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Research on the Application of Key Technologies for Environmental Governance and Resource Recycling

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Abstract. With the acceleration of urbanization and the increase of pollutant discharges in China, the pollution load of water body in many cities have exceeded the natural self-purification capacity of water bodies, resulting in the deterioration of water quality, or even the occurrence of black and odorous water bodies. The urban black and odorous water bodies, as current water environment issue in China, have aroused a strong public concern. In this paper, the origin and pollution source of black odor in water are analyzed from the aspects of point source, non-point source, endogenous and hydrodynamic conditions. Subsequently, the TiO_2/g-C_3N_5 composite photocatalytic material was prepared by hydrothermal method and high temperature calcination method. The results showed that the degradation rate of methylene blue (MB) reached 91.5%and the degradation rate of tetracycline hydrochloride (TCH) reached 92.4%in 105 min. The high degradation rate can be attributed to the effective combination of the introduced TiO_2 and g-C_3N_5 to form a heterojunction, with the excellent visible light response characteristics of g-C_3N_5, the photocatalytic performance is significantly improved.

Keywords. Urban black and odorous water body, pollution source, TiO_2, composite material, photocatalysis

1. Introduction

With the acceleration of industrialization and urbanization in developing countries, domestic and industrial wastewater has entered urban streams. If it is not treated or treated improperly, it will lead to serious ammonia nitrogen pollution in surface water [1]. Excessive ammonia nitrogen content in water bodies will cause eutrophication of urban river water bodies, resulting in seasonal or even year-round black and odorous water [2]. At the same time, excessive consumption of dissolved oxygen in water will also drastically deteriorate water quality [3]. The urban black and odorous water problem caused by ammonia nitrogen seriously affects the ecosystem structure and people's normal life, and is one of the environmental problems that the public is very concerned about.

The traditional methods for treating water pollution include ion exchange, oxidation-reduction, chemical precipitation, gravity sedimentation, coagulation, extraction, centrifugation and adsorption. However, these methods are not only high

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cost, high energy consumption and low efficiency, but also prone to secondary pollution [4-6]. Therefore, the development of high-efficiency, low-energy-consumption, and easy-to-operate methods to deal with water pollution has increasingly attracted social attention and attention. These methods include ultraviolet disinfection, sonication, and photocatalytic degradation. Among them, the photocatalytic degradation technology usually uses solar energy to degrade pollutants through photocatalytic reaction under the action of a specific photocatalyst, and this method has been considered as a sustainable development technology.

Since Fujishima and Honda [7] made the milestone invention of photoelectrochemical water splitting on TiO_2 electrode to generate hydrogen in 1972, a variety of new semiconductor photocatalytic materials have appeared one after another, such as TiO_2, $SrTiO_3$, g-C_3N_4, Fe_2O_3, etc [8,9]. Extensive research has been carried out in a variety of photocatalytic applications and great progress has been made. In particular, TiO_2 has the characteristics of strong redox ability, convenient source, low toxicity, good photochemical stability and environmental friendliness, and has been widely studied as a photochemical catalyst. However, TiO_2 has defects such as wide band gap, low response to visible light, and low mobility of photogenerated carriers, which limit the photocatalytic application of TiO_2 to a great extent. Therefore, it is of great practical significance to modify TiO_2 to enhance its photocatalytic degradation activity.

Photocatalytic technology uses solar energy to excite semiconductor photocatalysts and play a catalytic role. At this time, semiconductor photocatalytic materials play an important role in converting solar energy into chemical energy in the catalytic process. The characteristic of semiconductor materials is that the energy band is discontinuous, and the energy level has an unfilled region, and this region consists of a conduction band and a valence band. The valence band is filled with electrons, but the conduction band is empty. Usually what we call the forbidden band width (Eg) is the energy difference between the conduction band and the valence band. Different band gaps of semiconductor materials will also have certain differences, and the commonly used semiconductor band gaps are generally 1-4 eV. The size of the forbidden band width directly affects the light response range of the semiconductor. The smaller the forbidden band width of the semiconductor, the higher the light utilization rate. When light irradiates the surface of the semiconductor photocatalyst, if the incident light energy is higher than the band gap of the semiconductor, the electrons in the valence band will transition due to the excitation, and the electron transition to the conduction band is called photogenerated electrons (e-). The absence of electrons on the band will lead to holes in the valence band called photogenerated holes (h+), and the electrons and holes generated after illumination appear in pairs, so they can also be called photogenerated electron-hole pairs. The photogenerated electron-hole pair has strong reducing and oxidizing ability, which makes the adsorbed substances on the surface of the semiconductor photocatalyst undergo a deep redox reaction. Therefore, the photocatalytic reaction may convert harmful pollutants into harmless substances such as carbon dioxide and water, thus effectively solving some environmental pollution problems. The basic principle is shown in figure 1.

