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Innovative TiO_2 Photocatalysts: Advances and Strategies for Enhanced Hydrogen Evolution Efficiency

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Abstract:- As a photocatalyst, titanium dioxide (TiO_2) has attracted a lot of interest because of its remarkable qualities, including stability, affordability, and environmental friendliness. The latest developments in TiO_2-based photocatalysts are examined in this thorough overview, along with cutting-edge methods for increasing their effectiveness in a range of photocatalytic applications. The article discusses developments in TiO_2 modifications, such as surface functionalization, heterostructure, and doping, to increase charge separation, broaden the range of light absorption, and boost catalytic performance in general. Additionally, new methods for creating TiO_2 and how they affect photocatalytic activity are covered. The paper highlights the diverse possibilities of TiO_2-based photocatalysts in tackling modern issues by outlining applications ranging from solar fuel production to environmental remediation.

Keywords:- *Titanium Dioxide, Photocatalyst, Dye, Hydrogen, Efficiency, Reusability.*

I. INTRODUCTION

Hydrogen can be produced through a wide variety of raw materials. These raw materials include fossil sources, such as gas and coal, as well as renewable sources, such as biomass and water, using renewable energy sources (sunlight, wind, hydraulic). A diversity of technologies can be used, including chemical, biological, electrolytic, photolytic and thermochemical processes. Figure 1 describes some of the raw materials and technologies that can be used to produce hydrogen. Each technology is in a different state of development, and each offers unique opportunities, benefits and challenges. The availability of raw materials, the maturity of technology, political issues and costs are all factors that influence decision making about hydrogen production [1]. Numerous different source materials can be used to make hydrogen. These raw materials come from both renewable and fossil energy sources (sunlight, wind, and hydraulic energy), such as biomass and water, as well as fossil energy sources like gas and coal. A wide range of technologies, such as photolytic, electrolytic, chemical, biological, and thermochemical processes, can be employed [2].

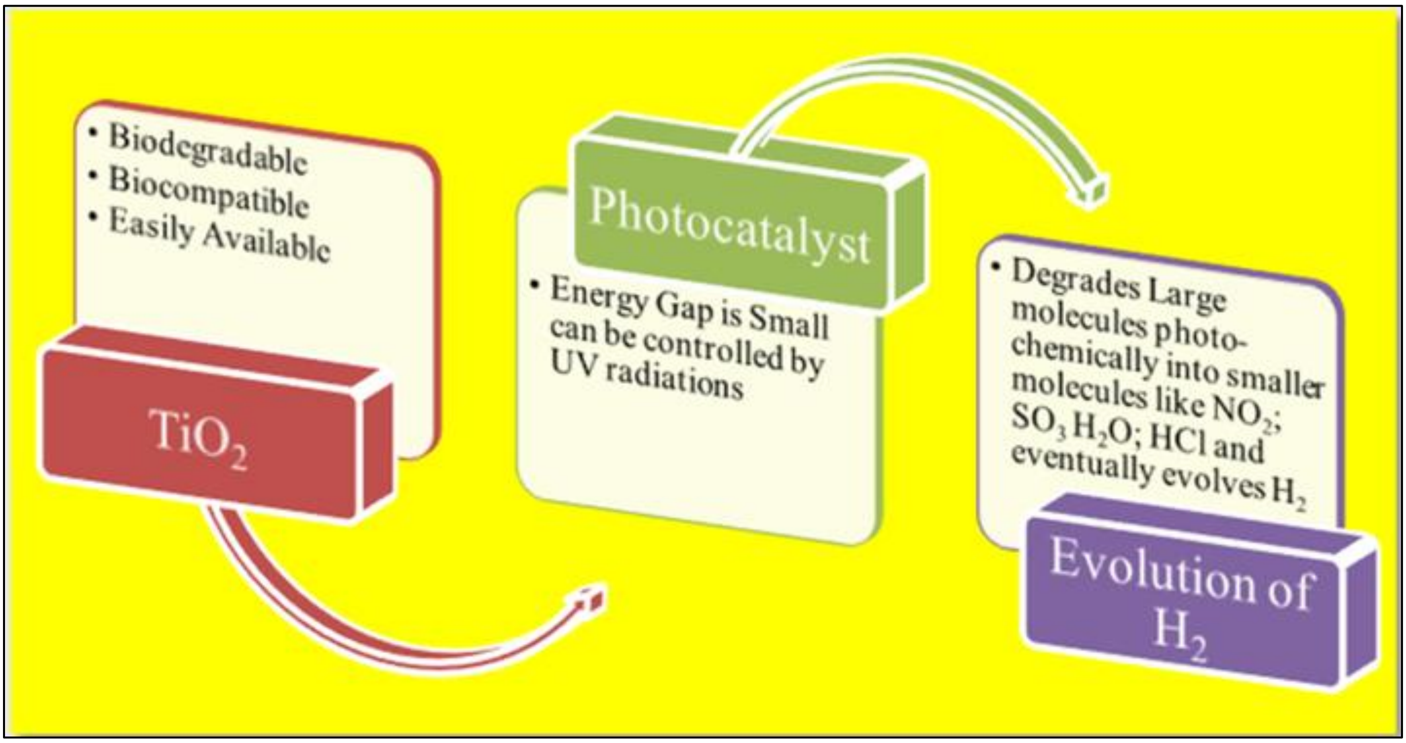

Fig 1 Hydrogen Evolution using TiO_2 as Raw Material

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A general overview of for the hydrogen evolution using TiO_2 as raw material is shown in Figure 1. Every technology presents various difficulties, rewards, and possibilities, and each is in a different stage of development. Costs, political concerns, technological maturity, and raw material availability all play a role in the decision-making process related to producing hydrogen. A few of these technologies are already on the market and can be used to produce hydrogen industrially [3-4]. The process of producing pure hydrogen by water electrolysis dates back to the 1920s and was the first commercial technique. The utilization of fossil fuel-based raw materials, which is currently the primary source of hydrogen generation, gradually replaced industrial hydrogen production in the 1960s.

II. HYDROGEN PRODUCED VIA WATER DISSOCIATION

There are various ways in which the dissociation of water might produce hydrogen. Among these techniques are photo-biological generation, electrolysis, and the breakdown of water at high temperatures [5].

Hydrogen from the dissociation of Water Hydrogen can be generated from the dissociation of water through several processes. Some of these methods are electrolysis, photo electrolysis, photo biological production and the decomposition of water at high temperatures.

Equation 1 illustrates the process of Water electrolysis, which splits water into hydrogen and oxygen by applying electrical energy. The temperature affects the overall amount of energy required for the electrolysis of water. For instance, electrical energy drops at increasing temperatures. Thus, when high temperatures are available as leftover heat from another process, a high-temperature electrolysis technique is preferred [2, 3].

$$H_2O + e^- \longrightarrow H_2 + 1/2O_2 \quad (1)$$

The majority of the electricity generated globally comes from fossil fuels. Researchers are currently working hard to find a renewable energy source that would be both environmentally benign and able to power the electrolysis.

Photosynthesis through photobiology (bio-photolysis): Photosynthesis and hydrogen production, which is catalyzed by hydrogenase, are the two processes that make up photo-biological hydrogen production. Bacteria and green algae, for instance, could be employed [2]. The following two reactions are part of the entire processes, *photosynthesis* in (2) and *hydrogen production* in (3):

$$2H_2O \longrightarrow 4H^+ + 4e^- + O_2 \quad (2)$$

$$4H^+ + 4e^- \longrightarrow 2H_2 \quad (3)$$

- *Water's Combustion at High Temperatures:*

At 300°C, water begins to dissociate at high temperatures. Only 10% of the water decomposes at this temperature; the other 90% needs to be recycled. Alternative processes for the dissociation of water at high temperatures (up to 850°C) have been proposed in order to lower the process thermal load. These include thermochemical cycles, hybrid systems coupling thermal decomposition, electrolytic decomposition, thermo-physical cycles, and water decomposition by chemical plasma. These techniques can achieve efficiencies of over 50%, which lowers the cost of producing hydrogen. The availability of materials that can withstand corrosion at high temperatures, along with the advancement of membranes, heat exchangers, and heat storage medium, present the primary technological barrier for these kinds of high temperature processes. Safety and design considerations are also crucial. [3].

- *Thermo-chemical Process:*

Water is converted into hydrogen and oxygen by thermochemical mechanisms that cause it to dissociate. This method makes use of several thermochemical processes. Equations (4–7) depict the iodine/sulfur cycle as an illustration of this kind of process:

(@ 850°C): $$H_2SO_4 \longrightarrow SO_2 + H_2O + 0.5O_2 \quad (4)$$

(@ 120°C): $$I_2 + SO_2 + H_2O \longrightarrow H_2SO_4 + + 2HI \quad (5)$$

(@ 450°C): $$2HI \longrightarrow I_2 + H_2 \quad (6)$$

Overall: $$\mathbf{H_2O \longrightarrow H_2 + 0.5O_2} \quad (7)$$

Research and development are still needed to determine the best ways to avoid secondary reactions and do away with the usage of hazardous materials while implementing thermochemical processes. The issues of corrosion that arise from handling these kinds of compounds still need to be closely monitored.

