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The Research and Application of Photoelectrochemical Biosensing Technology based on Wide-bandgap Metal Oxide Semiconductor Nanomaterials

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Abstract. Research on semiconductor nanomaterials has made significant progress over the past few decades. These materials, which possess numerous advantages, are now widely applied across various fields and have gradually become an indispensable part of human societal development. Among the various types of semiconductor nanomaterials, those based on wide-bandgap metal oxides are taking a dominant position. This paper primarily investigates the application of wide-bandgap metal oxides in the field of photoelectrochemical biosensing technology, along with a brief analysis of their fundamental physical properties. The aim of this study is to explore the potential of this semiconductor material in empowering the photoelectrochemical biosensing field and the feasibility of addressing related issues. Methods such as literature analysis, synthesis, and comparative analysis have been employed. The study reveals that semiconductor nanomaterials based on wide-bandgap metal oxides hold significant potential for development in photoelectrochemical biosensing technology, yet they also face some known challenges.

Keywords: wide-bandgap, semiconductor nanomaterial, photoelectrochemical biosensing

1. Introduction

Research on semiconductor nanomaterials based on metal oxides has made substantial progress over the past few decades. Since the pioneering work of Akira Fujishima and Kenichi Honda in 1972, which demonstrated the photocatalytic decomposition of water using titanium dioxide photocatalysis under ultraviolet irradiation, significant interest has been directed toward the unique properties of metal oxide semiconductors. With the emergence of nanotechnology in the late 1980s, the integration of these two fields has experienced rapid development. Studies from around the world have shown that such materials play crucial roles in energy, environmental science, information and electronics, and biomedical applications.

Metal oxide-based nanoscale semiconductor materials (MONMs) are still in the early stages of exploration and represent a frontier at the intersection of nanotechnology and semiconductor physics. The core concept of this technology lies in utilizing metal oxide semiconductors at the nanoscale as functional units, exploiting their size-dependent properties to develop novel materials

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with performance far exceeding that of conventional counterparts. However, research indicates that there remains considerable scope for further investigation into the application of MONMs in the field of photoelectrochemical biosensing. This study aims to evaluate the feasibility of applying MONMs to photoelectrochemical biosensing technologies through methods such as literature review, comparative analysis, and data-driven interpretation. Such an approach has the potential to significantly enhance the sensitivity of biomolecular recognition at different nanoscale levels. Moreover, MONMs can reduce the cost of photoelectrochemical biosensors without causing substantial degradation in detection performance. The application of these materials in photoelectrochemical biosensing is expected to exhibit broad and promising prospects in the future. This study highlights the potential of wide-bandgap metal oxide nanomaterials to improve the performance, stability, and cost-efficiency of PEC biosensors, benefiting medical, environmental, and food safety applications. It also identifies key challenges and offers strategies such as heterojunction design, providing valuable guidance for future research in biosensing and nanomaterials.

2. Characterization and property analysis of semiconductor nanomaterials based on wide-bandgap metal oxides

2.1. Concept and advantages of wide-bandgap metal oxides

2.1.1. Concept of wide-bandgap metal oxides

Wide-bandgap metal oxide semiconductors (WBG MOSs) constitute an important class of functional materials characterized by a bandgap energy typically greater than 3 eV. This intrinsic property endows them with unique optical and electronic behaviors, particularly their strong response in the ultraviolet (UV) region and high transparency in the visible spectrum. Representative materials in this category include titanium dioxide (TiO_2), zinc oxide (ZnO), tin dioxide (SnO_2), and tungsten trioxide (WO_3), all of which have been extensively investigated due to their excellent physicochemical stability and versatile electronic properties.

From a fundamental perspective, the electronic structure of wide-bandgap metal oxides is governed by the distribution of valence and conduction bands, which are primarily derived from oxygen 2p orbitals and metal cation orbitals, respectively. When incident photon energy satisfies the condition $h\nu \geq E_g$, electrons in the valence band can be excited to the conduction band, resulting in the generation of electron–hole pairs. These photogenerated charge carriers play a central role in photoelectrochemical (PEC) processes. The efficiency of such processes strongly depends on the separation, transport, and recombination dynamics of these carriers. At the nanoscale, metal oxide semiconductors exhibit distinct size-dependent effects, including quantum confinement, increased surface-to-volume ratio, and enhanced surface activity. These characteristics significantly improve light absorption efficiency and provide abundant active sites for interfacial reactions. Moreover, the shortened charge transport pathways in nanostructured materials contribute to reduced recombination losses, thereby enhancing overall photoelectrochemical performance.In addition, wide-bandgap metal oxides possess several intrinsic advantages, such as high chemical stability, resistance to photocorrosion, low toxicity, and cost-effective synthesis. These properties make them particularly suitable for applications in harsh environments and long-term operation. However, their relatively large bandgap also limits visible light utilization, which has prompted extensive research into bandgap engineering strategies, including doping, defect modulation, and heterojunction construction with narrow-bandgap semiconductors.

