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The research on photocatalytic semiconductor materials

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Abstract. A requirement for energy availability and environmental pollution control represents two critical challenges that necessitate immediate resolution. Among the multitude of alternative energy sources, solar green energy emerges as a distinct leader. Semiconductor materials are widely used in many fields of photocatalysis. Contaminant degradation and energy conversion using photoresponsive semiconductor materials. Furthermore, the creation of efficient photocatalysts is of paramount importance. In this paper, the basic principle of photocatalytic semiconductor and the whole process of photocatalytic reaction are introduced in detail. The process of photocatalytic reaction basically includes three stages, and the modification of photocatalytic semiconductor materials are also reviewed. In order to give full play to the excellent properties of semiconductor materials, optimizing the synthesis technology according to the different distribution of doping concentration is the main aspect of future research. It has been extensive used as a treatment of organic pollutants, photocatalytic water splitting and carbon dioxide reduction.

1 Introduction

Due to the rapid growth of global economy, environmental pollution and energy crisis are becoming more and more serious. The extensive utilization and exacerbated exploitation of fossil fuels are posing severe detrimental effects on both the earth's environmental integrity and human wellness. In an endeavor to foster a green economy and catalyze sustainable progression, it is of paramount urgency to discover novel materials, alternative energy sources, and avant-garde technologies to rectify these predicaments. Photocatalytic technology is the use of solar energy as a catalyst to decompose waste water and waste gas. High decomposition efficiency , no secondary pollution,and easy to use are the advantages of photocatalytic technology. Developing photocatalysts that are cost-effective, environmentally friendly, visible light responsive, high reactivity and good durability is a major challenge for solar hydrogen production.

Early research in photocatalysis development of photocatalysts based on metal oxide semiconductors. In 1972, Fujishima and Honda [1] published a famous article, which triggered a real revolution, and subsequently titanium dioxide (TiO_2) was widely used as a

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photocatalyst for various reactions. Since then, academic and industrial interest in such semiconductors has grown exponentially. During this time, titanium dioxide photocatalysts have been successfully applied to many reactions, including hydrogen production, wastewater purification, sterilization, and organic synthesis.

Inorganic semiconductor materials such as carbon materials, nitrides, phosphates and single atom catalysts are also used in the field of photocatalysis. Organic semiconductors have attracted wide attention because they can connect different functional groups and have adjustable band gaps and band positions. Common organic semiconductor photocatalytic materials include COFs, MOFs, CPs and ZIFs.

In this paper, the basic principle of semiconductor photocatalysis, the modification and optimization of photocatalytic semiconductor materials, semiconductor materials and their photocatalytic applications will be reviewed.

2 Basic principles of semiconductor photocatalysis

Semiconductors are characterized by their discontinuous energy band structure, which is attributed to the discontinuous value of electron energy. The conduction band (CB) of a semiconductor corresponds to the highest energy level, while the valence band (VB) represents the lowest energy level [2, 3]. Subsequent to the acquisition of an adequate energy supply, electrons are capable of transitioning from the Valence Band (VB) to the Conduction Band (CB). Consequently, vacancies or holes are generated within the VB, thereby effecting the differentiation of electrons and holes. The minimal energy required for an electron transition corresponds to the energy discrepancy between the apex of the valence band and the base of the conduction band, which is denoted as the band gap (Eg) [2-4]. Concurrently, the width of the bandgap in semiconductor materials is inextricably linked to the threshold for light absorption, and this relationship can be expressed mathematically as follows: λ(nm) =1240/Eg (eV) [5]. Therefore, a larger band gap means a smaller light absorption threshold and a higher REDOX potential of the corresponding photogenerated electron-hole. The whole process of photocatalytic reaction basically includes three stages.