- *Photolysis:*

A possible solution is artificial photosynthesis, which is harvesting solar energy from the environment and transforming it into a strategic and useful fuel like hydrogen. By utilizing a semiconductor material to receive and utilize solar energy by converting it into chemical species, artificial photocatalysis offers a method to simulate photosynthesis. Additionally, the method of dissociating water utilizing this kind of technology to make hydrogen is clean, inexpensive, and safe for the environment. Important topics for this work are presented in the following parts [6-11].

TiO_2 is anticipated to become more and more important in the near future in a variety of disciplines, including solar cells, chemical sensors, photocatalysis, and electrochromic devices, because of its outstanding optical, semiconductor, and chemical capabilities. TiO_2 can be employed directly under UV radiation as a photocatalyst with applications in various fields, including environmental remediation, water purification, air purification, and solar energy conversion [12].

Its photocatalytic properties are primarily attributed to its ability to generate reactive oxygen species (ROS) when exposed to light, typically ultraviolet (UV) light. The

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crystalline nature of TiO_2 in the form of rutile, anatase and brookite makes it a versatile photocatalyst materials shown in Figure 2. Among these, anatase and rutile are the most commonly used for photocatalytic applications due to their favourable properties. The crystal structure of titanium dioxide plays a crucial role in its photocatalytic activity due to its semiconductors like properties. The energy band gap is the energy difference between the valence band and the conduction band in a material. In the case of titanium dioxide, the band gap is around 3.2 eV for anatase and 3.0 eV for rutile. This energy gap corresponds to the energy of UV light, making titanium dioxide primarily responsive to UV radiation [13].

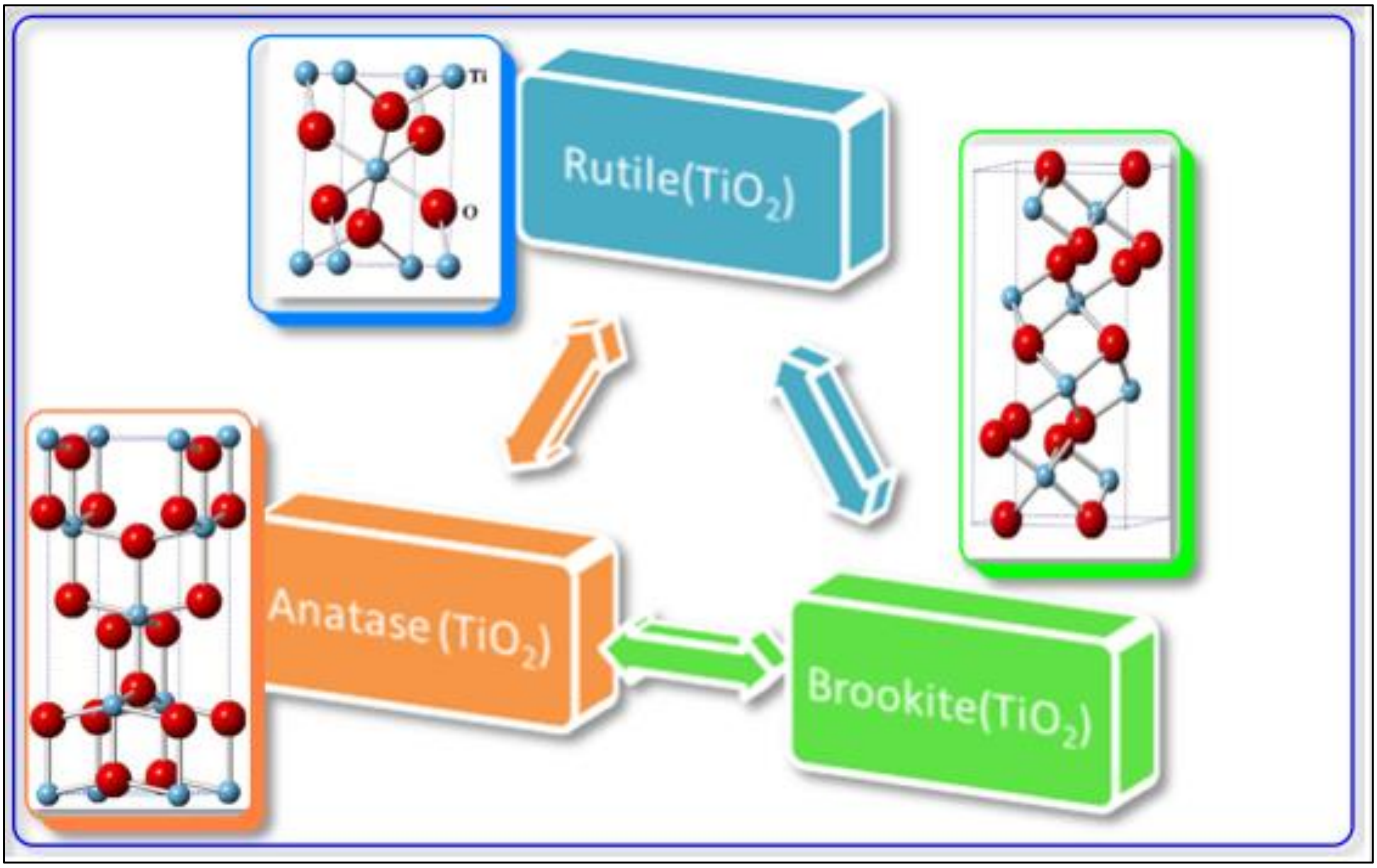

Fig 2 The Crystalline forms of TiO_2.

III. TiO_2 AS PHOTOCATALYST

Titanium dioxide (TiO_2) is widely recognized as a suitable photocatalyst due to its wide energy band gap, typically around 3.2 eV for anatase and 3.0 eV for rutile phases. This band gap allows TiO_2 to absorb ultraviolet (UV) light, making it effective for photocatalytic processes. It is chemically inert and stable under wide range of physiochemical conditions; therefore, it can be repeatedly used [14]. Due to its biocompatible nature and biologically safety, it is also safe to use in biomedical applications. It has high abundance and Titanium is one of the most abundant elements in the Earth's crust therefore, TiO_2 is readily available, contributing to its low cost. Hence, its abundance and cost-effectiveness of TiO_2 make it economically viable for large-scale applications. It has high photo stability and resistance to photodegradation and therefore exhibits good photo stability, maintaining its structural and chemical integrity over prolonged exposure to light. This characteristic is important for sustained photocatalytic activity. TiO_2 can be synthesized using various methods, including sol-gel, hydrothermal, and chemical vapor deposition, allowing for control over particle size, morphology, and crystalline structure. Its surface can be modified to enhance its properties, such as by introducing dopants or coupling with other materials, to improve its performance in specific applications [15]. It is widely used for the photocatalytic degradation of organic pollutants in air and water, contributing to environmental remediation. Its coatings on surfaces, such as glass or building materials, exhibit self-cleaning properties, as they can decompose organic contaminants when exposed to sunlight [16]. Due to its versatile nature, its photocatalysis has applications in water purification, air purification, self-cleaning surfaces, and solar energy conversion and therefore makes it applicable in diverse fields as shown in Figure 3.

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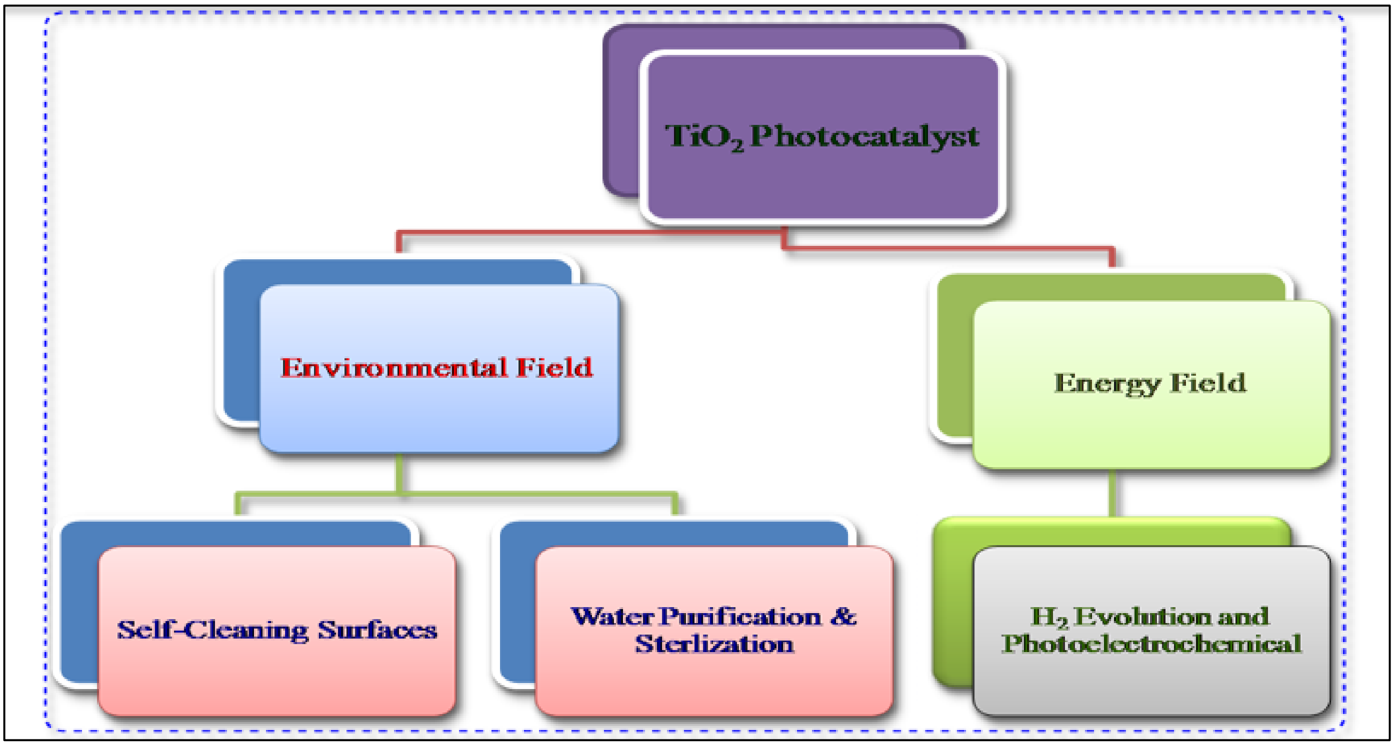