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Overall, the unique combination of optical, electronic, and surface properties of wide-bandgap metal oxide semiconductor nanomaterials provides a solid theoretical foundation for their application in photoelectrochemical biosensing systems. Understanding these fundamental principles is essential for the rational design and optimization of high-performance sensing platforms.

2.2. Advantage of wide-bandgap metal oxides

Compared with conventional narrow-bandgap semiconductors, wide-bandgap metal oxides exhibit a series of pronounced advantages in terms of their physical, chemical, and optoelectronic properties, thereby demonstrating broad application prospects in fields such as photoelectrochemistry and biosensing.

Wide-bandgap metal oxides possess excellent chemical stability and strong resistance to photocorrosion. During photoelectrochemical processes, materials are typically exposed to prolonged illumination, electrolyte solutions, and complex chemical environments. Owing to their large bandgap and stable crystal structure, wide-bandgap materials can effectively suppress self-corrosion induced by photogenerated charge carriers, thereby ensuring the long-term stability and reliability of devices. In addition, these materials exhibit strong absorption in the ultraviolet region while maintaining high transparency in the visible range. This characteristic contributes to a high signal-to-noise ratio during photoelectrochemical responses, which is beneficial for improving the detection sensitivity of sensors. Furthermore, the wide-bandgap nature implies a low intrinsic carrier concentration, thereby reducing dark current interference—an aspect that is particularly critical for high-precision biosensing applications. Wide-bandgap metal oxides also generally exhibit favorable electrical properties and relatively high electron mobility (e.g., TiO_2 and ZnO), which facilitate efficient separation and transport of photogenerated electron–hole pairs, ultimately enhancing photoelectric conversion efficiency. At the nanoscale, these advantages are further amplified, resulting in faster response times and reduced recombination losses in photoelectrochemical processes. Taking TiO_2 as an example, this n-type semiconductor material possesses the advantageous characteristics mentioned above, including non-toxicity, cost-effectiveness, and high physical and chemical stability. Generally, TiO_2 exists in three primary crystalline phases: rutile, brookite, and anatase, whose crystal structures are illustrated in Fig. 1. The wide bandgap of TiO_2 renders it relatively insensitive to visible and infrared radiation while exhibiting strong sensitivity to ultraviolet light, which endows this material with distinct advantages in ultraviolet detection. This behavior is reflected in the reflectance of the three phases across the ultraviolet, visible, and infrared spectral regions. As shown in Fig. 2, the reflectance of all three phases decreases significantly around a wavelength of 300 nm and approaches nearly zero at approximately 500 nm.

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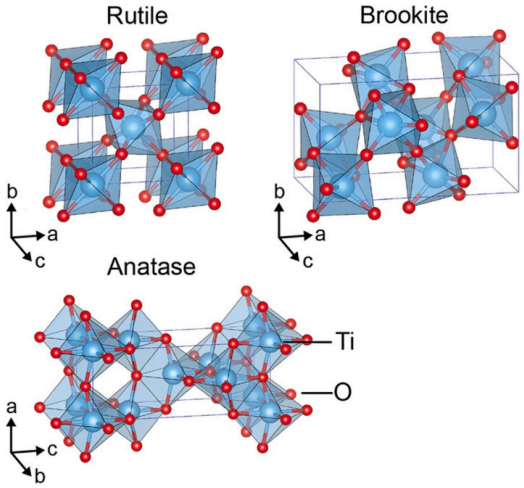

Figure 1. Three crystal structure of tio2 . Rutile (a), Brookite (b), and Anatase (c) [1]

