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Study on electronic structure regulation and charge migration in photoelectrocatalytic materials

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Abstract. With the increasing urgency of global energy and environmental challenges, photoelectrocatalytic technology has emerged as a promising approach for solar-driven energy conversion and environmental remediation. The electronic structure and charge carrier migration behavior of semiconductor materials critically influence their catalytic efficiency and stability. This study conducts a comprehensive analysis of three representative photoelectrocatalytic materials—TiO_2, g-C_3N_4, and MoS_2—highlighting their unique band structures, charge transport mechanisms, and photocatalytic properties. TiO_2 exhibits excellent chemical stability and strong reduction potential under ultraviolet light but is limited by a wide band gap and rapid charge recombination. g-C_3N_4 demonstrates visible light responsiveness and improved electron-hole separation through electronic tuning strategies. MoS_2 offers a narrow band gap, high carrier mobility, and broad-spectrum light absorption, though it requires further stability enhancement. The paper discusses current challenges, including interfacial charge dynamics and scalability issues, and proposes future directions focusing on advanced material design, multi-scale characterization, and practical application development. These insights provide a theoretical foundation for optimizing photoelectrocatalytic materials to achieve higher solar energy utilization and environmental benefits.

Keywords: semiconductor photocatalysts, charge transport, band structure engineering, solar energy conversion

1. Introduction

As the global energy crisis and environmental pollution become increasingly severe, the development of new and efficient energy conversion and environmental governance technologies has become the focus of academic and industrial attention. Photoelectrocatalytic technology offers distinct advantages in water purification, degradation of organic pollutants, carbon dioxide reduction, and hydrogen production, owing to its ability to harness solar energy directly to drive diverse chemical transformation processes [1]. Compared with traditional physical or chemical treatment methods, photoelectric catalysis is not only green and environmentally friendly, with mild reaction conditions, but also can achieve efficient conversion and utilization of solar energy, and has great application prospects and social value [1]. In the photoelectric catalytic system, the electronic structure and charge migration behavior of semiconductor materials are the core factors affecting their catalytic performance. The electronic structure determines the material's ability to absorb photons and the energy band position, thereby affecting the generation, separation and migration efficiency of photogenerated carriers; the charge migration behavior is directly related to whether the photogenerated electrons and holes can migrate to the reaction interface in time to participate in the redox reaction, thereby determining the catalytic efficiency and stability. Therefore, studying the electronic structure regulation and charge migration mechanism of photoelectric catalytic materials not only helps to understand their intrinsic photoelectric properties, but also provides a theoretical basis for the rational design and application promotion of efficient catalysts.

Over the last few years, conventional semiconducting materials (e.g. TiO_2, g-C_3N_4 and MoS_2) have received much attention because of their interesting band structures and good photoelectric properties [2]. TiO_2 has become a representative material in the photocatalytic field thanks to its high stability and large number of accessible surfaces, g-C_3N_4 has been widely used due to the visible light response and good electron-hole separation ability, and MoS_2 has showcased enormous potential in the next-generation photocatalysts because of its narrow band gap and good carrier mobility. The article focuses on these three material types, using literature analysis and theoretical comparisons, to explore the similarities and differences of their electronic structures and charge migration behaviours and how these characteristics collectively define the catalytic efficiency, which could provide a good foundation for the design and optimization of new photoelectrocatalytic materials.

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2. Electronic structure theory for photoelectrocatalysis

2.1. Significance of charge carrier separation in photocatalysis

The fundamental process of photoelectrocatalytic reaction is based on photons absorption by semiconductor materials and effective carrier separation. Generally, semiconductor materials have a Valence Band (VB) and a Conduction Band (CB), which are separated by a band gap [3]. When the material absorbs photons with energy higher than the band gap, the electrons in the valence band are excited to the conduction band to form photogenerated electrons (e^-), while leaving holes (h^+) in the valence band. The generation of this pair of electrons and holes is the basis of photoelectrocatalytic reaction.

However, if the photogenerated electrons and holes cannot be effectively separated, but quickly recombine in the bulk phase or on the surface, the probability of photogenerated carriers participating in the surface redox reaction will be greatly reduced, thereby limiting the catalytic efficiency [4]. Therefore, the optimization of the internal band structure of the material and the surface/interface design are the key to improving the electron-hole separation efficiency and improving the photoelectrocatalytic performance. Ideally, the photogenerated electrons should be able to efficiently migrate to the reaction surface to participate in the reduction reaction, and the holes should participate in the oxidation reaction, so as to achieve efficient energy and material conversion.

