extended light-harvesting range, efficient charge separation at the interface, and a high redox potential all at the same time. It was shown that realistic and smart choices of semiconductors and tailoring of well-suited energy band structures should be taken into full account when making heterojunction photocatalysts to meet the above factors. Until now, many methods have been used to improve the photocatalytic performance of semiconductors for efficient hydrogen production. These include homogenous and heterogenous methods, S-scheme, Z-scheme, and artificial photocatalysis.

2. METHODS

Materials can be divided into three groups based on how well they conduct electricity: conductors, semiconductors, and insulators. Materials that conduct electricity have conductivity on the order of 107 Ω^{m-1}, while materials that don't conduct electricity have conductivity on the order of 1010 Ω^{m-1}. Semiconductors are in between the other two groups. Their electrical conductivity ranges from 10 to 6 to 104 Ω^{m-1}. The energy bands cause this difference in conductivity. Electrons live in specific bands. In the ground state, valence electrons are in the lower energy valence band, while there are no electrons in the higher energy conduction band. The difference in energy between these two energy bands is called the bandgap, and its size is given by the bandgap energy (Eg). Note that electrons that are between the energy levels of the conduction band and the valence band cannot leave. Conduction happens when free electrons in the conduction band move above the

Fermi level. Figure 1 shows that the Fermi level is where the conduction and valence bands overlap in materials that conduct electricity.

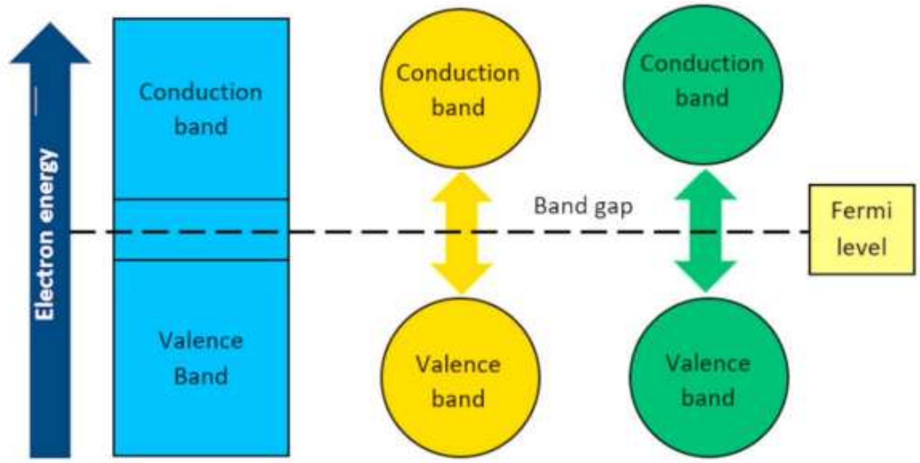

Fig 1. Band structures different conductors, semiconductors and insulators.

Semiconductor Photocatalysis

When photons with energies higher or equal to the bandgap (Eg) of the semiconductor hit it, an electron (e) moves from the valence band (VB) to the conduction band (CB), creating a hole (h+). Figure 2a shows that both the excited state in the conduction band and the holes in the valence band are thermodynamically and kinetically likely to recombine and use up the energy that was put in by making heat or light. If, on the other hand, electrons and holes move to the surface of the semiconductor without recombining, they can work together with species absorbed at the surface in electrochemical processes. In this situation, photogenerated electrons act as reducing agents and holes act as oxidising agents. This ability of electron–hole pairs to do redox can be used in photocatalytic processes like cleaning up water and air and making hydrogen.

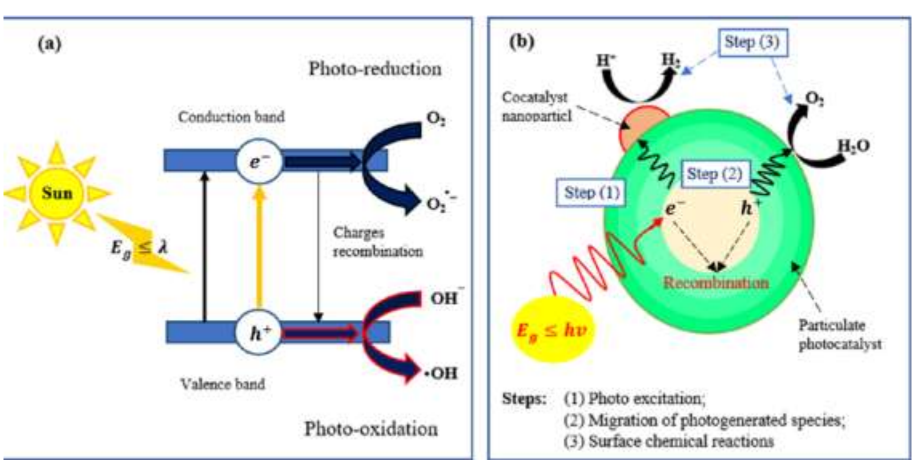

Fig 2 Photocatalytic reactions in semiconductors

Photocatalytic reactions in semiconductors have three basic steps as it is shown in fig 2b: (1) photon excitation, (2) migration of photogenerated species, and (3) surface chemical reactions.

