Research progress of semiconductor photocatalysis applied to environmental governance

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Abstract. A review of the current research situation of semiconductor photocatalysis at home and abroad, and a brief analysis of the existing problems and future development trends. Listed some of the achievements of photocatalysis research in the past 30 years, covering the research of photocatalysis mechanism, the application research of photocatalysis technology in the environmental field, and the contemporary problems of photocatalysis technology, etc. from basic to applied research.

Keywords: Semiconductor Photocatalysis; Environmental Pollution Control.

1. Introduction
A lot of pollution has been generated in the process of industrialization, and it is urgent to solve the problem of environmental pollution. Today environmental pollution treatment methods include adsorption methods, biological treatment, and membrane separation processes. Among them, semiconductor photocatalysis is an efficient, clean and environmentally friendly technology, which is one of the methods with great application prospects.

In 1972, Fujishima and Honda discovered the phenomenon of single-crystal TiO$_2$ electrode photocatalytic water splitting, which opened the era of semiconductor photocatalysis [1]. They designed an electrolyzed water device with n-type semiconductor TiO$_2$ electrode as anode and platinum black electrode as cathode. When ultraviolet light with a wavelength of less than 450 nm irradiates the anode, it can be seen that oxygen is released at the anode and hydrogen is released at the cathode. In 1997, Wang et al. discovered that TiO$_2$ coated glass with super-hydrophilicity has self-cleaning properties [2]. M Halmann [3] used the principle of photocatalysis to reduce CO$_2$ to CH$_3$OH, HCOH and other organic matter, which caused people to think about the application of photocatalysis in the field of environmental governance. For decades, semiconductor photocatalysis has developed rapidly. Shahed et al. chemically modified the n-type semiconductor TiO$_2$ by controlling the combustion of titanium in a natural gas flame to increase the maximum light conversion efficiency [4]. Chen et al. proposed to increase the degree of disorder of the surface layer of nano-phase TiO$_2$ through hydrogenation, thereby increasing the solar absorption efficiency [5]. Semiconductor photocatalysis has gradually been widely used in environmental protection, medical, chemical, biological and other application.
2. Principle of photocatalysis

2.1. Principle of photocatalysis

![Diagram of photocatalysis](image)

Fig. 1 Primary steps in the photoelectrochemical mechanism: (1) formation of charge carriers by a photon; (2) charge carrier recombination to liberate heat; (3) initiation of an oxidative pathway by a valence-band hole; (4) initiation of a reductive pathway by a conduction-band electron; (5) further thermal (e.g., hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products; (6) trapping of a conduction-band electron in a dangling surficial bond to yield Ti\(^{III}\); (7) trapping of a valence-band hole at a surficial titanol group [6].

At present, it is generally believed that there are seven primary steps in the photoelectrochemical mechanism[6].

(1) charge-carrier generation, that is, after light excitation, electrons in the valence band transition to the conduction band, and at the same time, an equal amount of holes are generated in the valence band, and the reaction process is:

\[
\text{TiO}_2 + \text{hv}(E \geq E_{bg}) \rightarrow h^+_v b + e^+_c b \quad (1)
\]

(2) charge-carrier recombination, and the reaction process is:

\[
e^+_c b + \{≡\text{Ti}^{IV} \cdot \text{OH}·\}^+ \rightarrow \text{Ti}^{IV} \cdot \text{OH} \quad (2)
\]

\[
h^+_v b + \{≡\text{Ti}^{III} \cdot \text{OH}\} \rightarrow \text{Ti}^{IV} \cdot \text{OH} \quad (3)
\]

where \(≡\text{TiOH}\) represents the primary hydrated surface functionality of \(\text{TiO}_2\), \(e^+_c b\) is a conduction-band electron, \(h^+_v b\) is a valence-band hole, \(\{≡\text{Ti}^{IV} \cdot \text{OH}·\}^+\) is the surface-trapped VB hole, \(\{≡\text{Ti}^{III} \cdot \text{OH}\}\) is the surface-trapped CB electron.