2.2. Band structure characteristics of photoelectrocatalytic materials and their impact on performance

The band structure of photoelectrocatalytic materials directly determines their light absorption range, photogenerated carrier migration, and separation efficiency, which are key factors affecting their performance. These materials have different band gap widths and band positions which leads to different advantages in terms of light responsiveness and catalytic activity.

Wide-bandgap semiconductors (TiO_2, 3.2 eV) have a high level of conduction band, allowing redox reactions such as hydrogen production [5] but respond mostly to ultraviolet light, this limits their ability to capture solar energy as they absorb very little visible light. Medium-bandgap materials (g-C_3N_4, 2.7 eV) able to absorb portions of the visible spectrum have a tunable band position allowing enhanced separation of charge carriers by manipulating the electronic structure of the material via doping or building heterojunctions [6]. Narrow bandgap materials (MoS_2, 1.8 eV) having a layered structure are capable of greater visible and near infrared light absorption, and greater charge carrier diffusion, creating a more efficient medium for photoelectric conversion and improved catalytic activity [7]. Overall, the width of the bandgap and the arrangement of bands of the material determine not only to which wavelengths light can be absorbed, but also largely determines the photogenerated electrons and holes separation efficiency and migration path, while also influencing the photogenerated carrier lifetimes. If the band structure can be designed rationally, if can provide enough redox potential, can elongate carrier lifetimes and suppress recombination to drive the reaction forward and improve the overall efficiencies of the photoelectrocatalytic reaction. As a result, band structure regulation is one of the major strategies for creating high-generate photoelectrocatalytic materials.

2.3. Theoretical foundations and key equations in photoelectrocatalysis

To understand both the electronic behavior and the charge transport mechanisms taking place in photoelectrocatalytic systems, it is important to rely on some key equations from semiconductor physics. These equations provide a theoretical basis to understand the fundamental processes of light absorption, charge carrier generation, charge carrier transport, and charge carrier recombination [8].

When a semiconductor absorbs photons with energy hv greater than its band gap E_g, electrons are excited from the Valence Band (VB) to the Conduction Band (CB) and issue holes in the VB. This can be described as:

$$h\nu \geq E_g \rightarrow e_{\mathrm{CB}}^- + h_{\mathrm{VB}}^+ \tag{1}$$

The ability of photogenerated carriers to undergo redox reactions is controlled by the placement of the CB and VB relative to the redox potentials of the reactions of interest. More specifically, the CB edge needs to be more negative than the reduction potential and the VB edge needs to be more positive than the oxidation potential:

$$E_{\mathrm{CB}} < E_{\mathrm{red}}, E_{\mathrm{VB}} > E_{\mathrm{ox}} \tag{2}$$

Both the Conduction Band (CB) and Valence Band (VB) positions must straddle the redox potentials of the target reaction, where E_{red} and E_{ox} representative of the reduction and oxidation potentials of the target reaction respectively.

In practical applications, efficient photoelectrocatalysis also depends on the diffusion length L of charge carriers, which determines how far electrons or holes can migrate before recombination. This is given by:

$$L = \sqrt{D\tau} \tag{3}$$

where D is the diffusion coefficient and τ is the carrier lifetime. The diffusion coefficient itself is linked to carrier mobility μ through the Einstein relation:

$$D = \mu \frac{k_B T}{q} \tag{4}$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, and q is the elementary charge.

The overall motion of charge carriers in semiconductors can be further described by the drift-diffusion current density equation, which combines the effects of electric field-driven drift and concentration gradient-driven diffusion [8]:

$$J = qn\mu E + qD\frac{dn}{dx} \tag{5}$$

In this expression, J denotes the current density, μ is the carrier mobility, E is the electric field strength, $\frac{dn}{dx}$ represents the spatial gradient of carrier concentration.

Finally, the recombination rate R of charge carriers, a critical loss mechanism, can be modeled as:

$$R = \frac{n}{\tau} \tag{6}$$

Among them, R is the recombination rate, n is the carrier concentration, and τ is the carrier lifetime.

The above theoretical models can provide a theoretical basis for subsequent material design, interface regulation and performance optimization of photocatalytic systems [8]. These formulas not only reveal the basic physical process of photoelectrocatalytic reactions, but also provide quantitative tools for improving quantum efficiency and charge utilization efficiency.

3. Comparative analysis of TiO_2, g-C_3N_4, and MoS_2 in photoelectrocatalysis

The performance of photoelectrocatalytic materials is fundamentally governed by their electronic structures, which determine light absorption properties, band alignment, and the efficiency of charge carrier generation and separation. Three representative materials—TiO_2, g-C_3N_4, and MoS_2—are presented in terms of their band gap, carrier transport and catalytic properties.