Fig 3 Versatile Nature of TiO_2 as Photocatalysts.

One mineral that is highly adaptable and has important applications in both energy and the environment is titanium dioxide, or TiO_2 as it is being depicted in the Figure 4. It is a significant participant in the energy sector because of its remarkable light-absorbing and charge-separation capabilities in solar cells and photovoltaics. Its effective solar energy conversion has aided in the development of renewable energy technology. Furthermore, because of its stability and electrochemical performance, it is very important in lithium-ion batteries and other energy storage applications. When exposed to ultraviolet (UV) radiation, TiO_2 exhibits exceptional efficacy in the destruction of organic pollutants, pigments, and even microbiological contaminants. This makes it a standout environmental photocatalyst for wastewater treatment [17]. This ability to purify water by photocatalysis is in line with eco-friendly methods and provides a long-term solution. It's dual relevance in the environmental and energy domains highlights how crucial it is for advancing technologies that support a more sustainable and environmentally friendly future.

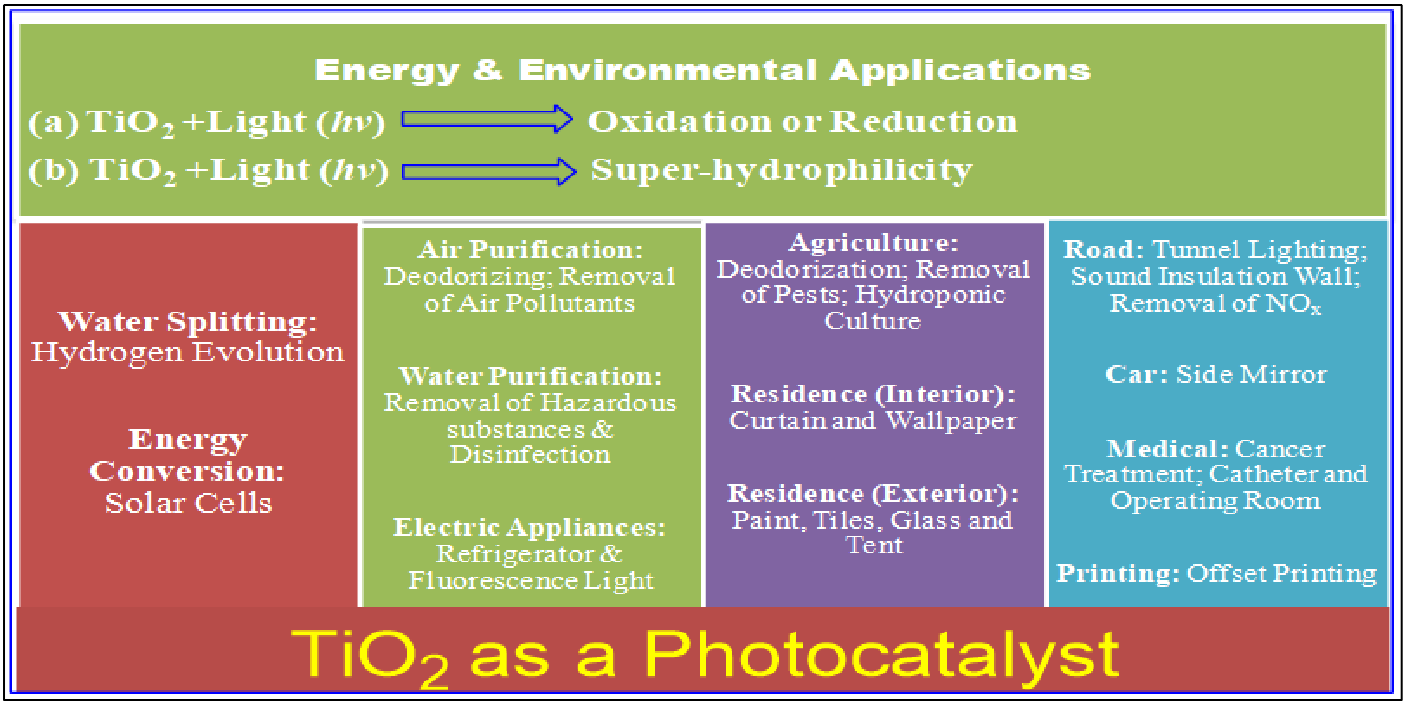

Fig 4 TiO_2: A Photon Sensitive Material.

Titania possesses remarkable photocatalytic properties, particularly when it is nanocrystalline, mostly due to its wide bandgap and potent UV reactivity. Titania is particularly helpful in decomposing organic pollutants found in water because of its special ability to use solar energy for catalytic reactions. Titania, also known as titanium dioxide, is a photocatalytic substance that is used in water treatment to significantly improve environmental sustainability.

Titanium starts a photocatalytic reaction that creates electron-hole pairs when UV photons are absorbed. When these charged species react redoxively with organic contaminants and water molecules that have been adsorbed onto the Titania surface, reactive oxygen species (ROS) such as hydroxyl radicals are produced. These ROS's potent oxidative qualities enable organic pollutants to decompose into safe metabolites [18].

➢ *Major Functions of TiO_2 as Photocatalyst*

- *Degradation:*

When light strikes a semiconductor like titanium dioxide, electrons and electron holes are created. After that, it combines with oxygen and water to form reactive oxygen and hydroxyl radicals (•OH), which enable the breakdown and breakdown of dangerous materials. Consequently, there is a self-cleaning effect. [19].

- *Super Hydrophilicity:*

A titanium dioxide-coated surface becomes covered in hydrophiles when light and water come into contact with it. By using water to rinse the surface free of oil, dirt, dust, and other contaminants, this super-hydrophilic method removes dirt and grime from the surface. When rain or other water comes into touch with the surface, this process occurs, causing the surface to clean itself [20].

Titania is used in water treatment to purify a range of water sources, including agricultural runoff, industrial effluent, and even potable water. When used, it aids in the removal of several contaminants, including organic dyes, pesticides, and harmful microorganisms. Titania is also a more appealing long-term water treatment technique because to its resilience, non-toxicity, and ease of regeneration. Thus, its use as a photocatalytic material in water treatment demonstrates how it can be used to effectively degrade various waterborne contaminants using solar energy, which can aid in resolving environmental issues and advancing the development of effective and sustainable water purification technologies [21].

Materials based on titanium have found extensive use in the gas sensing industry, where they are essential for detecting and tracking environmental pollutants. Titania's special qualities, especially its sensitivity to changes in the surrounding environment, make it an excellent material for gas sensor technology.

➢ *Important Applications of Titania-based Materials in Gas Sensors*

- *Titania is Prone to Gas:*

Titania is sensitive to a variety of gases, including carbon monoxide (CO), methane (CH_4), nitrogen dioxide (NO_2), and volatile organic compounds (VOCs). This sensitivity is the result of interactions between the gas molecules and the surface of titania, which alter the material's electrical and optical properties [22].

- *Surface Reactivity:*

The optical or conductivity properties of titania can be changed by the adsorption of gas molecules onto its surface. Due to modification, this phenomenon forms the basis for gas detection since alterations in these attributes may be measured and connected to the concentration of the target gas [23].

- *Selectivity:*

Titanium-based gas sensors can be made to be just slightly sensitive to specific gases. To increase the material's ability to distinguish between different gases, extra elements or dopants can be added, its shape can be altered, or its composition can be altered. Titania-based gas sensors are known for their rapid response times to target gases and their ability to recover well when the gas source is eliminated. Its dynamic reactivity is essential for real-time monitoring applications [24].

- *Operational Stability:*

Titania-based gas sensors are known for their longevity and dependability across a range of environmental conditions.

- *Versatility:*

Titania-based materials' versatility allows gas sensors to be tailored to each application's requirements. Due to their adaptability, they have been included in numerous sensor systems for environmental monitoring in industrial, commercial, and residential settings.