(3) At the Ti (IV) site, a CB electron is trapped to produce Ti(III) and the reaction process is:

\[
e^+_c b + \text{Ti}^{IV} \cdot \text{OH} \rightleftharpoons \{≡\text{Ti}^{III} \cdot \text{OH}\} \quad \text{shallow trap} \quad (4)
\]

\[
e^+_c b + \text{Ti}^{IV} \rightarrow \{≡\text{Ti}^{IV} \cdot \text{OH}·\}^+ \quad \text{deep trap} \quad (5)
\]

The dynamic equilibrium of eq 4a represents a reversible trapping of a conduction-band electron in a shallow trap below the conduction-band edge such that there is a finite probability that \(e^+_c\) can be transferred back into the conduction band at room temperature.

(4) The surface titanium alcohol group traps valence-band holes, which can exchange charge and energy with substances adsorbed on the surface of the semiconductor material to produce strong oxidizing active substances, such as \(\cdot \text{OH}, \text{H}_2\text{O}_2, \text{O}_2\), etc. These substances directly participate in the reduction oxidation reaction of decomposing organic matter, and the reaction process is:

\[
h^+_v b + \text{Ti}^{IV} \cdot \text{OH} \rightarrow \{≡\text{Ti}^{IV} \cdot \text{OH}·\}^+ \quad (6)
\]

(5) The valence-band holes participate in the initial oxidation reaction, and the reaction process is:

\[
\{≡\text{Ti}^{IV} \cdot \text{OH}·\}^+ \rightarrow \text{Red} \rightarrow \text{Ti}^{IV} \cdot \text{OH}^+ \text{ Red} \cdot \quad (7)
\]

(6) The CB electrons participate in the initial reduction reaction, and the reaction process is:

\[
e^+_c b + \text{O}_x \rightarrow \text{Ti}^{IV} \cdot \text{OH}^+ \text{ O}_x \cdot \quad (8)
\]

(7) Further thermodynamic and photocatalytic reactions produce mineralized products.
2.2. Photocatalytic materials

In 1972, the main process of single-crystal TiO$_2$ electrode photocatalytic water splitting discovered by Fujishima and Honda was that after the semiconductor TiO$_2$ electrode was exposed to ultraviolet light, photoproduction electron-hole pairs were generated, and these carriers further participated in the electrolysis process of water [1].

At present, the semiconductor materials used in photocatalysis mainly have the following five categories:

1. Metal oxides represented by TiO$_2$, WO$_3$, etc. TiO$_2$ has become the most studied photocatalyst due to its stable chemical properties, high catalytic activity, safety, non-toxicity, and environmental friendliness. Wan-Kuen et al. found that according to the principle of TiO$_2$ photocatalysis, the content of the main aromatic volatile organic compounds in the car can be degraded to almost zero in the range of air humidity [7].

2. The metal sulfide represented by MOS$_2$ [8]. MOS$_2$ is a two-dimensional layered structure material. When it consists of multiple layers and becomes a single layer, the forbidden bandwidth becomes wider, and the optical and electrical properties change accordingly.

3. Ag-based photocatalyst represented by Ag$_3$PO$_4$ and so on. Such materials have excellent light response performance, but are susceptible to photo-corrosion, so they often improve stability by building heterostructures [9].

4. g-C$_3$N$_4$ photocatalyst. The catalyst can respond under visible light, has good chemical stability and thermal stability, and its morphology can be adjusted. Wang et al. reported the photocatalytic hydrogen production performance of g-C$_3$N$_4$. The experiment found that g-C$_3$N$_4$ also has the activity of reducing water to H$_2$ or oxidizing water to O$_2$ even if noble metal promoter is used [10].

5. Metal organic framework materials (MOFs) [11]. The material has the characteristics of high specific surface area, multiple active sites, structure tailoring, and easy functionalization, etc. It has broad application prospects in the field of semiconductor photocatalysis.

2.3. Influencing factors of photocatalysis

The semiconductor photocatalytic reaction is a multiphase reaction system consisting of a series of complex surface physical and chemical processes, and many factors may affect it.