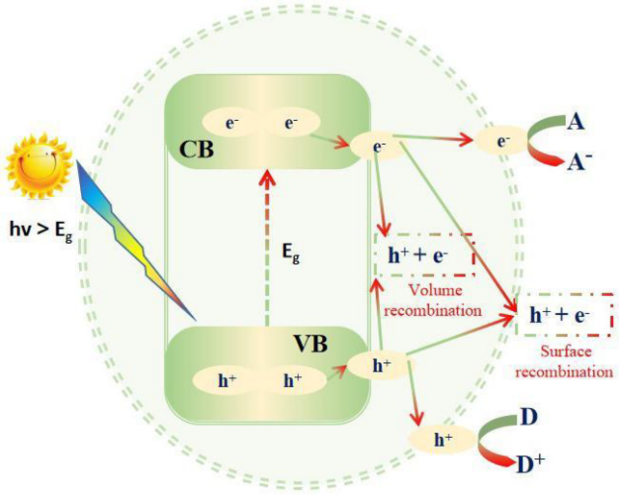

Figure 1. Schematic diagram of photocatalysis principle.

In order to achieve the objectives of water ecological and integrity restoration, low-carbon operation and environmental protection and pollution-free in the city, this study conducts field investigation on black and odorous water bodies in urban river basins, and analyzes the causes of black and odorous water bodies and pollution sources from the aspects of point source, non-point source, endogenous and hydrodynamic conditions; In addition, TiO_2 and g-c3n5 were coupled to form heterojunction by hydrothermal method and high-temperature calcination method, and TiO_2/g-C_3N_5 composite photocatalyst was synthesized to study its organic pollution degradation ability.

2. The Causes and Pollution Sources of the Black and Odorous Water Bodies

The causes of water body black and odor are complex. In essence, the pollution load of water body exceeds the self purification capacity of water body, which induces the water quality index to exceed the standard. It is found that the anaerobic decomposition of organic matter in water is the root cause of black and smelly water. When the concentration of oxygen consuming pollutants in the water body exceeds a certain range, the oxygen consumption rate of the water body will be greater than its reoxygenation rate, thus leading to hypoxia in the water body. In anoxic environment, organic matter is decomposed into H_2S, ammonia, thioether and other odorants under the action of microorganisms; At the same time, there are a large number of actinomycetes, algae and fungi in the water body, and their metabolism process will secrete a variety of alcohol odorants. The blackening substances in the water body are mainly ferrous metal sulfides such as FES and MNS formed by the reaction of metal ions such as Fe^{2+} and Mn^{2+} in the water with S^{2-} in the anoxic environment, and non-ferrous humus that can be dissolved in water. There are many reasons for the occurrence of black odor in water, and the overload pollution sources (external, internal and other pollution sources) are the main reasons.

2.1. External Pollution

A large number of pollutants (such as organic matter and ammonia nitrogen) are directly discharged into the water body, which is the main reason and the most direct reason for the black and odor of the water body. After the pollutants are discharged into the water body, the dissolved oxygen in the water is consumed, causing the concentration of dissolved oxygen in the water to decrease, and then decompose under the action of anaerobic bacteria and other microorganisms to produce black and smelly substances, resulting in black and smelly water. External pollution includes point source and non-point source pollution. Point source pollution is the most prominent pollution problem of black and smelly water bodies in cities. Its causes include: the rapid development of society and economy, many cities are facing development and construction, and the problem of insufficient collection capacity of urban industrial and domestic sewage has arisen, resulting in industrial and domestic sewage being directly discharged into the river without entering the sewage intercepting pipe network; Due to insufficient sewage treatment capacity, some cities have problems of direct sewage discharge or overload operation of sewage treatment facilities, resulting in substandard tail water flowing into the river; The rainwater and sewage hydration flow pipe network in the old urban area causes the overflow of the overflow outlet in the rainy season to pollute the river. The mixing and wrong connection of the rainwater and sewage pipes causes the sewage from the rainwater inlet to be discharged into the river in dry days. The initial rainwater of the diversion rainwater pipe is discharged into the river without effective control. The non-point source pollution sources of black and smelly urban water are relatively complex, mainly including: domestic and construction wastes randomly stacked on both sides of the river and garbage leachate discharged into the river with rainwater, causing pollution; Rainwater runoff pollution caused by rainfall scouring the surface, soil and pavement along the river; The loss of chemical fertilizer from agricultural farming along both banks of the river and the discharge of livestock and poultry breeding wastewater from individual farmers make a large number of nitrogen, phosphorus and other pollutants enter the water body with the rain, causing pollution.