Due to chemical stability and versatility, TiO_2 has been one of the first materials studied extensively as a photocatalyst. TiO_2 has a wide band gap (3.2 eV approximately) and thus responds primarily to ultraviolet light [5]. The Conduction Band (CB) edge of TiO_2 is approximately –0.5 V vs NHE, which is negative enough for many reduction reaction (including hydrogen evolution) [9]. However, the wide band gap restricts it to minimal visible light absorption, which diminishes the solar to hydrogen conversion efficiency. Another significant limitation to using TiO_2 as a viable photocatalyst for solar energy conversion is the analysis of the electron-hole pairs which will often rapidly recombine impacting the quantum yield.

g-C_3N_4 (graphitic carbon nitride) is a new, metal-free semiconductor with a moderate band gap around of 2.7 eV [6], allowing it to effectively absorb visible light. Its CB and Valence Band (VB) positions are between TiO_2 and MoS_2, and therefore having a more even redox capability, and being able to separate the charges better. g-C_3N_4 also has tunable electronic structures through heteroatom doping and defect engineering, which increases its performance in photoelectrocatalysis.

MoS_2 (molybdenum disulfide) is a common Transition Metal Dichalcogenide (TMD) with a narrow band gap of approximately 1.8 eV and a two-dimensional, layered structure [7]. Similar to other TMDs, the high carrier mobility and broad-spectrum light absorber (particularly in the visible and near-infrared regions) is enhanced by the band alignment that allows for an effective migration and separation of photogenerated carriers. MoS_2 also has large quantities of active edge sites that increase its reactivity with substrates through it is greater propensity for catalysis and chemical transformations of this type.

These materials highlight the importance of band structure design for photoelectrocatalytic activity. By using or designing materials with appropriate band gaps and alignment, we can utilize the solar spectrum efficiently for maximizing photoexcitation and promoting efficient charge separation, which is all necessary for high performing photoelectrocatalysis.

The differences in band structure and charge dynamics largely influence their photoelectrocatalytic properties. In Figure 1 show the band structures and light absorption ranges of TiO_2, g-C_3N_4, and MoS_2, showing the potential for complementary spectral responses which could lead to efficient composite catalysts. Depending on their band structures and light absorptions, TiO_2, g-C_3N_4, and MoS_2 exhibit photoelectrocatalytic properties associated with their individual band structures and charge dynamics. TiO_2 provides a robust chemical stability and strong reducing ability, but has limited visible light absorption and rapid charge recombination. g-C_3N_4 utilized more visible light and shifted the visible light spectrum but suffers from limited surface area and active sites for catalysis. MoS_2 is capable of light absorption throughout the visible to near-infrared region and has fast carrier mobility, but stability needs to be increased. The understanding of these complementary properties enables us to design the composite photocatalyst, exemplified through the TiO_2/g-C_3N_4 heterojunction and g-C_3N_4/MoS_2 heterojunction, to combine the benefits that prevent the issues seen with each system individually. The following sections discuss the performance, challenges, and strategies associated with each material in more detail.

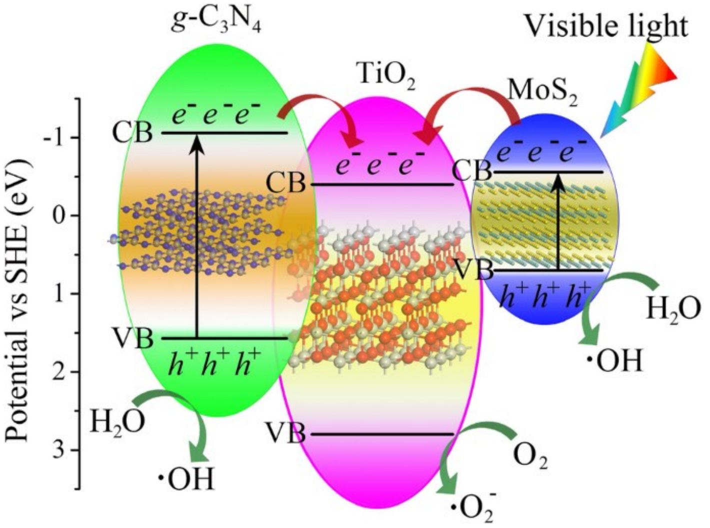

Figure 1. Band structures and light absorption ranges of TiO_2, g-C_3N_4, and MoS_2 [10]

4. Carrier migration mechanisms and performance optimization in photocatalytic materials

4.1. Mechanism of carrier migration impact on catalytic efficiency

The photocatalytic efficiency highly depends on the effective migration of photogenerated charge carriers (electrons and holes). Carriers must successfully migrate from the bulk of the material to its surface to participate in redox reactions [11]. Bulk or surface recombination during migration results in energy loss as heat, significantly reducing the quantum efficiency. Many wide-bandgap semiconductors such as TiO_2 have suitable band positions but exhibit low actual catalytic efficiency due to low carrier mobility and high recombination rates. Enhancing carrier mobility and lifetime through strategies like heterojunction construction, doping, and surface modification is an effective way to improve photocatalytic performance.