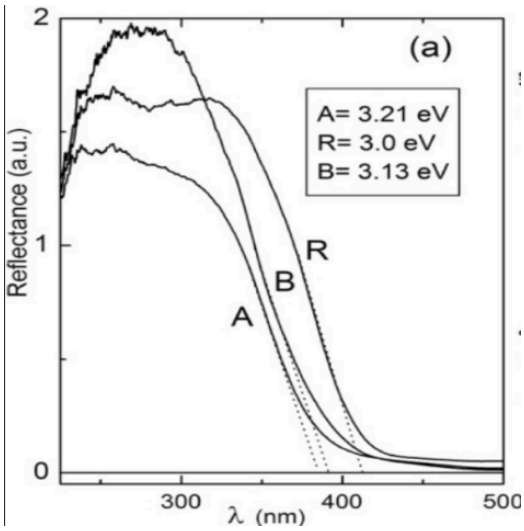

Figure 2. Reflectance of Rutile (R), Brookite (B), and Anatase (A) at Different Wavelengths of Light [1]

Beyond their intrinsic advantages in photoelectrochemical sensing, wide-bandgap metal oxides are also characterized by abundant raw material availability, relatively simple synthesis processes, and low cost, making them well-suited for large-scale production and practical applications. Various mature fabrication techniques, such as sol–gel methods, hydrothermal synthesis, and chemical vapor deposition, enable flexible control over their morphology and structure, thereby allowing performance optimization. This high degree of tunability provides an important foundation for their customized design in diverse application scenarios.

Most importantly, in the context of biological applications considered in this work, many metal oxides (such as TiO_2 and ZnO) exhibit good biocompatibility and low toxicity, enabling their safe use in biomolecular detection and medical diagnostics. This indicates that the application of such materials in biosensing is both feasible and highly promising. Moreover, their surfaces are readily amenable to functionalization, facilitating the immobilization of biomolecular recognition elements such as antibodies, enzymes, and nucleic acids, which in turn enhances the selectivity and specificity of the sensors.

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Nevertheless, it should be noted that wide-bandgap metal oxides still present certain limitations, including weak responsiveness to visible light and the persistence of photogenerated carrier recombination. Consequently, current research efforts are focused on strategies such as constructing heterojunctions, introducing defect states, and forming composites with narrow-bandgap materials to further improve their overall performance. These aspects will be discussed in greater detail in the latter part of this paper.

2.3. Core properties of semiconductor nanomaterials based on wide-bandgap metal oxides

Semiconductor nanomaterials based on wide-bandgap metal oxides inherit the intrinsic advantages of their parent materials while exhibiting a series of unique and essential characteristics arising from nanoscale effects. Among these, the nanoscale effect imparts a pronounced advantage in specific surface area. As the material dimensions decrease to the nanoscale, the surface-to-volume ratio increases significantly, thereby providing a larger number of active surface sites that facilitate the adsorption and immobilization of biomolecules such as enzymes, antibodies, and nucleic acids. This feature is of great importance for enhancing the sensitivity and detection efficiency of biosensors. Meanwhile, the increased surface activity also promotes interfacial reaction processes, thereby strengthening the output of photoelectrochemical signals. Another critical aspect is the quantum confinement effect that emerges at the nanoscale. When the material size approaches or becomes smaller than the exciton Bohr radius, its electronic band structure undergoes significant modifications, manifested as bandgap widening and energy level discretization. This effect not only enables the tuning of optical absorption properties but also optimizes the generation and separation behavior of photogenerated charge carriers, thereby improving photoelectrochemical response performance to a certain extent. In addition, nanostructuring effectively shortens charge transport pathways and enhances carrier separation efficiency. In conventional bulk materials, photogenerated electrons and holes are prone to recombination during transport. In contrast, nanostructured materials, owing to their reduced dimensions, significantly shorten carrier migration distances, thereby lowering the probability of recombination. Furthermore, by constructing one-dimensional (e.g., nanowires and nanorods), two-dimensional (e.g., thin films), or three-dimensional porous architectures, charge transport channels can be further optimized, leading to enhanced electron transport rates and overall photoelectric conversion efficiency.

It is also noteworthy that, as mentioned above, surface effects become dominant at the nanoscale. The surfaces of wide-bandgap metal oxide nanomaterials typically contain abundant defect states and unsaturated bonds, which can serve as active sites for photoelectrochemical reactions while also providing favorable conditions for surface functionalization. Through surface modification—such as the introduction of functional groups or the loading of noble metal nanoparticles—the interfacial properties of the materials can be significantly improved, thereby enhancing the selectivity and sensitivity of the sensors.