2.2. Internal Pollution

Internal pollution is another important cause of black and smelly water. The organic matter, nitrogen and phosphorus pollutants in the polluted water body can be deposited in the sediment by precipitation or particle adsorption. However, under appropriate conditions, a large number of pollutants will be released from the sediment, and CH_4, H_2S and other gases will be generated, causing the water body to be black and smelly. In addition, aquatic plants in the water body can absorb pollutants, but if the plants are not harvested in time, they will release pollutants into the water body again after decomposition, increasing the concentration of pollutants in the water body.

2.3. Other Pollution

Hydrodynamic conditions are one of the factors that affect the blackness and odor of water bodies. When the ecological runoff of the water body decreases, the fluidity of the water body will become poor, and the water circulation of the water body will be poor, resulting in the decline of the reoxygenation ability, forming the hydrodynamic

conditions suitable for the rapid reproduction of blue-green algae, increasing the risk of algal blooms, and causing the deterioration of water quality and even the occurrence of Black odor phenomenon. Temperature is also one of the factors that affect the black and odor of water bodies. The increase in temperature will accelerate the rate at which microorganisms in the water body decompose algal residues into organic matter and pollutants such as nitrogen and phosphorus, resulting in a decrease in the concentration of dissolved oxygen and aggravating the black and odor of water bodies.

3. Experimental

3.1. TiO_2 Photocatalytic Materials

TiO_2 is available in three crystalline forms, brookite, anatase, and rutile, as shown in figure 2. In these three crystal phases, the valence band is formed by the overlapping of the 2p orbital of oxygen, and the lower part of the conduction band is formed by the overlapping of the 3d orbital of Ti^{4+}. The application of brookite in the field of photocatalysis is limited due to its poor stability and difficult synthesis. Compared with rutile-type TiO_2, anatase-type TiO_2 possesses higher photoactivity, which is attributed to the dominant facets of two different structures. Anatase is an excellent traditional photocatalyst due to the large number of insufficiently bound Ti atoms on the {001} planes. In addition, six O^{2-} ions surround Ti^{4+} ions, forming TiO_6 octahedra in these two polymorphic oxides. The two crystalline forms have different electron band arrangements and mass densities resulting in their structural differences, resulting in higher photocatalytic activity of Anatase than Rutile. However, the fast recombination rate of charge carriers limits the light-induced response in Anatase. More importantly, Anatase possesses a wide bandgap of 3.2 eV, making it less efficient for sunlight.

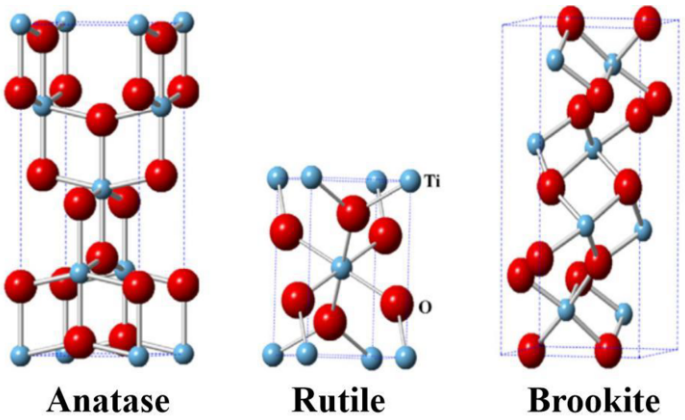

Figure 2. Schematic diagram of the crystal structure of TiO_2.

