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Recent Advances in Titanium Dioxide for Green Hydrogen Production

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Abstract

Green chemistry represents a proactive approach to preventing pollution and reducing environmental impact through thoughtful design and innovation in chemical processes and products. By adhering to its principles, chemists can create more sustainable and safer methods for manufacturing and using chemicals, which benefits human health and the environment. The ongoing research and application of green chemistry continue to drive progress towards a more sustainable future. Hydrogen is increasingly recognized as a crucial component in the transition to sustainable energy systems due to its high energy density and zero carbon emissions upon combustion. Titanium dioxide (TiO_2) has emerged as a prominent photocatalyst for hydrogen production through water splitting, leveraging its stability, non-toxicity, and relative abundance. This paper reviews recent advancements in the utilization of TiO_2 for green hydrogen production, focusing on enhancing its photocatalytic efficiency, extending its light absorption into the visible spectrum, and integrating it with other materials. The challenges and future prospects for TiO_2-based photocatalysts are also discussed.

Keywords: Green chemistry, (TiO_2), photocatalyst, hydrogen production, water splitting, stability,

Introduction

Hydrogen is considered an ideal solution to address this issue due to its sustainable, energy-dense, and eco-friendly properties (Baykara, 2018; Catapan et al., 2018; Im et al., 2009). It is employed in a wide range of applications, including petroleum refining, electricity production, gas welding, automotive fuel, and rocket fuel for space programs (Staffell et al., 2019; Tusek and Suban, 2000). Several countries, such as China, the United Kingdom, and the United States, have adopted hydrogen as an alternative fuel for transportation to reduce greenhouse gas emissions in major cities (Zhu et al., 2018). Green chemistry, also known as sustainable chemistry, is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. It aims to create more efficient, environmentally benign methods for chemical manufacturing and to minimize the impact of chemicals on human health and the environment. Green chemistry encompasses a wide range of scientific disciplines and practices, seeking to make chemical processes more sustainable and safer. Titanium dioxide (TiO_2) plays a significant role in green chemistry and sustainable development due to its unique properties and versatile applications. The increasing demand for renewable energy sources has highlighted hydrogen as a critical component of future energy systems. Green hydrogen, produced through water splitting using renewable energy, offers a sustainable alternative to fossil fuels. Titanium dioxide (TiO_2) has emerged as a leading photocatalyst for this purpose due to its chemical stability, non-toxicity, and cost-effectiveness. This paper examines the recent advancements in TiO_2 research aimed at improving its photocatalytic efficiency for green hydrogen production.

Here are some of the key aspects of its contribution:

1. Photocatalysis:

Environmental Remediation: TiO_2 is widely used as a photocatalyst to degrade organic pollutants in water and air. When exposed to UV light, it generates reactive oxygen species that can break down harmful substances, making it effective for wastewater treatment and air purification.

Self-Cleaning Surfaces: TiO_2 coatings on surfaces like glass and building materials can harness sunlight to break down organic dirt and pollutants, reducing the need for chemical cleaners and maintenance efforts.

2. Energy Production:

Dye-Sensitized Solar Cells (DSSCs): TiO_2 is a critical component in DSSCs, a type of solar cell that mimics photosynthesis. These cells offer a cost-effective and environmentally friendly alternative to traditional silicon-based solar cells.

Hydrogen Production: TiO_2 can be used in photocatalytic water splitting to produce hydrogen, a clean fuel. By utilizing solar energy, TiO_2 helps generate hydrogen without emitting greenhouse gases.

3. Green Synthesis:

Catalytic Reactions: TiO_2 can facilitate various chemical reactions under mild conditions, reducing the need for harsh chemicals and high energy inputs. This aligns with the principles of green chemistry, which aim to minimize the environmental impact of chemical processes.

4. Environmental Impact:

Non-Toxicity and Abundance: TiO_2 is non-toxic and abundant, making it a safer alternative to other materials that might have harmful environmental or health effects. Its wide availability and low cost further support its use in sustainable applications.

5. Innovative Applications:

Nano-TiO_2: The development of nano-sized TiO_2 particles has enhanced its photocatalytic efficiency and broadened its applications. Nanotechnology allows for more effective environmental cleanup, improved solar cell performance, and new methods of energy storage.

Mechanism of Photocatalytic Water Splitting

Photocatalytic water splitting involves the absorption of light by a semiconductor, leading to the generation of electron-hole pairs. These charge carriers then drive the redox reactions to produce hydrogen and oxygen. The overall reaction can be simplified as:

$$2H_2O + 4hv \rightarrow 2H_2 + O_2 \quad (1)$$

For TiO_2, the photocatalytic process is typically initiated by UV light due to its wide band gap (~3.2 eV for anatase). However, harnessing visible light, which constitutes a significant portion of solar radiation, is essential for practical applications.