2.1 Light absorption and charge carrier production

When the light of no less than the semiconductor band gap energy shines on the photocatalytic surface, the electron transition immediately occurs, and the photogenerated electron hole (e^-h^+) pair is generated [5]. In general, light with wavelengths between 200-400 nm and 400-800 nm ranges is considered ultraviolet and visible light. Whenever the Eg of semiconductor is below about 3.1 eV, visible ligh can be absorbed and achieve efficient use of sunlight (The main component of sunlight is visible light, which accounts for about 50 %). As a result, the ideal photocatalyst must have the ability of efficient light absorption, which is a prerequisite for photocatalytic reactions.

2.2 Carrier separation and transfer

Electrons are transferred from the valence band to the conduction band, with holes being left behind in the valence band, resulting in the separation of electrons from holes. Nonetheless, the recombination of photogenerated electrons and holes is an inexorable process that impedes the utilization of charge carriers and diminishes the catalytic efficacy of the photocatalyst. Consequently, a multitude of strategies have been devised to enhance the efficiency of carrier separation and transport within photocatalysts, including minimizing particle size, managing surface imperfections, exposing accessible active sites, and augmenting specific surface area [6].

2.3 Corresponding reactants undergo surface REDOX reactions

Electrons with reducing capacity and holes with oxidizing capacity quickly transfer to the reaction site, triggering REDOX reaction on the surface of the photocatalyst. As shown in Fig.1., the potential applications of common REDOX reactions in the realm of photocatalysis are comprehensively reviewed, including processes such as hydrogen evolution and CO_2 reduction. Thermodynamically, it is imperative that the band structure of the semiconductor aligns with the REDOX reaction potentials, necessitating that the conduction band minimum (CB) energy level exceeds the reduction potential, while the valence band maximum (VB) energy level surpasses the oxidation potential. Consequently, an appropriate band structure serves as the thermodynamic foundation for facilitating photocatalytic reaction.

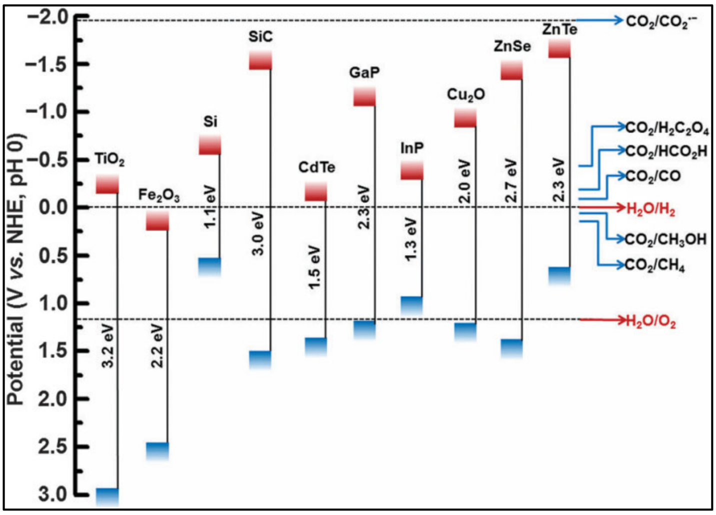

Fig. 1. Band structure diagram of common semiconductors [7].

3 Modification of photocatalytic semiconductor materials

Improving the separation efficiency of photogenerated carrier can improve the photocatalytic performance of semiconductor materials. This is usually achieved by building a built-in electric field. However, the construction of internal electric field in traditional heterojunction structures requires the matching of semiconductor energy levels, which is limited by many conditions. Another way to generate an intrinsic electric field is to construct an intrinsic electric field with a homojunction structure. Compared with heterojunction, homojunction can also effectively promote the separation of photogenerated carriers, and because only a single semiconductor material is required. Homojunction is easier to prepare, and has been applied in many fields such as solar cells and photocatalytic water decomposition to produce hydrogen [8].

3.1 Element doping technique

Doped elements with gradient concentration distribution are introduced into the semiconductor material (the concentration of doped elements gradually decreases or increases from the surface to the bottom surface), where different doping concentrations of foreign doped ions can change the position of Fermi level, so that Fermi level moves towards the valence band or conduction band. The contact of the same semiconductor with different doping concentrations causes band bending, which can create multiple homogeneous junction interfaces, which are distributed in a stepped band position, and thus accelerate the separation of photogenerated carriers. Homogeneous junction semiconductor materials constructed with different gradient doped ions and doping methods have made great progress in many fields [9].