3.2. Preparation of TiO_2 Composite Material

TiO_2 was prepared by hydrothermal method. The specific scheme was as follows: solution A was prepared by dissolving 5mL of tetrabutyl titanate in 10mL of absolute ethanol. Mix 17.5mL of absolute ethanol, 2.5mL of deionized water and 7.5mL of

glacial acetic acid, add 0.05g of cetyltrimethylammonium bromide (CTAB), dissolve and stir for 30 minutes to prepare solution B. In the vigorously stirred solution B, solution A was slowly added dropwise, after 5 minutes of dropwise addition, stirring was continued for 30 minutes, and then the solution was subjected to ultrasonic vibration for 30 minutes under normal temperature and pressure to obtain a mixed solution. The mixed solution was then transferred to a 100 ml stainless steel autoclave lined with polytetrafluoroethylene and heated at 140℃ for 14h. After naturally cooling to room temperature, the reaction mixture was centrifuged, and the precipitate was washed several times alternately with deionized water and absolute ethanol. The prepared precipitate was fully dried in a drying oven at 80℃, and the obtained product was TiO_2.

Pour 1.5g of 3-amino-1,2,4-triazole into a covered alumina crucible, place the crucible in a tube furnace, and calcine at 520℃ for 3h. The obtained brown solid is g-C_3N_5, which is ground into powder for use.

Put the prepared TiO_2 and g-C_3N_5 into an agate mortar in a certain mass ratio, fully grind for 30 minutes, grind to a powder without graininess, pour the ground mixed powder into a crucible, and calcine at a high temperature of 500℃ for 3h, the obtained powder is TiO_2/g-C_3N_5 composite material. The process of composite material preparation is shown in figure 3.

Figure 3. Flow chart of composite photocatalytic material preparation.

3.3. Catalytic performance of TiO_2 Composite Catalyst

The photocatalytic performance was evaluated by the degradation efficiency of the prepared photocatalytic samples for methylene blue (MB) as an organic pollutant and tetracycline hydrochloride (TCH) as an antibiotic pollutant.

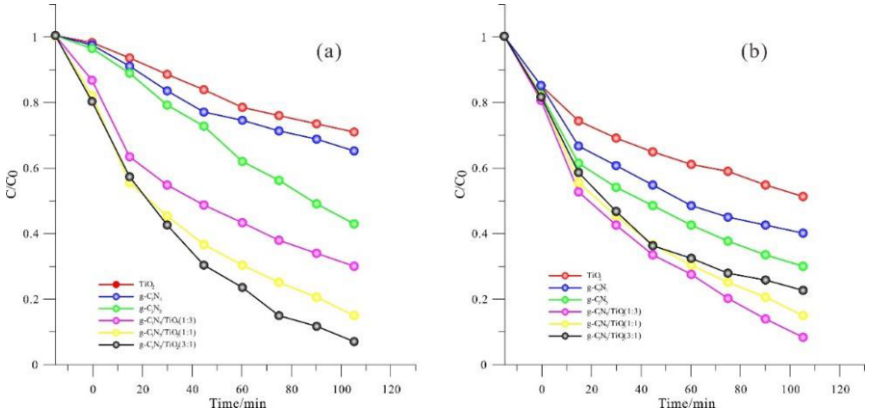

Figure 4. The sample's degradation map of methylene blue (a) and the degradation map of tetracycline hydrochloride (b).

Figure 4 (a) is the degradation diagram of methylene blue by different photocatalysts. For pure TiO_2 and pure g-C_3N_4, the MB removal rate is low when the light is 105 minutes. The photocatalytic performance of the prepared nitrogen rich carbon nitride (g-C_3N_5) is significantly improved compared with that of g-C_3N_4, which has been effectively improved. More importantly, the degradation performance of TiO_2/g-C_3N_5 composites was significantly improved under simulated visible light conditions compared with that of single component samples. Among them, the removal rates of MB were 77.4%, 85.1% and 92.4% respectively with different mass ratios of TiO_2 and g-C_3N_5(3:1, 1:1 and 1:3).

The photocatalytic degradation experiment of tetracycline hydrochloride was carried out under the same light source and under the same conditions. The results are shown in figure 4 (b). The TiO_2/g-C_3N_5 (1:3) composite still has the highest degradation efficiency.

4. Conclusions

The occurrence of black and odorous water bodies is an external manifestation of serious pollution of the natural environment. The cause of this problem is generally the random discharge of domestic and production sewage, etc., which eventually leads to a negative impact on the ecological environment in the water body.

The g-C_3N_5/TiO_2 composite photocatalyst was prepared by using the new photocatalytic material g-C_3N_5 and TiO_2 to successfully couple and construct a heterojunction. The prepared composite photocatalyst showed the highest photocatalytic activity for the degradation of methylene blue and tetracycline hydrochloride under simulated visible light conditions.

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