3. RESULTS AND DISCUSSION

Semiconductor Heterojunctions

Heterojunctions are generated at the interface between different semiconductors and they are utilized in the case of unequal bandgaps, discontinuities in the bandgap, or the existence of an abrupt barrier in a specific band as shown in figure.

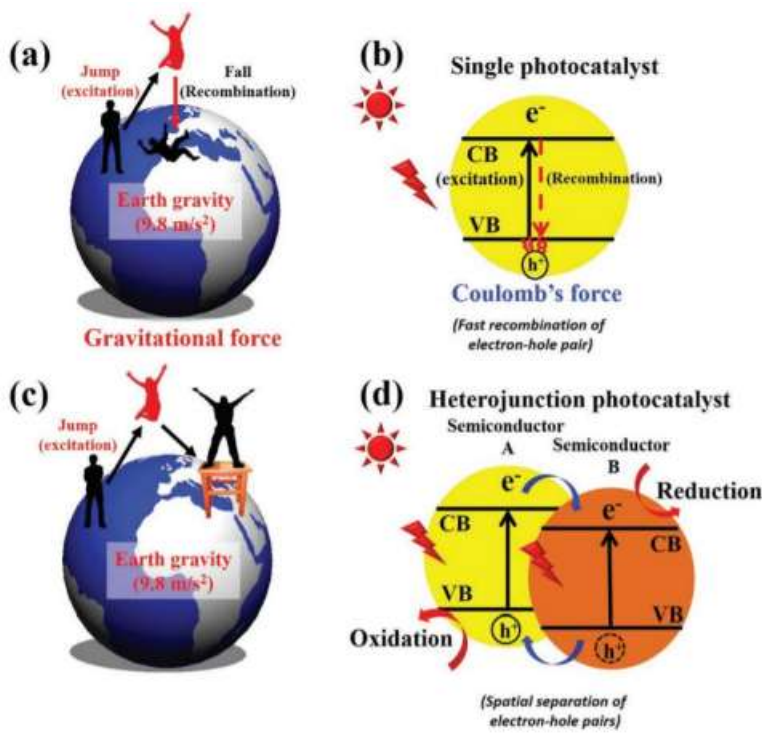

Fig 3 Illustration of (a) the gravitational force on a jumping man; (b) electron-hole recombination on a single photocatalyst; (c) keeping a man off the ground using a stool; and (d) electron-hole on a heterojunction photocatalyst adapted from.

Because of Coulomb attraction, the electron (the man in Figure 3a) must instantly recombine with a hole (the ground) as it moves from the valence band to the conduction band (the sky) (the gravity of the Earth). Thus, a semiconductor B is required to separate photogenerated electron–hole pairs and hold the man off the ground

(Figure 3c,d). The composite photocatalyst or heterojunction was developed to maximise charge carrier recombination and minimise visible-light activity. Photogenerated electron–hole pairs may easily migrate to the surface to participate in electrochemical processes, as shown in Figure 4.