1. The energy band structure of the photocatalyst essentially determines the reaction process. The oxidation-reduction capacity of the photocatalyst depends on the position of the conduction band and the valence band, and its photo-responsiveness depends on the forbidden bandwidth. For example, anatase TiO$_2$ has a forbidden bandwidth of 3.2 eV and has photocatalytic properties only under ultraviolet light.

2. The size of the photocatalyst, the crystal facet exposed on the surface, the crystal structure, crystal defects and other crystal structures affect the reaction. O.cap et al. proposed that compared with rutile TiO$_2$, anatase TiO$_2$ has lower electron mobility, lower density, and lower dielectric constant [12]–[15].

3. System pH. Different organic substances have different pH in solution, and the similarities and differences between the charge and the surface charge of the catalyst directly affect the adsorption performance and subsequent catalytic degradation. S. Sakthivel et al. found that the amphoteric behavior of semiconductor oxides affects the surface charge of the photocatalyst, thereby affecting the catalytic performance. The photodegradation rate of TiO$_2$ increases with the decrease of pH, while the photodegradation rate of ZnO reaches at pH=10. Peak [16].

3. Application of photocatalysis technology in environmental governance

3.1. Self-cleaning film

In 1997, Wang et al. found that after ultraviolet light irradiated TiO$_2$, the surface of the material would show a microstructure of hydrophilic phase and lipophilic phase, thus making anti-fog and self-cleaning TiO$_2$ coated glass[2]. The water contact angle of this kind of glass before ultraviolet light irradiation is 72°±1°, and after ultraviolet light irradiation, the water contact angle is reduced to 0°±1°. Takeuchi et
al. proposed a structural model of H$_2$O clusters composed of multilayer H$_2$O molecules adsorbing TiO$_2$ solid surface, as shown in Figure 2 [17]. H$_2$O molecules chemically adsorb on the surface of TiO$_2$ (such as surface cations or surface hydroxyl groups) to form a single H$_2$O molecular layer; H$_2$O molecules connected by hydrogen bonds are physically adsorbed to form a multi-molecular layer (as shown in S1, S2, S3); H$_2$O molecules without active hydrogen bonds cover the polymer chain H$_2$O molecules, forming the shell of H$_2$O clusters (S0 in the picture). The polymerized chain H$_2$O molecules are called "hydrogen-bonded water", and the water molecules without hydrogen bonding in the outermost shell are called "free water".

![Fig. 2](image)

**Fig. 2** (a) Two H$_2$O molecules interact through hydrogen bonds. (b) Composition model of different numbers of H$_2$O molecules. (c) Structural model of H$_2$O clusters adsorbed on a solid surface [17]

R. Molinari et al. used TiO$_2$ Degussa P25 catalyst to degrade Congo Red and Patent Blue in a photocatalytic membrane reactor, and they found that the degradation rate of immersing a UV lamp in a dye solution was about 50 times that of an external UV lamp[18]. Djafer et al. used commercial TiO$_2$ hydrosol and Al$_2$O$_3$ carrier to prepare a photocatalytically active TiO$_2$ film, which directly couples separation and photocatalytic degradation and can effectively achieve the degradation of smaller organic molecules [19]. CP Athanasekou used chemical vapor deposition to prepare a composite TiO$_2$ photocatalytically ultrafiltration membrane. Both sides of the membrane were covered with TiO$_2$ photocatalyst[20]. The experiment found that on both sides Under ultraviolet light, the common cross-flow membrane operation mode doubles the degradation of pollutants such as methyl orange.

### 3.2. Air purifications

Currently, one of the main pollutants in the air is Volatile Organic Compounds (VOCs), which mainly come from industrial emissions, urban public facilities, and agricultural and animal husbandry emissions, etc. VOCs have a wide range of pollution and difficult treatment. As an emerging pollution treatment technology, photocatalysis has been widely favored.