Enhancements in TiO_2 Photocatalysts

1. TiO2 -based photocatalysts for HER

1.1. Fundamental of photocatalytic HER

The separation of water occurs under UV, visible, or UV–Vis irradiation through several key steps (Fig. 1) (Jafari et al., 2016). First, a photocatalyst absorbs solar energy equal to or greater than the bandgap of TiO2, forming excitons. Second, this energy causes an electron to move from the valence band (VB) to the conduction band (CB), leaving a hole in the VB. Third, protons adsorbed on the surface of TiO2 receive the newly generated electron to produce hydrogen (Eq. (2)), while water is oxidized by the holes to form oxygen (Eq. (3)).

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = 0.00 \text{ eV} \quad (2)$$

$$H_2O + 2h^+ \rightarrow 2H^+ + 1/2O_2 \quad E^0 = 1.23 \text{ eV} \quad (3)$$

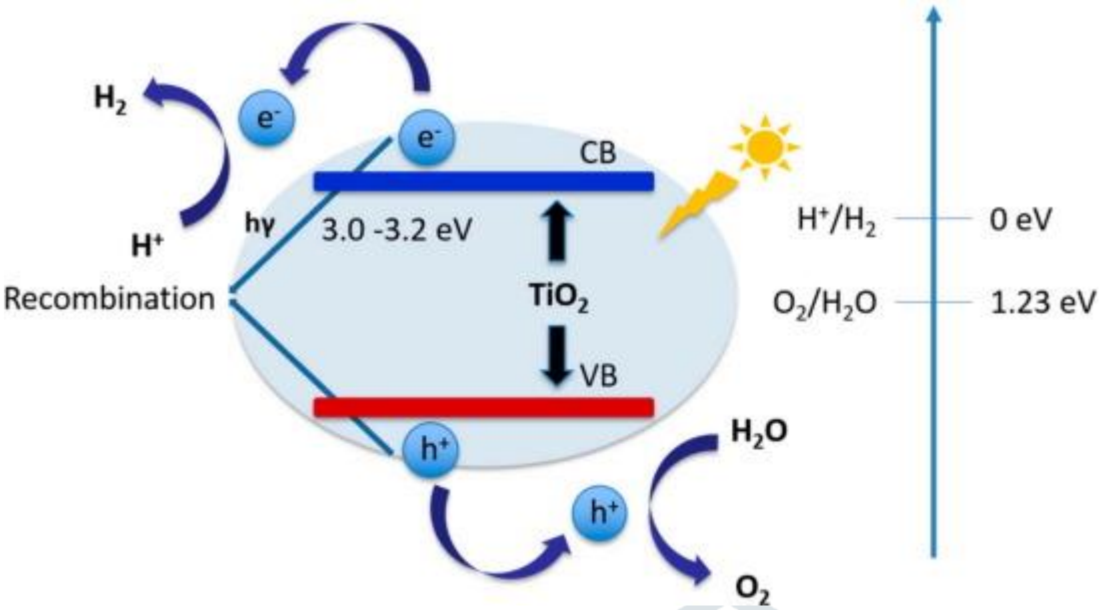

Fig. 1. Schematic illustration of TiO_2 for photocatalytic hydrogen evolution reaction (Jafari et al., 2016).

The Initial Condition for Photocatalytic Reactions

The initial condition for a reaction under light irradiation requires the catalyst to have a conduction band (CB) value smaller than the reduction potential of H^+/H_2 (0 eV) and a valence band (VB) level higher than the reduction potential of O_2/H_2O (1.23 eV). TiO_2 is a promising candidate for photocatalytic HER, with a CB level of -0.3 eV and a VB level of 2.9 eV. TiO_2 as a catalyst for solar water splitting was first reported by Fujishima and Honda in 1972. They evaluated the photocatalytic performance under UV light in a photoelectrochemical system, using TiO_2 as the anode and platinum as the cathode. Oxygen was generated at the TiO_2 surface, while hydrogen was produced at the Pt electrode, paving the way for the field of photocatalysis. However, due to its large bandgap, TiO_2 is only active under UV light, which constitutes about 4% of solar energy. Additionally, charge recombination during the photoreduction reaction reduces catalytic efficiency. To overcome these challenges, various strategies have been implemented to enhance the photocatalytic activity of TiO_2 for HER.