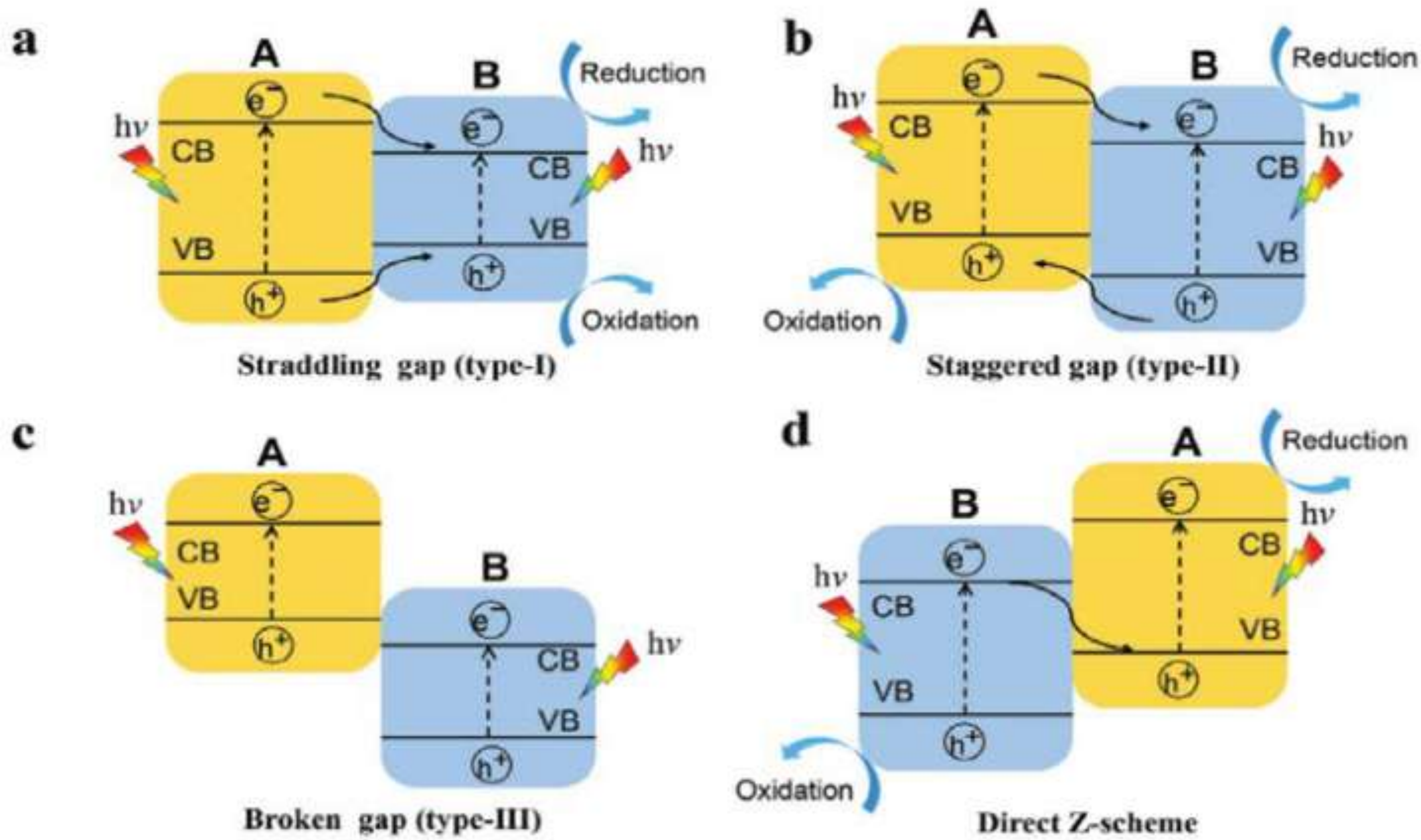

Fig 4 The electron–hole pairs' migration under irradiation in various type of heterojunction photocatalysts: (**a**) type-I, (**b**) type-II, (**c**) type-III, and (**d**) direct Z-scheme, adapted from.

2D semiconductors are suitable for photocatalytic research and commercial applications due to their unique physical and chemical features. Heterojunctions increase light adsorption, energy carrier separation, and photocatalytic activity. Heterojunction design optimises component functionality and synergy. 0D setups activate more sites and reduce charge migration distances. They may be built with flexible adjustable bands to boost catalytic activity. One-dimensional designs efficiently carry charge ballistically. They also prevent 2D material aggregation. Charge transfer efficiency increases contact areas for 2D/2D heterojunctions. Three-dimensional arrangements improve energy usage by transporting reacting molecules to reaction sites. By enhancing photocatalytic activities, 2D/0D, 2D/1D, 2D/2D, and 2D/3D designs may enhance characteristics. Two semiconductors may make p-n or non-p-n heterojunctions.

Morphology effect in Heterojunctions

Heterojunctions shape catalytic activity. Heterojunction photocatalyst size and arrangement may also effect performance. Two-dimensional (2D) materials are good candidates for photocatalysis due to their structural and electrical features, however electron–hole recombination and limited redox ability need to be addressed. In this regard, wise and objective construction of 2D heterojunction photocatalysts with various arrangements and morphologies can improve photocatalytic activity; Figure 5 shows the design of proficient photocatalysts with different configurations, applications, and properties, each of which has pros and cons.