Takeda et al. loaded TiO$_2$ on zeolite, Al$_2$O$_3$, SiO$_2$ and other inert carriers to perform photocatalytic decomposition of gaseous propionic aldehyde [21]. Experiments have found that the carrier can remove pollutants in the atmosphere through adsorption, thereby increasing the photodegradation rate. C.H.Ao et al. loaded TiO$_2$ material on activated carbon AC to degrade SO$_2$ and NO$_2$[22]. When SO$_2$ is present, TiO$_2$/AC has a 10% increase in NO conversion rate compared with TiO$_2$ alone; at the same time, AC can inhibit water vapor pollution. Therefore, in a high-humidity environment, it is feasible to remove many pollutants in indoor air at the ppb level. Irokawa Y et al. studied the photodegradation efficiency of N-doped TiO$_2$(TiO$_2$,N$_x$) photocatalyst to toluene[23]. Under visible light irradiation, toluene is first
oxidized to benzaldehyde, and then organics such as carboxylic acid and aldehyde are formed. Finally, it gradually degrades into CO$_2$ and H$_2$O. Li et al. reported a zinc-imidazolate MOF (ZIF-8) composite film [24]. The air purifier prepared by the film, as shown in Figure 3, has a particulate matter removal rate of 97%.

3.3. Water purifications

The waste water, domestic sewage and agricultural sewage such as pesticides and fertilizers discharged from the pharmaceutical industry and other industrial fields contain a large number of difficult-to-degrade organic and inorganic pollutants, such as dyes, heavy metals, and pharmaceutical solutions. Traditional treatment methods, such as adsorption method, coagulation sedimentation method, biochemical method, etc., have low efficiency in degrading pollutants and are likely to cause secondary pollution. Photocatalytic technology does not cause secondary pollution when degrading pollutants and is environmentally friendly, which is a pollution treatment technology with broad application prospects.

Yu et al. used the dip-coating technique to prepare porous TiO$_2$ anatase coatings, which can decompose dimethyl-2,2-dichlorovinyl phosphate solution under visible light [25]. V. Kavitha et al. synthesized copper-doped TiO$_2$ nanoparticles by sol-gel method [26]. Under natural light, the degradation efficiency of 0.6%Cu-TiO$_2$ to rhodamine B aqueous solution can reach 97% within 180 minutes. Kamran et al. added the leaf extract of cestrum nocturnum to both the AgNO$_3$ solution and the TiO$_2$ suspension to prepare Ag/TiO$_2$ nanocomposite materials [27]. The degradation of methylene blue reached 90% within 40 minutes. The degradation mechanism is shown in Figure 4.

Inorganic pollutants are mainly heavy metal ion pollution. Zhang et al. developed a TiO$_2$ modified sewage sludge carbon[28]. The removal rate of mercury increased from 87 g/kg to 151 g/kg, and the removal rate of Hg$^{II}$ increases of pH. Srimala et al. prepared Cu-TiO$_2$ nanotubes by electrochemical anodic oxidation, which can degrade Pb$^{II}$ heavy metal ions by 97% [29].

4. Problems to be solved in the application of photocatalysis technology

The electron-hole pair recombination rate of photocatalytic semiconductor materials is relatively high, resulting in low photocatalytic activity and catalytic efficiency. Jung et al. prepared Au-doped ZnO flower-like photocatalysts, and realized the material's response to visible light through the surface
The plasmon resonance effect of Au atoms, which can quickly degrade methyl blue under natural light[30]. The photocatalytic reaction has low selectivity for the degradation of pollutants, and cannot effectively degrade low-content and highly toxic organic pollutants in water. The surface of the photocatalyst is modified to selectively adsorb target pollutants and selectively synthesize target substances. The structure of compound semiconductor materials can improve selectivity. When degrading liquid pollutants, the suspended photocatalyst has a large specific surface area, but it is difficult to recycle. The fixed photocatalyst is easy to separate solid and liquid, but the photocatalytic ability is weakened. The photocatalyst can be solved by constructing nano-magnetic powder or photoelectric combined catalysis. The contradiction between immobilization and catalytic performance.

5. Conclusions and prospects
Semiconductor photocatalysis technology has obvious advantages in the field of environmental governance, and has great application prospects in the fields of self-cleaning membranes, air purification, and water purification. At present, improving the efficiency of photocatalysis is still the key to the development of semiconductor photocatalysis technology. Future research should focus on the research of catalytic materials to promote the development and application of semiconductor photocatalysis technology.

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