Efficient separation of photogenerated electrons and holes is critical for enhancing photocatalytic efficiency. The driving force for separation mainly arises from the band structure and interfacial barriers of the materials, such as built-in electric fields, band offsets, and heterojunction energy level differences. For example, in the g-C_3N_4 or MoS_2 heterostructure, band misalignment drives electrons and holes to migrate in opposite directions, achieving spatial separation; interfaces like Schottky junctions and p-n junctions also enhance built-in electric fields to promote carrier separation. Band engineering and interface modulation have become important approaches to prolong carrier lifetimes and improve reaction efficiency [12].

4.2. Theoretical models and material migration characteristics

Carrier migration in photoelectrocatalytic materials is primarily described by drift-diffusion models and recombination kinetics. Drift is the movement of charge carriers from an internal or external electric field, while diffusion is the result of concentration gradients of electrons and holes. The recombination kinetics models show how electrons and holes recombine through several mechanisms such as, radiative, Auger and defect-related Shockley-Read-Hall recombination which decreases the number of charge carriers available for surface reactions which restricts the overall photocatalytic efficiency [12].

Different semiconductor materials will perform differently based on their inherent properties and structures that determine how carriers will migrate. TiO_2 is a classic example of a wide-bandgap semiconductor with low carrier mobility and rapid electron-hole recombination which occurs due to bulk defect states and surface defect trap states that have a direct impact on availability of photogenerated carriers during with photocatalytic processes. Several methods exist for surface modification of

TiO_2 for photocatalytic applications, including doping and formation of heterojunctions, to aid charge separation and enhance the lifetimes of photogenerated carriers. Conversely, g-C_3N_4 falls into the category of moderate-bandgap semiconductors with increased two-dimensional layered structure beneficial for electron transport properties leading to moderate carrier mobility, and relatively longer carrier lifetimes, decreasing recombination by multiple pathways of electron transport. $MoS_2$is a narrow bandgap, transition metal dichalcogenide which has a layered and two-dimensional morphology most beneficial for electron transport properties, and is able to achieve broadband light absorption. MoS_2has many more active edge sites than g-C_3N_4 or TiO_2, leading to the greatest catalytic activity and facilitating fast separation and migration of photogenerated carriers, ultimately reducing the recombination losses encountered in other semiconductor materials.

5. Conclusion

This study provides a detailed overview of the electronic structures and charge carrier migration mechanisms of three photoelectrocatalytic materials—TiO2, g-C3N4, and MoS2. From the perspective of individual activity and performance level as a series of photocatalytic application, we have provided a summary of how the encouraged or prevented charge generation, migration, and recombination types provided benefits to the candidates as well as inherent disadvantages which affect their photocatalytic performance in different ways. TiO2 is ideal because of its great chemical stability, capacity to generate a strong enough reduction potential, the efficiency via ultraviolet light photodecomposition, but is hindered by a large band gap limiting visible light and fast charge carrier recombination. g-C3N4 provides moderate electronic stability (that can be enhanced), partial visible light absorption through tuning of the electronic structure (doping, building heterojunctions), and partial efficiency because it can separate the electron hole pairs to increase the stability of the charge carriers. MoS2 has a narrow band gap, exhibits a 2D layered crystalline structure, along with potentially the greatest charge carrier migration and absorption of broadband light. However, changes to the synthesis pathway and ali-teration of its delivery method like aqueous stability would greatly enhance by altering its performance and photocatalytic efficiencies. Heterojunctions synthesis route of each of the different compositions, surface modifications, and design around interface will allow for improvements in carrier migration and retainment are required to further enhance the efficiencies of photoelectrocatalysis and the electron hole carrier lifetimes.

Even with those advancements, there are still major limitations. The complex interfacial effects and carrier dynamics, which are taking place during the photoelectrocatalysis process, are still not completely understood primarily due to limited and hardly any in situ monitoring/quantification. Additionally, the gap between the lab and field comes with major challenges in translating material performance to real systems. And, more development in the stability and larger scale, low-cost synthesis must be made to support long-term and large-scale application. Future research should focus on multi-scale and multi-physics investigations of carrier transport mechanisms, integrating advanced characterization techniques and computational modeling to elucidate the relationship between carrier dynamics and catalytic activity. The design of novel composite materials and functionalized interfaces to expand light absorption ranges, improve charge separation efficiency, and enhance catalyst stability is essential.

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