Research Progress in the Development and Application of Photocatalysis Technology and Materials

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Abstract: In recent years, photocatalytic technology has become a research hotspot for the treatment of organic wastewater, uranium containing wastewater, and Cr (VI) containing wastewater due to its advantages of environmental friendliness, simple reaction process, and high degradation efficiency. Uranium, as the main component of nuclear fuel, is an important strategic resource. The separation and enrichment technology of uranium is of great significance for the sustainable development of nuclear energy. Previously, a series of solid adsorption materials for uranium extraction have been developed, such as inorganic minerals, mesoporous silica, magnetic nanomaterials, carbon based materials, and advanced porous materials. However, due to the comprehensive performance of stability, removal kinetics, adsorption capacity, selectivity, and reusability, the practical application of these materials is still inevitably limited. And photocatalytic technology can reduce easily soluble and easily flowing U (VI) to more difficult to dissolve and relatively non-flowing U (IV), thus overcoming the above problems and achieving the reduction and fixation of uranium. Moreover, this technology only relies on inexhaustible solar energy as energy source, and has the advantage of green and clean. Therefore, the use of photocatalytic technology to separate and enrich uranium is of great significance for the sustainable development of nuclear energy. However, most semiconductor photocatalysts have shortcomings in terms of light absorption capacity and charge separation ability, which limits their practical application in wastewater treatment. In addition, there are many difficulties in photocatalytic treatment of wastewater, such as the fast recombination speed of photo generated electron hole pairs generated by the catalyst, the weak visible light response of most single semiconductor materials, the need to introduce additional sacrificial agents to capture holes in the reaction, and the introduction of inert gases to eliminate the interference of oxygen. This article provides a certain scientific basis for expanding the application of various photocatalytic technologies in wastewater treatment.

Keywords: Photocatalytic Technology; Photocatalytic Materials; Uranium Containing Wastewater.

1. Introduction

With the continuous development of modern society, the environmental and energy issues faced by humanity have become increasingly prominent. On the one hand, the rapid development of industrialization has led to the gradual deterioration of environmental pollution, with higher levels of pollutants in the air and water bodies; On the other hand, the demand for clean energy that can replace fossil fuels is becoming increasingly urgent under the national strategic goal of "carbon peaking and carbon neutrality"[1]. These issues pose unprecedented challenges to the development of contemporary science and technology.

Among various radioactive waste, uranium is a representative act series element with a half-life of millions to billions of years, and is a common pollutant widely present in the ground and surface water near contaminated sites. Nowadays, countries often load nuclear waste into HIC high integrity containers or solidify it for deep geological treatment. Technologies such as separation and transmutation, and space processing are still being further developed[2]. Therefore, the treatment of medium and low level nuclear waste is the urgent problem to be solved. The technical requirements for the disposal of medium and low level radioactive waste are relatively low, and their large quantity makes the task even more arduous. The traditional methods for treating uranium wastewater include chemical reduction, adsorption, membrane filtration, and biological treatment. These methods have more or less limitations, such as high costs and secondary pollution. A low-cost strategy for efficient nuclear waste removal and waste minimization is essential, and the emergence of photocatalysis has opened up a new continent for nuclear waste treatment[3].

2. Photocatalysis

2.1. Principles of Photocatalysis Technology

The term "photocatalysis", as the name suggests, refers to the conversion of solar energy into chemical energy in the presence of a photocatalyst. During this process, the photocatalyst can absorb light and cause chemical changes in the reactant. The excited photocatalyst can react multiple times with the reactant to form intermediate substances, while ensuring that it remains unchanged before and after the reaction. When the quantum energy of the incident light is equal to or greater than the bandgap width of the semiconductor, the valence band electrons are excited and transition to the conduction band, corresponding to the generation of holes h+vb in the valence band, and the formation of photo generated electrons e−cb in the conduction band. The photogenerated electrons formed on the conduction band have strong reduction ability, while the photogenerated holes on the valence band have strong oxidation ability, which can migrate to the semiconductor surface and undergo corresponding redox reactions with the pollutants adsorbed on the surface [4].

The generated photogenerated electrons are mainly transmitted in the following forms: 1) electrons and holes are
Photocatalytic technology can remove toxic substances, especially heavy metals, from water bodies. On the other hand, photocatalytic technology can also mineralize them into CO2, H2O, and other non-toxic or chemical energy. Selectively oxidize pollutants in wastewater, organic pollutants, catalysts convert solar energy into aliphatic hydrocarbons, phenolic organic compounds, ciprofloxacin, tetracycline, etc., surfactants, pesticides, antibiotics (norfloxacin, methylene blue, methyl orange, etc.), and disinfection all have drawbacks[6].

2.2. Research and Development of Photocatalytic Materials

The selection of photocatalysts is the core of photocatalytic technology, and the structural, chemical, and optical properties of semiconductors themselves are key factors affecting photocatalytic activity. Commonly used semiconductor photocatalysts include TiO2, ZnO, SnO2, WO3, CdS, etc. However, traditional photocatalysts mostly have large bandgap widths, such as the most widely used TiO2 (with an Eg of 3.2 eV of anatase TiO2), which only responds to ultraviolet light and cannot effectively utilize visible light, which accounts for about 43% of the solar spectrum; Although ZnO, CdS, and others have high photocatalytic activity, their structures are unstable under illumination and are prone to photo corrosion. These shortcomings greatly limit their practical application in the field of photocatalysis. Therefore, designing and developing semiconductors with good chemical stability and visible light response ability is the key to ultimately achieving the industrial application of photocatalysis [5].