- *Advancements in Technology:*

Nanoscale engineering has been applied to titania materials to further improve their gas-sensing properties, such as titania nanoparticles or nanotubes. Because of their larger surface area and nanoscale reactivity, titanium-based gas sensors have higher sensitivity and perform better overall. Their ability to recognize and quantify various toxins contributes to enhanced environmental health, air quality, and occupational safety.

IV. PHOTOCATALYSIS MECHANISM AND ITS MODIFIED FORMS

The idea behind titanium dioxide (TiO_2) photocatalysis is to use light energy to start catalytic processes on the surface of TiO_2. Applications for this phenomenon are numerous and include solar energy conversion, water purification, air decontamination, and environmental remediation. The

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fundamental idea is that when exposed to light, electron-hole pairs are created, which results in redox reactions and the creation of reactive species that power different catalytic processes [24, 25].

A. Principle of TiO_2-Based Photocatalysts:

Using Light to Promote Catalysis The following procedures are involved in the photocatalysis of TiO_2, and they are depicted in Figure 5 as a flowchart. The process is dependent on the availability of light (hv).

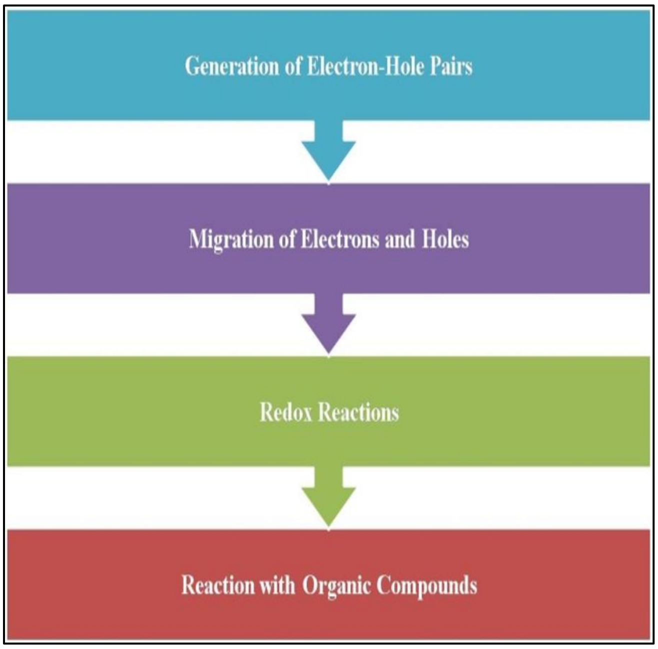

Fig 5 Flowchart involving Photocatalytic Pathway.

➤ *Step I: Light Absorption:*

TiO_2 is a semiconductor with a bandgap, typically around 3.2 eV for the anatase phase. When titanium dioxide is exposed to UV light with energy equal to or greater than the bandgap, electrons in the valence band are excited to the conduction band, electron-hole pairs (excitons) are generated by the absorption of photons with energy equal to or greater than the band gap. These electron-hole pairs contribute to the photocatalytic activity of TiO_2 [26-28] are shown in the Figure 6.

➤ *Step II: Generation and Migration of Electron-Hole Pairs:*

Photons with energy greater than the band gap are absorbed, leading to the creation of electron-hole pairs in the material. The absorbed photons promote electrons (e^-) from the valence band to the conduction band, leaving behind positively charged holes (h^+) in the valence band. These electron-hole pairs are highly reactive and play a crucial role in the photocatalytic process. Electrons and holes migrate to the surface of the TiO_2 particle due to the influence of the internal electric field [29-31].

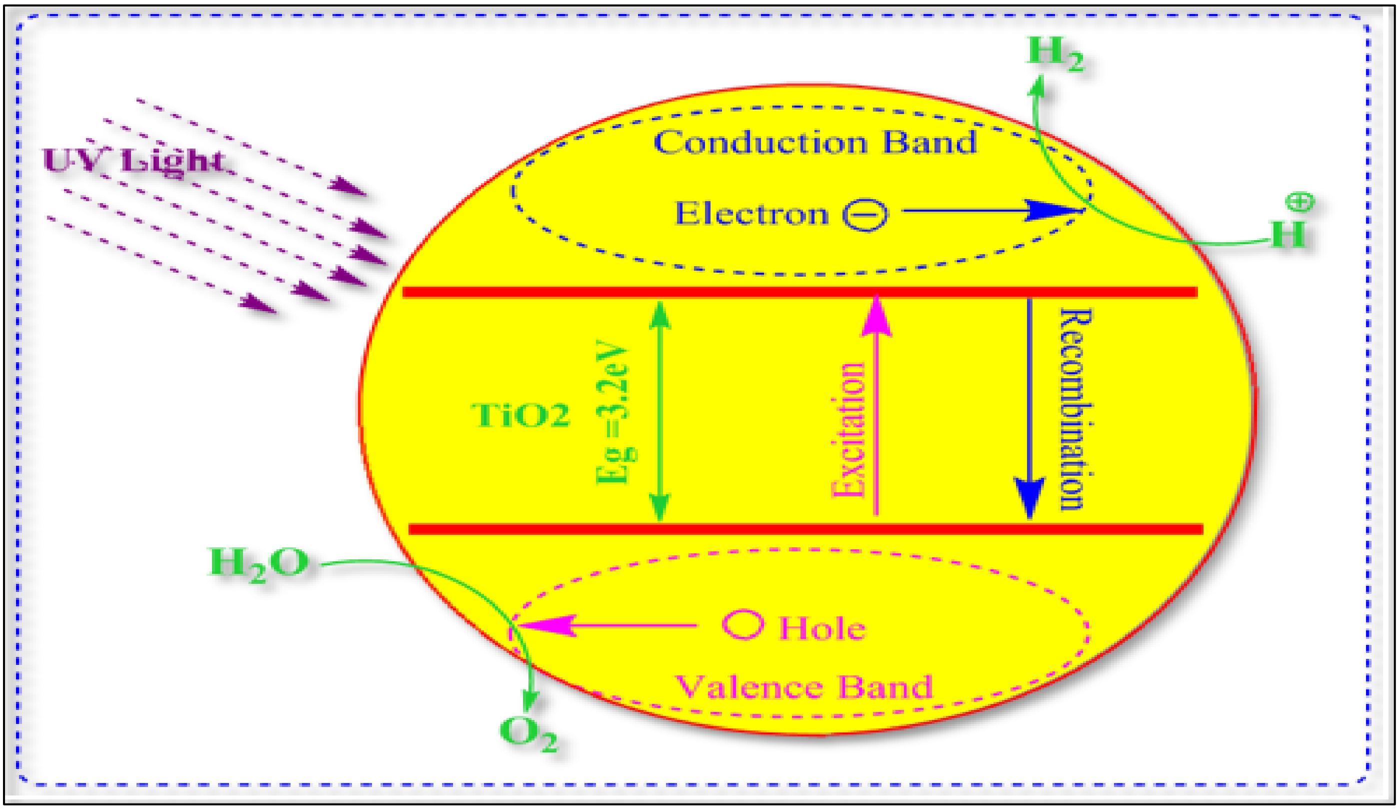

Fig 6 Role of Band Gap of TiO_2 Photocatalytic Reactions

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- **Redox Reactions:** At the surface, electrons react with oxygen molecules to produce superoxide radicals (O^{2-}), while holes react with water molecules to produce hydroxyl radicals (OH^{-}) as shown in the Figure 7.
- **Reactive Oxygen Species (ROS) Generation:** The superoxide radicals and hydroxyl radicals are examples of reactive oxygen species (ROS) that possess strong oxidizing properties. These ROS are responsible for the degradation of organic pollutants or the activation of catalytic reactions.

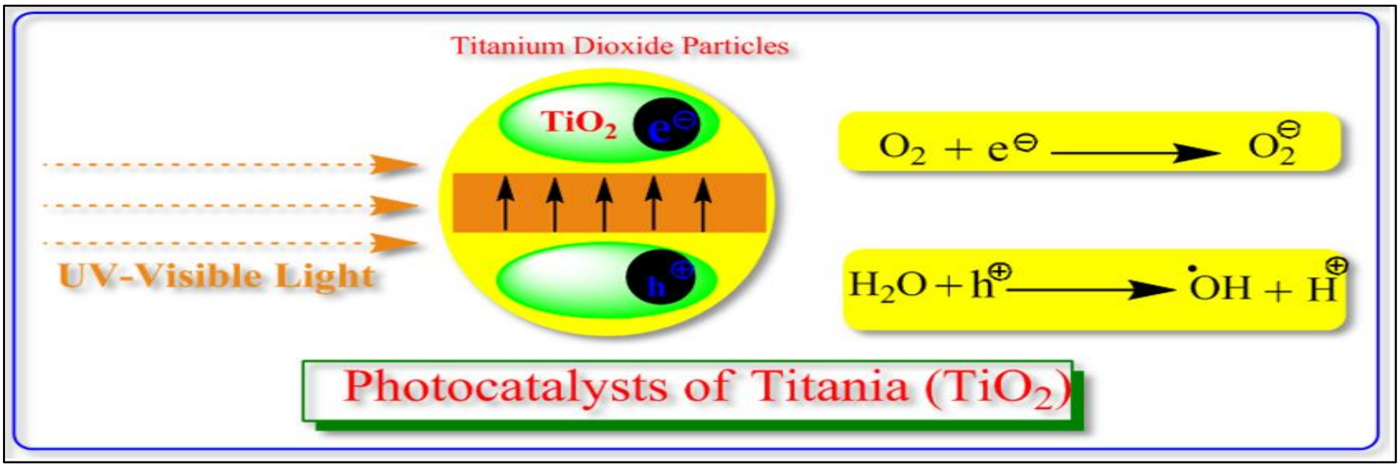

Fig 7 Principle of Photocatalysis of (TiO_2) and Generation of ROS.