1.2. TiO_2 Photocatalyst for HER

1.2.1. Structural Engineering

1.2.1.1. TiO_2 Nanostructure Engineering

TiO_2, a well-known n-type inorganic semiconductor, can form a p-n heterojunction structure when paired with a p-type semiconductor like p-Si, facilitating electron movement from p-Si through TiO_2 to active sites. For instance, Andoshe et al. fabricated TiO_2 nanorods on a p-type silicon plate as a cathode material for photocatalytic water splitting. These TiO^2 nanorods (NRs) were created through a hydrothermal process using tetrabutoxytitanium as a precursor. The use of TiO_2 significantly increased the optical absorption of the p-Si sample, with reflectance values at 550 nm decreasing from 37.5% for p-Si to 1.4% for the TiO_2 NRs/p-Si pattern. TiO_2 NRs/p-Si also showed better light absorption than TiO_2 seed layer/p-Si. When Pt nanoparticles were deposited on these samples, the photoelectrochemical (PEC) performance was remarkably enhanced, achieving a saturation current density as high as 40 mA cm−2 and an onset potential of approximately 440 mV. These heterojunction devices also demonstrated durability over a 52-hour test.

Another study by Yoon et al. in 2019 reported the deposition of MIL (125)–NH2 on the surface of TiO_2 NRs grown on FTO/glass. This device operated as an anode for water splitting under solar energy. Evaluated in an alkaline solution (pOH = 0.4) under AM 1.5 G irradiation, the photocurrent density reached 1.63 mA/cm² at 1.23 V vs. RHE, about three times higher than that of bare TiO2 NRs. The improved performance was attributed to the large specific surface area, high crystallinity of TiO_2 NRs, and the appropriate bandgap width of the MOF (MIL (125)–NH2). The combination of MIL (125)–NH2 and TiO2 NRs created a type (II) heterojunction structure, facilitating electron transport to the active area for HER.

Mesoporous TiO_2 materials have also attracted significant attention in photocatalytic applications due to their low cost, high stability, and excellent electronic and optical properties. Studies have focused on enhancing the photocatalytic activity of mesoporous TiO_2 materials. Zheng et al. synthesized and investigated rutile mesoporous single-crystal NRs (R-MSC) and anatase mesoporous single-crystal nanosheets (A-MSC) for their photocatalytic activity in water splitting. The morphology and size of mesoporous TiO_2 were influenced by seeding concentration, hydrohalic acid conditions, and temperature. The results showed that R-MSC with a seeding concentration of 0.3 mM (R-MSC-0.3) exhibited the best photocatalytic performance for hydrogen generation from water, surpassing rutile single-crystal (R-SC). Similarly, A-MSC-0.3 outperformed A-SC. The enhanced catalytic activity was due to the increased specific surface area and monocrystalline solid. The active facets of R-MSC played a crucial role in photocatalytic reactions. With tunable structures and models, mesoporous TiO_2 holds significant potential for various photocatalytic applications.