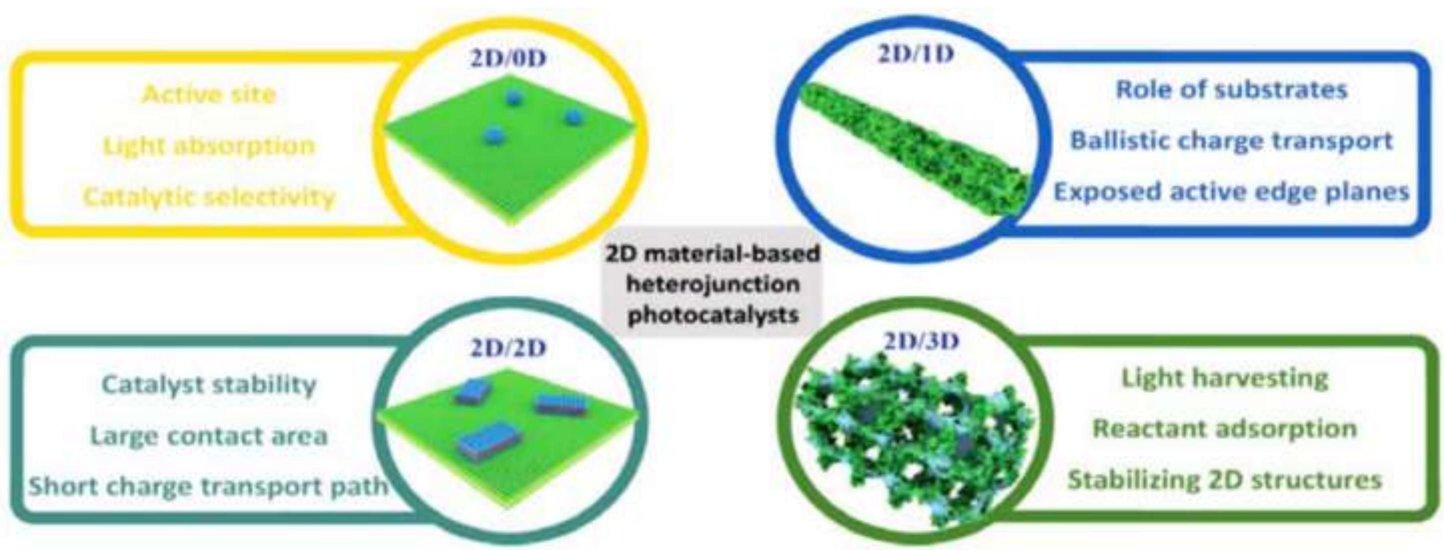

Fig 5 The schematic illustration of 2D heterojunction photocatalysts with various configurations, applications, and properties, adapted from.

4. CONCLUSION

The presented review paper aimed to introduce and discuss the semiconductor-based routes to fabricate novel photo catalysts stimulated by visible-light irradiation in order to generate green and renewable solar fuels such as H2. Hydrogen is considered to be one of the most advantageous sustainable energy carriers with great potential to substitute for fossil fuels because of its substantial gravimetric energy density. In addition, it is very clean and its combustion, fortunately, is CO2 free and leads to water production. In this regard, semiconductor-based photocatalysis procedures have been proven to be a promising scheme in hydrogen production. The catalysis process can be performed using homogeneous and heterogeneous procedures, but the heterogeneous processes are preferred. In semiconductor-based photocatalysis, the photon energy is utilized to generate an electron–hole pair, leading to redox reactions. One of the main issues in achieving enhanced quantum efficiency in photocatalysis procedures is the recombination of photoinduced species. Until now, various strategies have been proposed and explored to overcome the high recombination rate issue; hence, reducing the recombination rate is crucial to allow the photogenerated electron–hole to migrate to the surface and carry out reduction and oxidation reactions with high efficiency. In this regard, the main goal of this review paper is to discuss the design, synthesis, and characteristics of the novel high throughput, visible-light-driven, heterojunction composite photocatalysts for environmental remediation applications. It was seen that many variables are involved in the achievement of these targets, such as crystal structure, morphology, size, composition, element oxidation states, optical absorption properties, electrochemical properties of the proposed heterojunction photocatalysts, photocatalytic mechanism, catalyst dosage, temperature, and initial pH. Therefore, it is of eminent importance to thoroughly understand and wisely tailor the produced semiconductor for the desired application. This important issue requires accurate knowledge of the possible advantages and disadvantages, challenges, and benefits of each parameter and mechanism. It must be noted that the introduction of heterojunction materials has a substantial impact on the improvement in conversion efficiency; for instance, just a slight amount of Ag/WO3/Bi2WO6 heterojunction can improve the conversion rate by up to 250% compared to pristine counterparts. This up-graded activity can be related to the generation of a three-component heterojunction that improves visible-light absorption and increases the separation efficiency of the photogenerated electrons and holes. Moreover, 3% of CuO/ZnO heterojunction can lead to considerable photoreduction with substantial removal efficiency toward Hg(II), reaching 100%, which is 24 times higher than that of pristine ZnO .

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