Moreover, wide-bandgap metal oxide nanomaterials exhibit excellent compatibility in the construction of composite structures, offering extensive possibilities for further research and broader applications. By forming heterostructures with narrow-bandgap semiconductors, conductive polymers, or carbon-based materials (such as graphene), it is possible to effectively broaden the spectral response range and promote the separation and transport of photogenerated charge carriers. Such composite strategies provide an important pathway for overcoming the intrinsic limitations of single-component materials and represent a major focus of current research efforts.

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3. Applications of monms in photoelectrochemical biosensing technology

3.1. Fundamental principles of photoelectrochemical biosensors

The fundamental structure of a photoelectrochemical (PEC) biosensor can generally be simplified as consisting of a light source, electrodes, a photosensitive material, a biorecognition unit, an electrolyte, and a charge carrier transport system. As shown in Fig. 3(b), since PEC biosensors require a stable potential, a three-electrode configuration is typically employed, comprising a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). Among these, the working electrode is primarily responsible for interacting with the target analyte.

This configuration effectively minimizes the influence of solution resistance on the measurement, reduces signal distortion, and, due to the absence of current flow through the reference electrode, provides a stable reference potential, thereby improving measurement accuracy. When light emitted from the source irradiates the photosensitive material on the working electrode, electrons in the valence band (VB) absorb photon energy and are excited to the conduction band (CB), generating electron–hole pairs (see Fig. 3(a)). These photogenerated charge carriers, upon reaching the surface of the photosensitive material, participate in redox reactions with electroactive species in the electrolyte, producing a photocurrent that can be detected by an external detector. By analyzing the electrical signal obtained from the detector, quantitative determination of the concentration or presence of target biomolecules in the sample can be achieved.

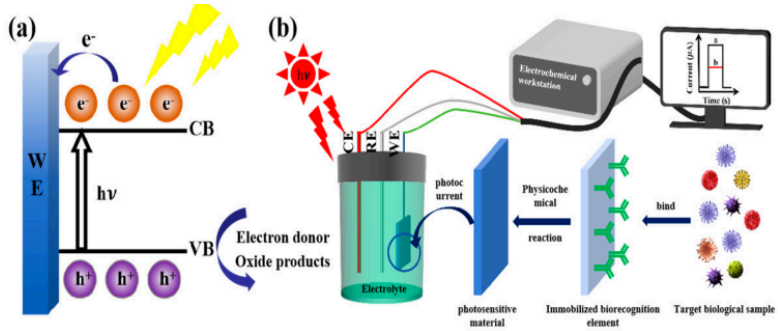

Figure 3. (a) Energy band diagram, (b) schematic illustration of the PEC biosensor [2]

Photoelectrochemical (PEC) biosensors can be broadly classified using two approaches: based on the target analyte and based on the recognition process, as illustrated in Fig.4.

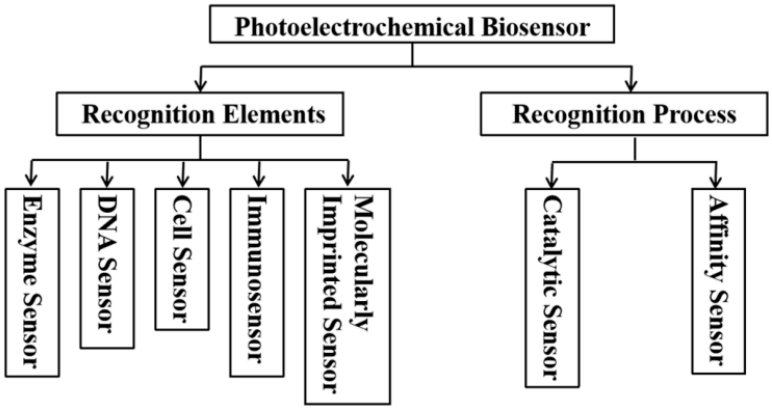

Figure 4. Diagram of the classification system of PEC biosensors [2]

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3.2. Advantages of photoelectrochemical biosensors based on semiconductor nanomaterials using wide-bandgap metal oxides as the substrate

The integration of metal oxide semiconductor nanomaterials with photoelectrochemical biosensors is primarily reflected in the photosensitive material distributed on the working electrode. Considering the strong chemical stability, excellent resistance to photocorrosion, relatively high electron mobility, and low cost of metal oxide semiconductor nanomaterials (MONMs), employing them as photosensitive materials to perform the processes described in Section 3.1 can significantly enhance both the operational efficiency and service lifetime of the sensors.