B. Types of TiO_2 Photocatalysis

- *Direct Photocatalysis:*

One potent and extensively used method for using sun energy to propel chemical reactions on titanium dioxide surfaces is direct photocatalysis. TiO_2 experiences photo-excitation in the presence of ultraviolet (UV) light, which results in the creation of electron-hole pairs on its surface. Then, these active charge carriers engage in redox reactions with species that have been adsorbed, like organic contaminants or dyes.

The production of reactive oxygen species (ROS), primarily hydroxyl radicals, via electron interactions with oxygen and water molecules is the distinguishing feature of direct photocatalysis on the titanium dioxide surface.

These extremely reactive species are essential for the breakdown and mineralization of organic pollutants, which turns them into innocuous byproducts. Direct photocatalysis on the TiO_2 surface is a straightforward and effective method that has been applied to a variety of environmental remediation processes, such as air purification and wastewater treatment, demonstrating its importance in the advancement of environmentally friendly and sustainable technology [32-33].

- *Indirect Photocatalysis:*

On the surface of titanium dioxide, indirect photocatalysis occurs via a unique process in which molecular species interact with photo-excited electrons and holes in the semiconductor to produce reactive intermediates that catalyze chemical changes.

In contrast to direct photocatalysis, indirect photocatalysis depends on co-catalysts or sacrificial agents to help produce reactive species.

Organic substances or inorganic species that easily take or donate electrons to stop the recombination of electron-hole pairs are common sacrificial agents. Co-catalysts, like metal nanoparticles, can improve charge carrier separation, which will encourage the production of reactive species even more.

These intermediaries, which are usually radicals and superoxide ions, react redoxically with organic contaminants to break them down due to the fact that indirect photocatalysis extends titania photo-activity to visible light, it can overcome the restrictions imposed by its bandgap. This sophisticated method improves the adaptability and efficiency of TiO_2-based photocatalysis, making it a useful instrument for applications including sustainable energy and environmental cleanup [34].

V. FACTORS INFLUENCING PHOTOCATALYTIC ACTIVITY

- *Crystal Structure:*

The photocatalytic capabilities of titanium dioxide (TiO2) are largely determined by its crystal structure. There are three primary crystalline phases of TiO2: rutile, brookite, and anatase. Each of these phases has unique structural properties. Of them, anatase is well known for having higher photocatalytic activity than brookite and rutile. When anatase is exposed to light, its distinct crystal structure increases the density of surface defects and increases its reactivity, which facilitates the effective creation and separation of electron-hole pairs. Reactive oxygen species (ROS), especially hydroxyl radicals, are produced more intensely as a result of this increased photoactivity. ROS play a crucial role in the breakdown of organic contaminants.

In contrast, rutile has a bigger bandgap and a smaller surface defect density than other minerals, which results in less photocatalytic activity despite its higher stability. Since its surface reactivity and electrical characteristics are directly influenced by its crystal structure, anatase is the favored phase for applications needing strong photocatalytic performance, like solar energy conversion and environmental cleanup. Scientists frequently modify the crystal structure using synthetic techniques to maximize its photocatalytic effectiveness for certain uses [35-36].

- *Surface Area:*

The efficacy of titanium dioxide (in environmental remediation and solar energy conversion applications is directly impacted by its surface area, which is a crucial element influencing its photocatalytic capabilities. More surface area typically translates into more active sites that are available for catalytic reactions and adsorption. Because of their smaller particle size, nanoscale TiO_2 compounds have a greater surface area and work better as photocatalysts.

When exposed to ultraviolet (UV) radiation, the larger surface area facilitates the formation of electron-hole pairs and more efficiently absorbs light. As a result, more reactive oxygen species (ROS) are created, including hydroxyl radicals, which improve its capacity to break down organic contaminants. More surface area also makes it easier for TiO_2 and target molecules to make better contact, which encourages effective photocatalytic reactions. Therefore, one typical tactic to customize its nanoparticles or films' photocatalytic performance for particular applications is to manage and optimize their surface area. This helps to promote efficient and sustainable photocatalytic technologies [37-38].

- *Bandgap Engineering:*

One important factor that greatly affects titanium dioxide's photocatalytic capabilities is its band gap. The energy difference between the valence and conduction bands, or band gap, establishes the lowest energy needed for electrons to go from the valence to conduction band. TiO_2 is found in various crystalline phases, the most common being rutile and anatase, each of which has a unique band gap value. Anatase is more sensitive to ultraviolet light than rutile because it has a shorter band gap, which facilitates effective absorption and the consequent creation of electron-hole pairs during photocatalysis. Reactive oxygen species, like hydroxyl radicals, are produced as a result of this increased photo-activity and play a crucial role in the degradation of organic contaminants. Therefore, the absorption spectrum and its capacity to use solar energy for catalytic reactions are directly influenced by the band gap. Optimizing band gap via different techniques, including doping or changing the crystalline structure, is a popular approach to maximize its photocatalytic efficiency, for the particular energy and the various environmental applications [39-40].

- *Surface Modification:*

Titanium dioxide's photocatalytic capabilities can be tailored and enhanced in large part through surface changes. By introducing certain functional groups, coating, doping, or other alterations, TiO_2 nanoparticles' surface properties can be finely adjusted. These changes affect the material's surface energy, reactivity, and electronic structure, which all affect how well it photocatalyzes. By altering the band structure, doping with alien elements such as metals or nitrogen reduces the band gap and increases photoresponse into the visible light spectrum. Enhancing the effectiveness of charge separation and light absorption, it can be coated with semiconductors or polymers. Surface functional groups can enhance adsorption capacity and encourage specific interactions with contaminants. The overarching goal of surface modifications is to improve the overall efficiency and adaptability of TiO_2-based photocatalysts by addressing issues including restricted absorption in the visible light spectrum and quick electron-hole recombination. This strategy has great potential to advance the use of it in solar energy conversion, water purification, and environmental remediation procedures [41, 42].

- *Strategies for Enhancing Photocatalytic Efficiency through Surface Modification*

The surface modification of TiO_2 can be done by following techniques which are as shown in the pictorial form of the Figure 8 and the various methods are as explained below:

- *Surface Functionalization:*

The surface modification techniques by functionalization method also led in tailoring of TiO_2 surface which eventually influencing its interaction with reactants [43].

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Fig 8 Modification of TiO_2 into Better Photocatalyst.

- *Metal Deposition:*

One well-known method for improving titanium dioxide's (TiO_2) photocatalytic capabilities is metal deposition on its surface. Through this modification, the performance of TiO_2 is significantly enhanced by the introduction of metal nanoparticles or clusters onto its surface. Metal deposition improves charge carrier separation, fosters particular redox reactions, and extends the absorption spectrum into the visible light range, among other functions. Silver, gold, and platinum are examples of noble metals that are frequently used because of their capacity to function as electron sinks, reduce electron-hole recombination, and increase the lifespan of charge carriers. Furthermore, metal nanoparticles have the ability to function as localized surface plasmon resonators, which enhance photocatalytic activity by absorbing and focusing light energy. The combination of deposited metals and TiO_2 produces a platform for customized catalytic reactions, broadening the range of potential uses in solar energy conversion and environmental remediation. This method shows how selective metal deposition can be used to optimize TiO_2's photocatalytic characteristics for increased effectiveness and adaptability. TiO_2 composites can be created by modifying TiO_2 with CdS, ZnO, PbS, Cu_2O, Bi_2S_3, and CdSe. It is theoretically possible to increase the photoelectric TiO_2 conversion efficiency by mixing n-type TiO_2 with p-type semiconductors. Since many of these modified materials can undergo Photo-corrosion (e.g., dissolution of Zn^{2+} or Cd^{2+}) when exposed to radiation and water, they have not received as much attention as they should [15]. An effective substitute for enhancing photoelectric conversion is to incorporate noble metals (such as Pt, Au, Ag, and Pd) into the semiconductor manufacturing process. Given that: a) near-UV and visible light can activate the surface plasmon resonance of noble metal particles; the energy band gap is minimized; and the noble metal nanoparticles operate as electron traps, noble metal addition favors water splitting. Platinum is an excellent option when it comes to potential noble metal co-catalysts because of its capacity to capture photo-generated electrons. When trapped electrons and H^+ interacts with each other then, molecular hydrogen and $H^•$ radicals are produced [44-46].