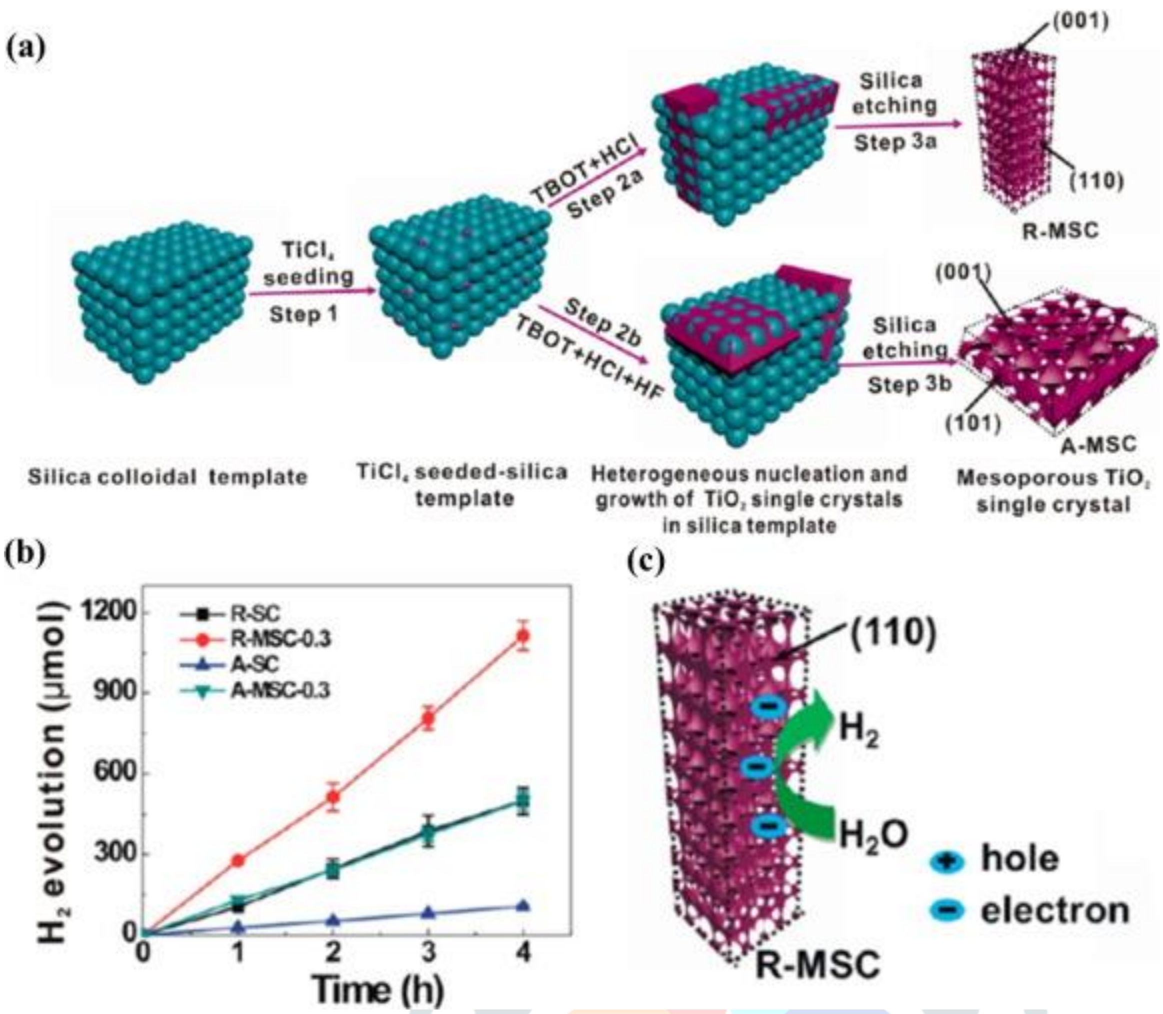

Fig. 2. (a) Schematic diagram of the synthesis of R-MSC and A-MSC in silica template. (b) Comparison of H2 formation rate by different catalysts. (c) The proposed mechanism for photocatalytic hydrogen evolution on R-MSC (Xiaoli Zheng et al., 2013).

Bandgap Engineering

To extend the light absorption of TiO_2 into the visible spectrum, various strategies have been employed:

Doping: Recent studies have focused on doping TiO_2 with non-metal and metal elements to reduce its bandgap and improve visible light absorption. For instance, nitrogen-doped TiO_2 (N-TiO_2) has shown enhanced photocatalytic activity under visible light due to the creation of mid-gap states that facilitate photon absorption in the visible range. A study by Zhang et al. 2023 demonstrated that nitrogen and sulfur co-doped TiO_2 exhibited a significant increase in hydrogen production under visible light, attributed to synergistic effects that enhance charge separation and light absorption.

Sensitization: Dye-sensitization involves adsorbing dye molecules onto the TiO_2 surface, which absorb visible light and inject excited electrons into the TiO_2 conduction band. Recent advancements include the use of metal-organic frameworks (MOFs) combined with TiO_2 to enhance light absorption and charge transfer, as reported by Wang et al. in 2022.

Morphological Control

The design of TiO_2 nanostructures, such as nanorods, nanotubes, and nanoflowers, has been a key strategy to increase surface area and improve charge transport properties. Liu et al. 2021 synthesized TiO_2 nanorods with a hierarchical structure, achieving a significant increase in photocatalytic hydrogen production due to improved light absorption and reduced charge recombination.

Composite Formation

Combining TiO_2 with other materials, such as graphene, carbon nanotubes, or other semiconductors (e.g., CdS, ZnO), has shown synergistic effects in enhancing photocatalytic efficiency. These composites can facilitate better charge separation and extend light absorption.

A study by Kim et al. 2022 demonstrated that a TiO_2-graphene composite exhibited enhanced photocatalytic hydrogen production, leveraging graphene's high electrical conductivity and large surface area to facilitate electron transport. Nanostructuring TiO_2 to form nanorods, nanotubes, or nanoflowers increases the surface area and enhances charge separation, leading to improved photocatalytic activity.

Recent Studies and Developments

Visible Light Activation

Recent studies have focused on developing TiO_2-based materials that are active under visible light. For example, nitrogen-doped TiO_2 (N-TiO_2) has demonstrated significant photocatalytic activity under visible light, attributed to the narrowing of the bandgap and the creation of mid-gap states that facilitate visible light absorption.