Metal oxide nanoparticles can be effectively immobilized onto the working electrode through various methods, including physical adsorption, electropolymerization, covalent bonding, and electrodeposition. Figure 5 illustrates in detail the functional mechanism of metal oxide nanomaterials as photosensitive materials in electrochemical analyte detection. In this context, the carbonaceous matrix and the metal oxide nanomaterials jointly interact with the analyte, ultimately generating a cyclic voltammogram that reflects the proportion of specific biomolecular components present in the analyte.

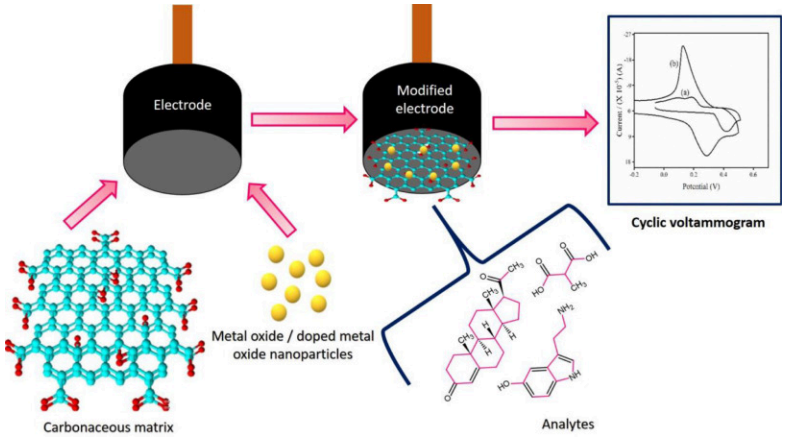

Figure 5. Characteristics of different MONMs in biosensing applications [3]

Table 1 presents the distinctive characteristics and applicable targets of various widely used typical metal oxides. Although these materials share the common properties of metal oxides discussed above, their differing responses to specific wavelengths of light make each metal oxide more suitable for particular research targets. This also highlights another advantage: by selecting different metal oxides for different analytes and biological components, a broad range of research objectives can be effectively covered, thereby significantly expanding the scope of experimental investigations.

Table.1 The characteristics of different metal oxides in biosensing applications [3]

MONMs	TiO_2	SnO_2	Fe_3O_4	CeO_2	SiO_2	ZrO_2	NiO	ZnO
IEP	3.9-8.2	4.5-5.0	6.7	6.7-9.5	1.7-3.0	4-11	10.7	9.5
PZC at pH 7.6	6.4	4	7.2	7.8	1	5.8	11.4	9.6

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Table 1. (continued)

ξ-zeta potential (mV) at pH 7.6	−25.8 ± 0.5	−40.5 ± 1.7	−29.1 ± 3.0	−4.2 ± 0.6	−38.1 ± 0.8	−32.3 ± 2.0	17.2 ± 0.2	23.5 ± 0.7
Bandgap (eV)	3.1	3.67	3.1	3.19	8.76	5-7	3.6-4.0	3.37
Features	Biocompatible, photocatalysis, wide bandgap	Low working potential, electron transfer	Superparamagnetic and affinity with oxygen atom of proteins	Biocompatible, fast electron transfer	Biocompatible, photocatalysis, wide bandgap	Biocompatible, binding with phosphorous atom of DNA	High adsorption, electron transfer	Biocompatible, fast electron transfer, nanomorphology
Target	ChOx, GOx, lipase, HRP, IgG, and DNA	ChOx, GOx, lipase, IgG, and DNA	ChOx, GOx, Urs, IgG, and DNA	ChOx, GOx, lipase, HRP, IgG, and DNA	ChOx, GOx, lipase, HRP, IgG, and DNA	ChOx, GOx, lipase, HRP, IgG, and		

3.3. Frontier applications of photoelectrochemical biosensors

Taking TiO_2 as an example, it is a highly representative metal oxide nanomaterial. In addition to the general properties discussed above, TiO_2 exhibits several unique advantages, including exceptionally high catalytic efficiency, a high redox potential, and strong adsorption capability.