- *Doping Strategy:*

In recent developments the doping strategies for the surface modification of TiO_2 with various elements basically modify its electronic structure and enhance photocatalytic activity. Doping titanium dioxide (TiO_2), or purposefully adding foreign elements to its crystal lattice, is a potent way to modify and improve its photocatalytic effects. The process of doping affects TiO_2's electrical structure, band gap, and surface reactivity, which in turn affects how well it can use solar energy for photocatalysis. Common dopants that impart certain functions are carbon, nitrogen, and transition metals. For example, nitrogen doping reduces the band gap, increasing the absorbance of visible light and the photoresponse range of TiO_2. By adding energy levels to the band structure, transition metal dopants can lower the rates of electron-hole recombination and help in charge carrier separation. Because of this increased photoactivity, reactive oxygen species (ROS), which are essential for the breakdown of organic contaminants, are produced more effectively. Thus, the doping strategy offers precise control over TiO_2's photocatalytic efficacy, providing a flexible and adaptable method for applications in sustainable energy conversion and environmental remediation [47-49].

- *Hetero-structuring:*

The incorporation of hetero-junctions with other semiconductors to improve charge separation and enhance catalytic performance of TiO_2 also modify its surface

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properties for the photocatalysis. Hetero-structuring is a transformative technique that greatly affects titanium dioxide's (TiO_2) photocatalytic capabilities. It entails combining various semiconductor materials. TiO_2's photocatalytic effectiveness can be significantly increased by forming heterojunctions with other semiconductors, such as metal oxides or sulfides. The enhanced charge separation and transfer facilitated by the synergistic effects at the heterojunctions reduce the recombination of electron-hole pairs. This increases the spectrum range of light absorption and improves photocatalytic activity, making it possible to use visible light for catalytic reactions. A cooperative and effective photocatalytic system is produced by the hetero-structuring approach, which takes advantage of the complementing qualities of many materials. Through the expansion of light absorption and the mitigation of rapid charge carrier recombination, this novel technique has the potential to advance TiO_2-based photocatalysis in a number of applications, such as environmental remediation and solar energy usage [50].

- *Dye-Anchoring:*

One tactical alteration that has the potential to greatly impact titanium dioxide's (TiO_2) photocatalytic characteristics is dye anchoring. This method creates a synergistic system by chemically attaching or adsorbing organic dyes onto the TiO_2 surface. This combines the dye's light-harvesting properties with the photocatalytic activity of TiO_2. The dye makes it easier for a wider range of light to be absorbed—particularly in the visible range—which TiO_2 might not be able to effectively use on its own. The photocatalytic process's overall efficiency is improved by this wider absorption range. Additionally, the dye molecules start photocatalysis by acting as sensitizers, introducing excited electrons into the TiO_2 conduction band. This dye anchoring technique maximizes sunlight use and expands the photocatalytic response into the visible light spectrum, making it very useful for utilizing solar energy for energy conversion and environmental remediation applications [51].

- *TiO_2 in Energy and Environmental Applications*

Titania is a versatile material with numerous applications in energy and environmental fields and therefore its unique properties make it suitable for various applications that contribute to sustainability and clean technologies. In energy applications it is used in photocatalysis in water splitting reactions to generate hydrogen through the absorption of light energy. This process is a key component in the development of clean and renewable energy sources. It is also used as Dye-Sensitized Solar Cells (DSSCs), where they serve as the photoanode. The semiconductor properties of TiO_2 contribute to the conversion of solar energy into electricity [52, 53]. In photovoltaic devices, it is contributing to the development of lightweight and flexible solar panels. Titania-based materials are investigated for use in supercapacitors and batteries due to their high surface area, stability, and potential for improved energy storage and conversion. Its photocatalytic properties are harnessed for the degradation of organic pollutants and the removal of harmful gases from air, contributing to air purification technologies. Titania coatings on surfaces such as glass and building materials exhibit self-cleaning properties.

Fig 9 TiO_2 Coating: Hydrogen Evolution Pathways.

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The photocatalytic activity of TiO_2 helps break down and remove organic contaminants when exposed to sunlight. Figure 9 shows that how do Titanium dioxide Coating work for various methods like anti-staining, sterilization, oxidative decomposition and air-water purification eventually lead to hydrogen evolution.

➢ *Economic and Environmental Implications in Hydrogen Evolution*

Utilizing titanium dioxide's photocatalytic activity for hydrogen evolution has significant potential consequences for the environment and economy. Economically speaking, the widespread use of TiO_2-based photocatalysis for hydrogen production offers the potential to lessen dependency on traditional, frequently carbon-intensive techniques. The cost-effectiveness of TiO_2 photocatalysis may increase with further developments, particularly with continuous research aimed at improving catalyst efficiency and streamlining production procedures. TiO_2 is also widely available and reasonably priced, which adds to the viability of large-scale hydrogen evolution economically. Regarding the environment, the photocatalytic characteristic makes it possible to use solar energy to propel the evolution of hydrogen, providing a clean and renewable energy source. It can reduce the carbon footprint associated with hydrogen generation by facilitating the splitting of water into hydrogen and oxygen without releasing harmful emissions by harnessing sunlight. This lessens the environmental effects of traditional hydrogen production techniques and is consistent with worldwide initiatives to shift towards sustainable energy sources. All in all, its photocatalysis for hydrogen evolution is economic and environmental outcomes make it a viable path toward a more eco-friendly and sustainable energy landscape. TiO_2 photocatalysis is widely employed for the degradation of organic pollutants (including dyes, pesticides, and pharmaceuticals), removal of inorganic pollutants, such as heavy metals and metalloids, through TiO_{--*+} photocatalysis, contaminants from water, and air decontamination [54-55].

- *Solar Cells:*

In photovoltaic applications, TiO_2 is utilized in dye-sensitized solar cells (DSSCs) to facilitate electron transport and enhance the efficiency of solar energy conversion.

- *Water Splitting:*

TiO_2-based photocatalysts play a crucial role in solar-driven water splitting, generating hydrogen as a clean and sustainable fuel.

VI. SYNTHESIS AND CHARACTERIZATION TECHNIQUES

Analysis of the novel synthesis techniques, include sol-gel, hydrothermal, and template-assisted methods, and their impact on the morphology and structure of TiO_2 photocatalysts. The various characterization techniques can be used to confirm the TiO_2 backbones which are suitable for photocatalytic activity are FTIR, CHNS elemental analysis and^{1}HNMR. etc. Structural Analysis is conducted by X-ray diffraction (XRD) or SEM -to confirm the crystalline phase of Titania. The surface analysis use techniques such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM) to analyze the external and internal surface morphology. Photocatalytic activity testing helps to evaluate the photocatalytic activity of the titania-biopolymer composite using a suitable model reaction under UV or visible light. The synthesis parameters (e.g., precursor concentration, pH, temperature) may need to be optimized based on the specific biopolymer and titania properties. The amount of biopolymer added should be optimized to ensure effective immobilization without hindering the photocatalytic activity of titania.To perform the photocatalytic activity tests using a standard reaction (e.g., degradation of a dye) to assess the efficiency of the titania-biopolymer composite. This general procedure provides a starting point, but adjustments may be necessary based on the specific requirements of the photocatalytic application and the characteristics of the biopolymer chosen. It's crucial to conduct thorough characterization and testing to validate the performance of the prepared titania-biopolymer composite as a photocatalyst [56].

In the literature titania, has shown to be an useful substance in the photocatalytic destruction of dyes, offering a safe and efficient way to treat wastewater. Titania exhibits exceptional photocatalytic characteristics, especially in the presence of ultraviolet (UV) radiation. Titania produces electron-hole pairs when exposed to radiation, which causes reactive oxygen species (ROS) such hydroxyl radicals to develop. Because of their extreme reactivity, these ROS can disintegrate organic substances—including dyes—into smaller, less dangerous molecules.

➢ *Dye Breakdown Mechanism:*

Dye molecules adhere to the surface of titania particles during the photocatalytic breakdown process. ROS are produced as a result of the photocatalytic reaction, which is started by further exposure to UV radiation. The adsorbed dye molecules are subsequently reacted with by these ROS, resulting in the dissolution of their molecular structures and the creation of simpler, non-toxic byproducts [57-60].

➢ *Broad Applicability:*

Titania is effective against a wide range of dyes, including synthetic organic dyes used in printing, textiles, and effluent from dyeing processes, among other industries. Titania is a useful tool for handling a variety of pollution concerns because of its adaptability.

- *Minimization of Residuals:*

Dyes usually mineralize and change into simpler, inorganic compounds as a result of the photocatalytic processes that titanium dioxide facilitates. By doing this, the production of leftover byproducts is minimized, lessening the treatment process's negative environmental effects.

- *Long-Term Stability:*

Titania has a reputation for stability and resistance to deterioration, which guarantees its efficacy over time. For applications requiring continuous and sustainable wastewater

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treatment, this makes it a dependable and long-lasting solution.

- *Integration into Water Treatment Systems:*

Titania's applicability and ease of integration into the current wastewater treatment infrastructure can be increased by immobilizing it onto other supports, such as membranes or nanoparticles, or by incorporating it into water treatment systems. Titania can be incorporated into water treatment systems or immobilized onto various supports, such as membranes or nanoparticles, enhancing its practicality and facilitating its integration into existing wastewater treatment infrastructure.