3.1.1 Gradient doping of monmetallic elements

There are many kinds of metal elements used for gradient doping, among which Ti, Sn, W, Mg and Cu are widely used. The gradient doping of metal ions can change the transfer path of photogenerated carriers, effectively improve the charge transfer and thus change the catalytic effect. Metallic elements are easier to deposit gradients than non-metallic elements, and are easy to observe and not easy to decompose. Ti is the most widely used nitrogen metal element in gradient doping. The Ti element, employed in gradient doping, enhances the material's visible light absorption performance. The gradient distribution of Ti elements can also improve the charge separation ability of materials. Rasouli et al. [10] prepared gradient Ti-doped hematite photoanodes by liquid phase deposition. As shown in Fig. 2., it is confirmed that the composition of Ti elements is in gradient distribution, and the visible light absorption performance of the material is also significantly improved.

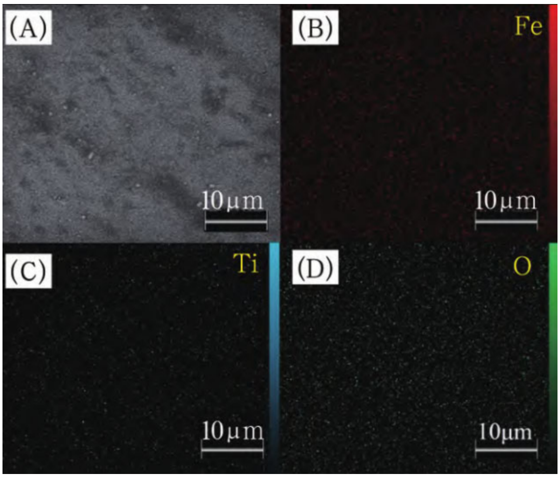

Fig. 2. SEM image of Ti gradient doping Fe_2O_3 [11].

3.1.2 Single nonmetallic element gradient doping

Gradient doping of nonmetallic ions can change the flat band potential of semiconductor materials, affect the change of valence band conduction position, and form a step distribution of energy band change inside the material, thus expanding the internal electric field range of photo-generated carrier separation. Nowadays, the non-metallic elements used as gradient doping include O, N, Cl, S, P and other elements, of which N and S are used more frequently. For instance, Wang et al. [9] prepared an N-gradient doped ZnO nanorods array (ZnO NRAs) for photoelectrochemical water decomposition. As shown in Fig. 3 ., the concentration of N element gradually rises along the vertical direction of ZnO NRAs, and the gradient distribution of N element is proved by SEM. The photocurrent density of lightly doped ZnO NRAs is about 2 orders of magnitude higher (160 μA·cm^{-2}) than that of undoped ZnO NRAs.

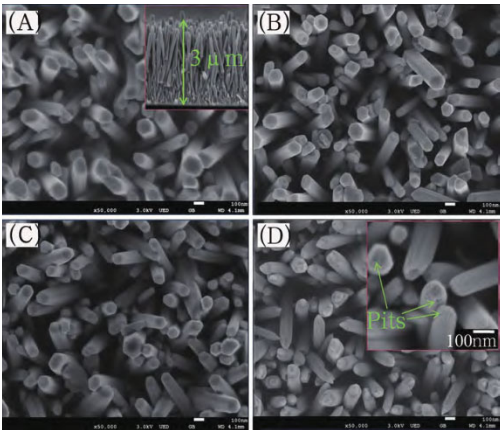

Fig. 3. SEM image of gradient N-doped ZnO [12].

3.1.3 Gradient co-blending of bimetallic elements

On the basis of single metal gradient doping, bimetal gradient co-doping is studied. Gradient co-doping usually involves gradient concentration doping at different interface positions. It is usually composed of transverse gradient diffusion and longitudinal gradient diffusion, which form the gradient concentration change of bimetal ion in the overall position. Relative to mono-metal doping. Bimetal gradient coblending can further promote charge separation and improve material properties [13].