In general, to apply TiO_2 in sensor fabrication, it can be obtained by washing sodium titanate nanotubes with a diluted hydrochloric acid (HCl) solution (0.1 mM). The specific preparation process and corresponding chemical reactions are as follows [4]:

$[TiO_2]$nanoparticle+2NaOH→2Na++TiO_{2-3}+H_2O

2Na++TiO_{2-3}→$[Na_2TiO_3]$nanosheets

$[Na_2O_3]$nanotubes→$[Na_2TiO_3]$nanotubes

$[Na_2TiO_3]$nanotubes+2HCl(dil)→$[TiO_2]$nanotubes+2NaCl+H_2O

In practical applications, TiO_2-based electrochemical biosensors have been widely employed for the detection of various biomolecules, such as uric acid, cholesterol, and viral proteins, demonstrating excellent performance including rapid response, low detection limits, and wide linear ranges. However, it should be noted that the use of metal oxides alone still presents limitations in terms of detection accuracy and target scope. With ongoing technological advancements, numerous researchers have identified a more effective strategy: constructing heterojunctions by combining metal oxides with other semiconductors or carbon-based materials. This approach can significantly enhance redox reaction efficiency and overall sensor performance.

For example, in a study by Khaliq et al., titanium dioxide nanotubes (TNTs) were fabricated via anodization of titanium foil, followed by the deposition of cuprous oxide (Cu_2O) nanoparticles onto their surface using a chemical bath deposition method. The resulting electrode exhibited high sensitivity toward cholesterol oxidation. Compared with the pristine electrode, the sensitivity of this composite electrode increased by five times, reaching 6034.04 $\mu A \cdot mM^{-1} \cdot cm^{-2}$. The limit of

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detection (LOD) and response time were 0.05 μM and 3 seconds, respectively. This study demonstrates that TNTs modified with Cu_2O nanoparticles can be used to fabricate stable, reusable, and selective biosensors.

3.4. Effect of heterojunctions on the performance of photoelectrochemical biosensors

As discussed above, heterojunctions play a crucial role in enhancing sensor performance. In this section, the construction of heterojunctions and their performance improvement mechanisms will be investigated in detail.

A heterojunction is a composite structure formed at the interface between two or more semiconductor materials with different band structures. Its fundamental function lies in regulating the band alignment to achieve efficient separation and transport of charge carriers, thereby significantly improving photoelectric or electrochemical performance. When two semiconductor materials come into contact, differences in their Fermi levels lead to a redistribution of electrons at the interface until thermodynamic equilibrium is reached. During this process, electrons migrate from the side with a higher Fermi level to the side with a lower one, resulting in the formation of a space charge region and the establishment of a built-in electric field near the interface. This built-in electric field provides the driving force for the subsequent separation of photogenerated charge carriers.

Under illumination, semiconductor materials absorb photon energy, causing electrons in the valence band (VB) to be excited to the conduction band (CB), thereby generating electron–hole pairs. Due to the band alignment differences at the heterojunction interface, these photogenerated carriers undergo directional migration under the influence of the built-in electric field, leading to effective spatial separation (see Fig.6).

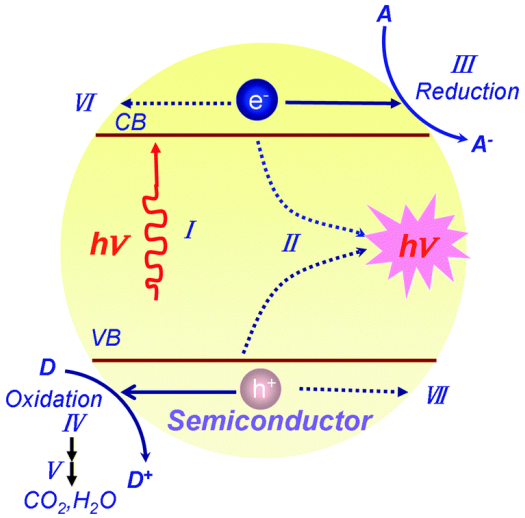

Figure 6. Detailed schematic diagram of the principles of semiconductor-catalyzed redox reactions

According to different band alignment configurations, heterojunctions can generally be classified into the following typical types:

Type I (straddling gap) heterojunction: both electrons and holes tend to migrate into the same material, which is suitable for light-emitting devices but unfavorable for charge separation;

Type II (staggered gap) heterojunction: electrons and holes migrate into different materials, achieving spatial separation, and is the most commonly used structure in photoelectrochemical and

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biosensing applications;

Z-scheme heterojunction: mimicking natural photosynthesis, this structure preserves high-energy electrons and holes, maintaining strong redox capability while achieving charge separation.