➢ *Model Dyes Selected for the photocatalytic Evolution of Hydrogen*

Different model dyes, cationic [(methylene blue (MB), crystal violet (CV) and malachite green (MG)) as well as anionic [Congo red (CR)], from their aqueous solutions were considered and reported for their decomposition and eventually degraded into water, oxygen, hydrogen and small molecules using the photocatalytic activity of Titanium Dioxide based hybrid material. Their structures are as shown in the Figure 10.

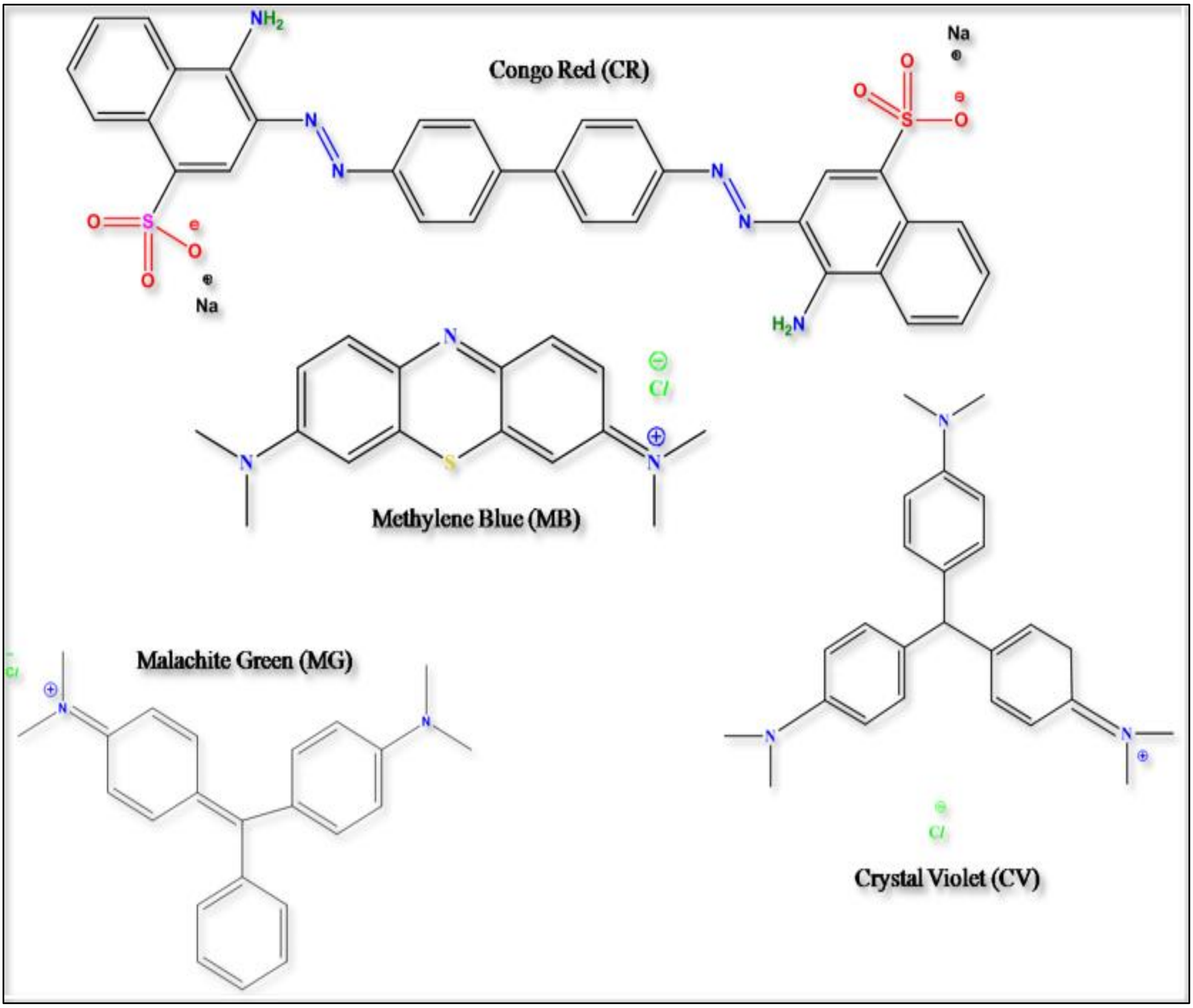

Fig 10 Structure of Model Dyes.

Congo Red (CR) is a water-soluble anionic acid dye and it is a secondary diazo dye. Crystal Violet (CV) is a triarylmethane dye and widely used in colour industry Also known as Basic violet-3/Methylrosaniline chloride/Hexamethyl Violet /Hexamethylpararosaniline chloride/Aniline Violet. Malachite Green (MG) is a water-soluble basic cationic dye, it is also known as aniline green/basic green 4/Diamond green B/ Victoria green B.

It is a triarylmethane dye and widely used in pigment industry and methylene blue (MB) is also a water-soluble basic cationic dye.

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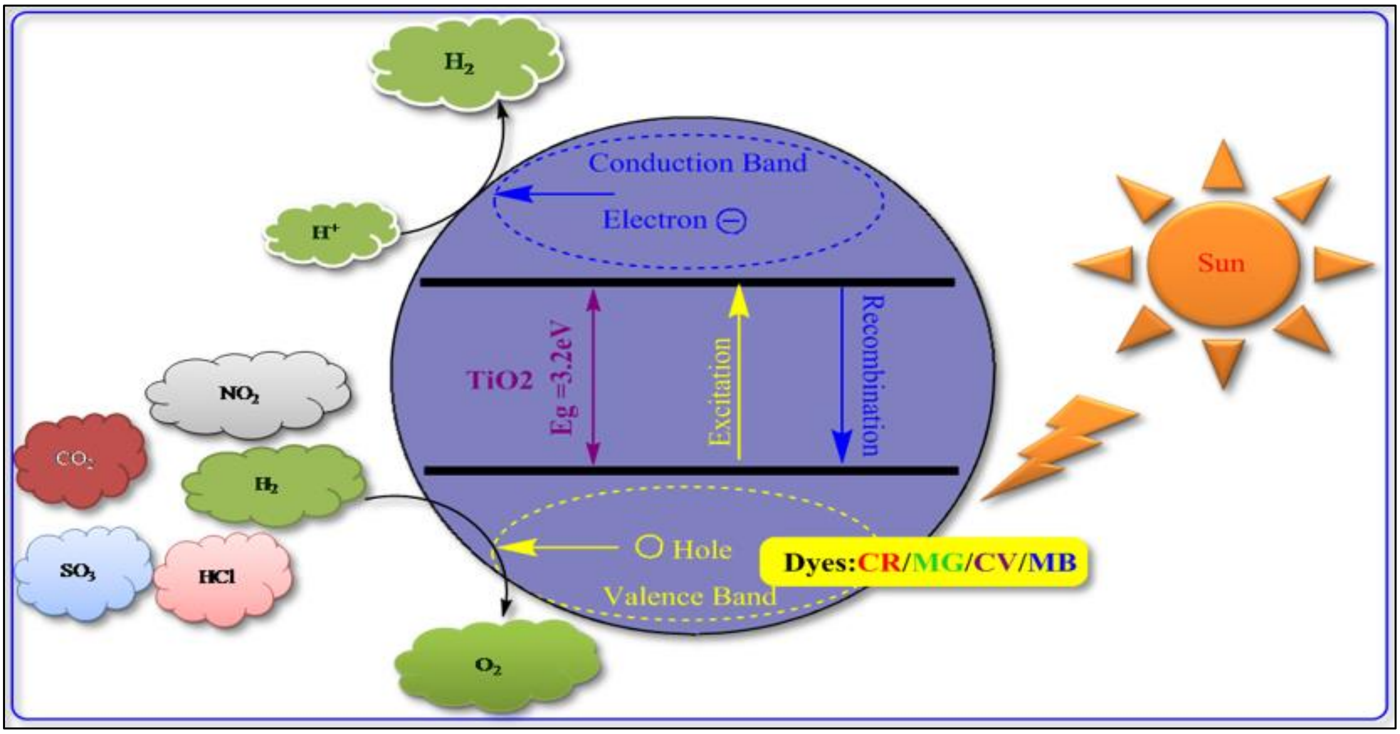

Fig 11 Mechanism for Photocatalytic Decomposition of Dye

- *Dye Degradation:*

Dye degradation can be accomplished using a variety of techniques, including chemical degradation, ozonation, photocatalytic degradation, biodegradation, adsorption through hydrogels, etc. However, the most frequent ways include photocatalytic degradation of dye containing NPs that use UV light to break down the dye molecules into smaller and less toxic components, most often water and carbon dioxide and eventually this released water can be very essential in . NP-based photocatalytic degradation has a number of benefits over alternative techniques, including high selectivity, cost-effectiveness, eco-friendliness, versatility, and efficiency. The TiO_2-based NPs can boost the degradation efficiency even at lower dye concentrations because of their large surface-area-to-volume ratio, which provides many active sites in a limited area. Using TiO_2-based NPs for photocatalytic breakdown, particular chemicals are targeted while the other compounds in the food matrix remain intact. This is due to the fact that light at a certain wavelength, which can be adjusted to suit particular dyes, activates the photocatalysts. The primary benefit of photocatalysis over other methods is its environmental friendliness. As carbon dioxide and water are typically produced as byproducts, they pose no environmental harm, and as a result, we can reduce the toxicity of the dyes to a greater extent. Because photocatalytic degradation is so adaptable, it can be used to break down a wide range of harmful chemical molecules, including ones that are resistant to conventional approaches. Since this procedure does not require the use of any expensive material or compound, it is comparatively less expensive. All that is needed are nanoparticles based on TiO_2 or ZnO and exposure to UV light, which may be achieved by being outside in the sun. The expected mechanism for the photocatalytic degradation of these dyes is as shown in the Figure 11.