3.1.4 Gradient co-blending of double nonmetallic elements

Non-metallic gradient coblending can not only further improve charge separation, but also enhance the conductivity and cycle stability of the material. For example, Sun et al. [14] prepared a N-P layer doped heterogeneous carbon material under a gradient electric field. DFT calculations show that N and P gradient co-doping can change the electrical structure of carbon materials, and induce the construction of gradient energy levels to form internal electric fields, thus enhancing the conductivity of MOF-derived carbon.

3.2 Making a heterojunction

Due to the limited diffusion range of the electron-hole pairs, the possibility of their recombination in the semiconductor is high, which greatly reduces the photocatalytic efficiency. The development of a heterojunction is identified as one of the efficacious approaches to augment the separation of photogenerated charges. Heterojunction refers to the interface between two semiconductor phases with different energy band structures. Based on the varying conductive properties of the two substances, heterojunctions may be categorized into homotype heterojunctions (such as P-p or N-n junctions) and heterotype heterojunctions (such as P-n or p-N junctions). Generally,the formation of heterojunctions is contingent upon the two semiconductors possessing analogous crystal structures, nearly identical atomic spacings, and comparable thermal expansion coefficients. Techniques such as interfacial alloying, epitaxial deposition, and vacuum evaporation may be employed to fabricate heterojunctions.

4 Semiconductor materials and their photocatalytic applications

4.1 Treatment of organic pollutants

Some organic matter is present in the environment and resists decomposition, which can lead to chronic poisoning and even cancer [15]. In 1976, Frankarnk and Bard successfully applied the technology to the degradation of pollutants in aqueous solutions. Subsequently, photocatalysts like titanium dioxide, zinc oxide, g-C_3N_4, cadmium sulfide have been widely studied in environmental treatment and energy applications. The composite of semiconductor photocatalytic materials can effectively improve the efficiency of solar energy utilization and quantum efficiency.

4.2 Photocatalytic water splitting

In recent years, the use of semi-conductive photocatalysts to decompose water to produce hydrogen has attracted extensive attention and research because of its low cost and great potential for clean hydrogen production. When the energy of the light exceeds or is equal to the bandgap of the semiconductor material, electron transitions occur within the semiconductor, resulting in the generation of holes in the valence band and the accumulation of electrons in the conduction band. The electrons are separated from the holes to reduce water to hydrogen or oxidize water to oxygen in the valence and conduction bands of the semiconductor. Photocatalytic water splitting production is an effective strategy to solve the growing energy and environmental problems[16].

4.3 Carbon dioxide reduction

Photocatalysis technology is considered to be one of the most advantageous and cleanest methods for converting carbon dioxide. The use of sunlight and photocatalytic materials to reduce the impact of the greenhouse effect, but also provide hydrocarbon fuel, thereby solving the problem of energy shortage.

5 Conclusion

Using solar energy as energy drive, semiconductor composite materials can achieve photocatalytic hydrogen production and photocatalytic CO_2 reduction reaction, which can cope with the increasingly serious energy crisis and environmental pollution problems such as greenhouse effect. The whole process of photocatalytic reaction basically includes three stages: light absorption and carrier generation, carrier separation and transfer, and surface REDOX reaction of corresponding reactants. The modification of photocatalytic semiconductor materials can be optimized by constructing homojunction structure and heterojunction structure through semiconductor gradient doping technology. Semiconductor materials and their photocatalytic applications, including the treatment of organic pollutants, photocatalytic water splitting, and carbon dioxide reduction. Photocatalysis to reduce CO_2 and convert CO_2 into carbon-based fuels is an attractive way to reduce the greenhouse effect and provide sustainable energy. Photocatalytic materials bring more possibilities and opportunities for future development. This paper lays the foundation for a wider application of semiconductor materials.

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