Nanoarchitectures

The synthesis of TiO_2 nanostructures with controlled morphology has been a critical area of research. Nanotubes and nanowires offer high surface area and enhanced charge transport properties. For instance, TiO_2 nanotube arrays prepared by anodization techniques have shown promising results in photocatalytic hydrogen production.

Hybrid Materials

TiO_2-based hybrid materials have shown remarkable improvements in photocatalytic performance. Graphene-TiO_2 composites, for example, benefit from the excellent electrical conductivity and large surface area of graphene, which enhance charge separation and reduce recombination rates. Combining TiO_2 with other materials, such as graphene or carbon nanotubes, has shown promise in enhancing its properties for various green applications, including more efficient solar cells and better performance in environmental cleanup.

Enhanced Photocatalytic Efficiency: Researchers are developing TiO_2 composites and doping TiO_2 with other elements (e.g., nitrogen, carbon) to extend its light absorption range into the visible spectrum, increasing its photocatalytic efficiency under natural sunlight.

Circular Economy: Innovations in recycling and reusing TiO_2 from industrial processes contribute to a circular economy, reducing waste and the environmental footprint of TiO_2 production and use.

Challenges and Future Prospects

TiO_2 photocatalysts are regarded as promising materials for hydrogen production via photocatalytic hydrogen evolution reaction (HER). Numerous studies have demonstrated that TiO2 -based photocatalysts exhibit excellent performance. However, the primary challenge with TiO2 is its wide bandgap, which leads to the rapid quenching of photo-induced excitons, thereby reducing its photocatalytic activity. Additionally, the impact of synthetic methods on catalytic activity requires further investigation, and the mechanisms of electron transfer are not fully understood. Although TiO2 materials have shown high activity, the recycling of TiO2 -based photocatalysts has not been extensively studied, which is crucial for reducing manufacturing costs in industrial applications. Moreover, further research is needed on mesoporous TiO2 with high porosity and well-defined pore channels to enhance proton transport to catalytic centers. The incorporation of two-dimensional materials (e.g., graphene, transition metal dichalcogenides) and metal-organic frameworks (MOFs) with TiO2 can also create promising candidates for solar hydrogen production. Finally, with the advancement of computational methods, properties of TiO2 -based catalysts such as electronic density of states, band structures, and active sites can be comprehensively studied and designed to improve photocatalytic HER performance. Therefore, a combination of empirical and theoretical studies is essential for a better understanding and enhanced development of TiO2 photocatalysis for the HER.

Despite its potential, the application of TiO_2 in green chemistry faces several challenges:

Charge Recombination: Rapid recombination of photogenerated charge carriers limits the efficiency of TiO_2 photocatalysts.

Scalability: The synthesis of advanced TiO_2 nanostructures and composites at a large scale remains challenging and cost-intensive.

Durability: Long-term stability and resistance to photocorrosion are critical for practical applications.

Efficiency under Visible Light: TiO_2 primarily absorbs UV light, which is a small fraction of the solar spectrum. Enhancing its visible light absorption is crucial for broader applications.

Scalability and Cost: The production of advanced TiO_2 nanostructures and composites can be expensive and challenging to scale up.

Environmental and Health Impact: While TiO_2 is generally considered safe, the long-term effects of nanoparticles on health and the environment need further investigation.

Future Direction: Comprehensive studies on the environmental and health impacts of nano-TiO_2 will help ensure its safe and sustainable use.

Future research directions include the development of more efficient co-catalysts, exploration of novel TiO_2 polymorphs, and the use of advanced fabrication techniques to create highly ordered nanostructures. Additionally, integrating TiO_2 photocatalysts into photoelectron -chemical cells (PECs) and tandem systems could offer pathways to more efficient solar-to-hydrogen conversion systems.

Summary:

Titanium dioxide plays a crucial role in advancing green chemistry and sustainability, showcased by its applications in photocatalysis, energy generation, and environmental cleanup. Its versatility underscores its potential to shape a more sustainable future, with ongoing research continually improving its efficiency and expanding its utility, reinforcing its significance in addressing global environmental concerns.

Conclusion:

In the pursuit of sustainable hydrogen production, titanium dioxide remains a cornerstone material. Recent progress in doping, morphological control, and composite development has notably bolstered its photocatalytic efficacy under visible light. However, confronting challenges like charge recombination, scalability, and durability is paramount for the practical deployment of TiO_2-based photocatalysts. Continuous research and innovation are poised to further enhance TiO_2 capabilities, paving the way for green hydrogen to become a feasible and widespread energy solution.

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