- *Recyclability and Reusability of TiO_2-Based Materials in Photocatalysis*

The recyclability and reusability of TiO_2-based materials in photocatalysis are essential aspects for sustainable and cost-effective environmental remediation. This comprehensive review explores the current state of knowledge regarding the recyclability and reusability of TiO_2-based photocatalysts, focusing on their performance over multiple cycles and strategies to maintain or enhance their activity. The review discusses factors influencing recyclability, such as photo-corrosion and surface fouling, and presents various approaches employed to address these challenges. Additionally, it evaluates the economic and environmental implications of recycling TiO_2-based materials. The insights provided in this review contribute to the development of more efficient and eco-friendly photocatalytic processes. Recyclability and reusability in TiO_2-based photocatalysts are very significant for the sustainable and economically viable environmental applications [61].

- *Factors Influencing Recyclability*

Photo-corrosion is a major factor affecting the stability and recyclability of TiO_2-based materials, particularly under prolonged exposure to light. The accumulation of contaminants on the TiO_2 surface, leading to reduced photocatalytic activity and hindered recyclability. The protective coatings also mitigate Photo-corrosion and improve the stability of TiO_2-based materials. The surface modifications, like doping and functionalization, are also considered to be good strategies to enhance the recyclability and reusability of TiO_2 photocatalysts [62].

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- *Recyclability and Reusability of TiO_2-Based Photocatalysts for Hydrogen Evolution*

The recyclability and reusability of TiO_2-based photocatalysts play a pivotal role in realizing sustainable and economically viable hydrogen evolution processes. This comprehensive review explores the current state of knowledge regarding the recyclability and reusability of TiO_2-based materials specifically for hydrogen evolution. It delves into factors influencing recyclability, such as Photo-corrosion and catalyst deactivation, and presents various strategies to enhance and maintain their activity over multiple cycles. This article review also evaluates the economic and environmental implications of recycling TiO_2-based photocatalysts for hydrogen production. Insights from this article contribute to the development of efficient and eco-friendly photocatalytic processes for sustainable hydrogen generation. Figure 12 shows the recyclability and reusability of the TiO_2 and gelatin-based hybrid nanomaterial for photocatalytic activity for five repeated uses and for the maximum adsorption capacity for five cycles.

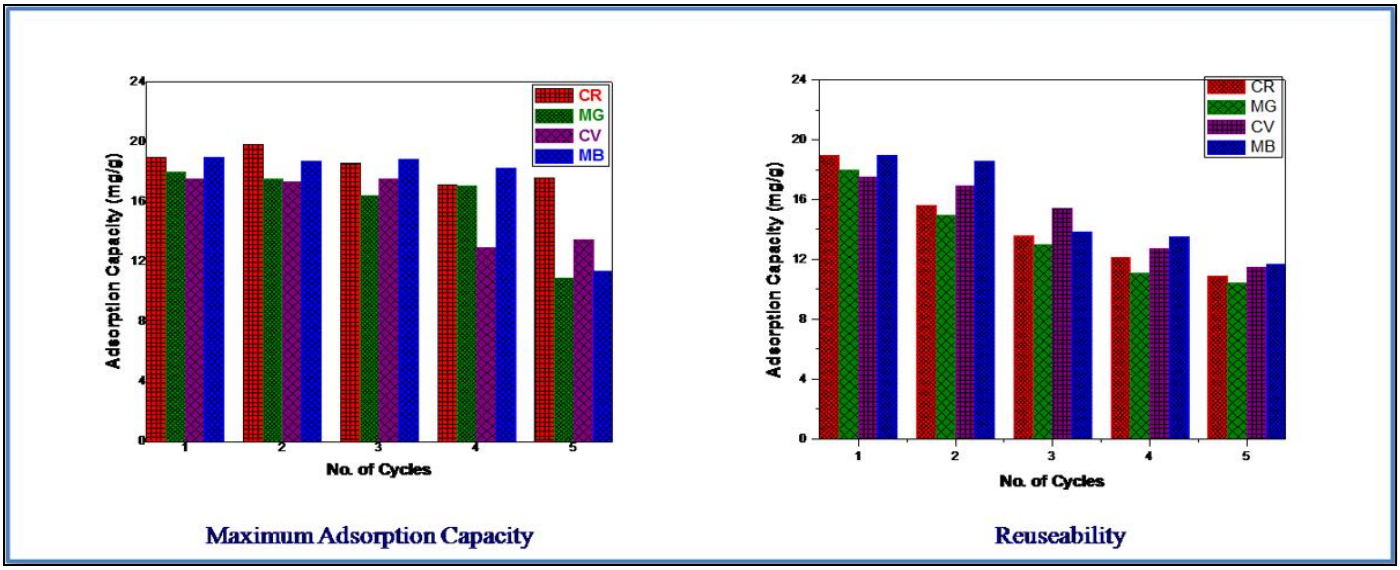

Fig 12 Recyclability and reusability of the TiO_2 based Material for Photocatalytic Activity.

Table 1. draws a comparison between the maximum adsorption capacity whereas Table 2. draws a comparison of conductivity and percentage uptake (P_u) of dye solutions as a function of repeated use all the four model dyes for 5 cycles [56, 62].

Table 1 Maximum Adsorption Capacity

Dye	λ_{max}	Total Cycles	Adsorption Capacity (mg/g)
Congo Red	481 *nm*	5	71
Malachite Green	595 *nm*	5	67
Crystal Violet	598 *nm*	5	75
Methylene Blue	628 *nm*	5	77

Table 2 Conductivity and Percentage Uptake (P_u) of Dye Solutions as a function of Repeated Use

Congo Red Dye (λ_{max}~598)					
Cycle	**I**	**II**	**III**	**IV**	**V**
Conductance	1043 μS	894 μS	1338 μS	1407 μS	1569 μS
P_u	76 %	79 %	74 %	69 %	70 %
Malachite Green Dye (λ_{max}~595)					
Cycle	**I**	**II**	**III**	**IV**	**V**
Conductance	4.36 *m*S	15.27 *m*S	16.31 *m*S	16.12 *m*S	16.89 *m*S
P_u	72 %	70 %	66 %	68 %	44 %
Crystal Violet Dye (λ_{max}~598)					
Cycle	**I**	**II**	**III**	**IV**	**V**
Conductance	780 μS	773 μS	1245	1180 μS	1070 μS
P_u	70 %	69 %	70 %	52 %	54 %
Methylene Blue Dye (λ_{max}~628)					
Cycle	**I**	**II**	**III**	**IV**	**V**
Conductance	4.0 *m*S	4.9 *m*S	13.9 *m*S	13.4 *m*S	16.52 *m*S
P_u	76 %	75 %	75.367%	72.904%	45.501%
Pure Water	**373 μS**				

VII. CONCLUSION

The principle of TiO_2-based photocatalysts revolves around the excitation of electrons and holes upon exposure to light, initiating redox reactions and the generation of reactive species. This unique property has led to a wide array of applications, and ongoing research continues to explore ways to improve efficiency and expand the scope of TiO_2 photocatalysis in sustainable technologies. In conclusion, the use of Titania in the photocatalytic degradation of dyes represents a promising and eco-friendly approach for treating wastewater, aligning with the principles of sustainable and environmentally conscious practices. In conclusion, titanium dioxide photocatalytic dye degradation is a viable and environmentally responsible wastewater treatment method that adheres to the ideas of sustainable and ecologically friendly practices.

CHALLENGES AND FUTURE DIRECTIONS

Identification of challenges related to achieving high efficiency in both pollutant degradation and hydrogen evolution, while maintaining selectivity. Ongoing research aims to improve the efficiency of TiO_2 photocatalysts, addressing challenges such as recombination of electron-hole pairs and limited visible light absorption.

Nanostructuring of TiO_2 materials, including nanotubes and nanoparticles, are a promising avenue for enhancing surface area and optimizing catalytic performance. Future research explores the integration of TiO_2 photocatalysis into multifunctional systems for applications in energy conversion, sensing, and more.

Exploration of future directions involving the development of novel materials and integration with emerging technologies to overcome current challenges. The discussion on the challenges associated with scaling up TiO_2-based photocatalysts for practical environmental remediation and hydrogen production applications.

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