For photoelectrochemical biosensors, Type II and Z-scheme structures are particularly important. In Type II heterojunctions, the material with a lower conduction band acts as an electron acceptor, while the material with a higher valence band serves as a hole acceptor, thereby significantly reducing electron–hole recombination. In Z-scheme systems, although some low-energy carriers recombine, the remaining high-energy electrons and holes exhibit stronger reduction and oxidation abilities, which enhances interfacial reaction activity. In practical systems, constructing composite heterostructures by introducing narrow-bandgap semiconductors or conductive materials (such as carbon-based materials) can further broaden the light absorption range and enhance photoresponse performance.

Carbon was initially employed as a support for TiO_2 in photodegradation studies. Its exceptionally large specific surface area, together with its intrinsic properties, endows it with strong adsorption capability, enabling the adsorption of a greater amount of pollutants and thereby enhancing reaction efficiency when applied in sensors. Among various carbon structures, carbon nanotubes have been identified as possessing the largest specific surface area and the greatest potential for improving sensor performance.

In addition, carbon nanotubes exhibit metallic conductivity, and their substantial electron storage capacity allows them to accept photogenerated electrons, forming hybrid or nanocomposite structures that can delay or suppress charge recombination. It is therefore evident that constructing a heterojunction by combining such materials with Ti O_2 can effectively compensate for the limitations associated with using TiO_2 alone as a photosensitive material. Therefore, we can understand this compound as an extremely effective behavior of amplifying electrical signals. Hoffmann et al.proposed a mechanism to explain the enhancement of the photocatalytic properties of Ti O_2 –CNT composites(see Fig.7). A high-energy photon excites an electron from the VB to the CB of anatase Ti O_2 . Photogenerated electrons formed in the space-charge regions are transferred into the CNTs until the Fermi levels of the Ti O_2 and that of the CNTs are on the same level, and holes remain on the Ti O_2 to take part in redox reactions.

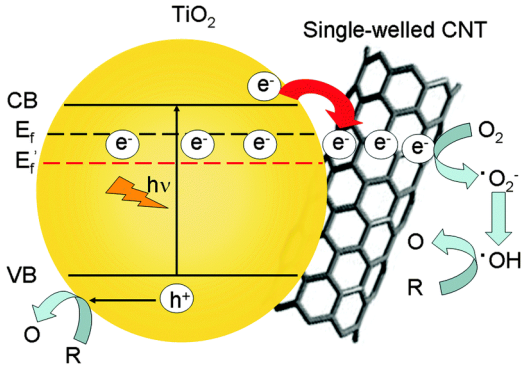

Figure 7. Working principle of the heterojunction formed by titanium dioxide and carbon nanotubes [5]

4. Conclusion

In conclusion, wide bandgap metal oxide nano-semiconductor materials have developed rapidly in the field of photochemical biosensors. The current development direction has shifted to forming

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heterojunctions by combining more diverse metal oxides or other semiconductor materials with high conductivity materials to conduct more efficient scientific research activities. However, it should be noted that merely using metal oxide nano-materials has already demonstrated increasing limitations, and the formation of heterojunctions is also limited by cost and the complex manufacturing process. This field still requires much effort to seek more convenient, efficient, and cost-effective solutions for further development. This study can be improved by incorporating more experimental validation, quantitative modeling, and advanced characterization techniques to support its conclusions. Additionally, deeper exploration of charge transfer mechanisms in complex heterojunctions and real-world application conditions like long-term stability and large-scale manufacturability is needed. Future research should focus on enhancing visible light utilization, charge separation efficiency, and sensor selectivity. Integration with portable devices for real-time detection and improving biocompatibility and stability in practical applications are also key areas for further exploration. Advanced techniques like in situ characterization, machine learning, and multi-scale simulations can help optimize sensor performance.

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