2.3. Application of Photocatalysis Technology

(1) Treating organic matter in wastewater

So far, many literatures have applied photocatalytic technology to the degradation of organic pollutants in wastewater, including organic dyes (Rhodamine B, orange G, methylene blue, methyl orange, etc.), surfactants, pesticides, aliphatic hydrocarbons, phenolic organic compounds, polychlorinated biphenyls, etc. In the degradation process of organic pollutants, catalysts convert solar energy into chemical energy, selectively oxidize pollutants in wastewater, and mineralize them into CO2, H2O, and other non-toxic or low toxic substances.

(2) Treating inorganic substances in wastewater

Photocatalytic technology can remove inorganic substances, especially heavy metals, from water bodies. On the one hand, photocatalytic technology can remove toxic heavy metal ions, such as Mn2+, Cr6+, Hg2+, Pb2+, Co2+, Zn2+, etc; On the other hand, photocatalytic deposition can be used to recover precious metals such as Au, Ag, and Pt. (3) Air purification

Photocatalytic technology can achieve effective catalytic degradation of common pollutants in the air, such as sulfur compounds, NOX, VOC, and photocatalytic reduction of CO2.

(4) Hydrogen production through hydrophotolysis

Photocatalytic hydrogen production technology is considered one of the best ways to solve energy and environmental problems. Semiconductors are excited by light to generate photo generated electrons and holes, which migrate to the conduction band of the material to reduce water to hydrogen. At the same time, photo generated holes are captured by scavengers or oxidized to oxygen by water.

(5) Disinfection and sterilization application

In addition to non biological pollutants such as organic pesticides, antibiotics, and heavy metals in water, the harm caused by biological pollution such as medical sewage and domestic sewage cannot be underestimated. Most pathogenic microorganisms can cause harm to human health through ingestion, respiration, or skin contact. Traditional disinfection methods such as chlorination, ozone oxidation, and ultraviolet disinfection all have drawbacks[6].

3. Overview of Wastewater

3.1. Uranium Containing Radioactive Wastewater

Uranium (U) is a common radioactive nuclide in soil and groundwater related to uranium mining, nuclear research, nuclear fuel production, nuclear weapon manufacturing, and radioactive material disposal. The naturally occurring uranium is a toxic weakly radioactive actinide element that is widely distributed and can be found in low concentrations in almost all rocks, soils, and water bodies. The naturally occurring uranium is a mixture of three radioactive isotopes (234U, 235U, and 238U), but most of them are 238U isotopes, with a relative abundance of 99.27% and a half-life of 4.5 ×109, it was one of the important raw materials for nuclear fuel manufacturing. Uranium (U) in the natural environment has many chemical valence states, such as U5+, U3+, U4+, and U6+, but mainly consists of insoluble tetravalent uranium (U (IV)) and soluble hexavalent uranium (U (VI)), the latter being much more toxic to organisms. The migration and fate of uranium in the environment are closely related to the morphology and redox conditions of its matrix. U (VI) usually exists in the form of soluble UO22+ cations, and free U (VI) ions have strong migration ability and are easy to enter the natural environment, posing a threat to human health and biological survival. In contrast, the main existing form of U (IV) is solid UO2, with low solubility (Ksp=252.0) and difficulty in migration.

3.2. Printing and Dyeing Wastewater

Printing and dyeing wastewater is the wastewater discharged from printing and dyeing factories that mainly process cotton, linen, chemical fibers, and their blended products. The amount of printing and dyeing wastewater is relatively large, with 100-200 tons of water consumed per ton of textile processing, of which 80-90% becomes wastewater. Textile printing and dyeing wastewater has the characteristics of large water volume, high organic pollutant content, high
alkalinity, and significant water quality changes, making it one of the difficult to treat industrial wastewater. Wastewater contains dyes, slurries, additives, oils, acids and alkalis, fiber impurities, sand substances, inorganic salts, etc. The water quality of printing and dyeing wastewater varies depending on the type of fiber used and processing technology, with significant differences in pollutant components.

### 3.3. Cr (VI) Wastewater

Chromium is a hard silver white metal. Chromium is an essential trace element in the human body and plays a special role in glucose and lipid metabolism. Trivalent chromium is a beneficial element for the human body, while hexavalent chromium is toxic. The absorption and utilization rate of inorganic chromium by the human body is extremely low, less than 1%; The utilization rate of organic chromium by the human body can reach 10-25%. Chromium has a low content in natural foods and exists in a trivalent form. Hexavalent chromium is a highly toxic substance that can be ingested or inhaled, and skin contact may cause allergies; It is more likely to cause genetic defects, inhalation may cause cancer, and has a persistent risk to the environment. But these are the characteristics of hexavalent chromium, and chromium metal, trivalent or tetravalent chromium do not have this toxicity.

Hexavalent chromium is easily absorbed by the human body and can invade the body through digestion, respiratory tract, skin, and mucous membranes. When breathing air containing different concentrations of chromic anhydride, there may be varying degrees of hoarseness, atrophy of the nasal mucosa, and in severe cases, perforation of the nasal septum and bronchiectasis. When invading through the digestive tract, it can cause vomiting and abdominal pain. Infectious and eczema can occur when invaded through the skin. The greatest harm is the risk of cancer when exposed to or inhaled for a long or short period of time.

Hexavalent chromium compounds have carcinogenic effects in the body and can also cause many other health problems, such as inhaling certain high concentrations of hexavalent chromium compounds that can cause runny nose, sneezing, itching, nasal bleeding, ulcers, and perforation of the nasal septum. Short term high dose exposure can have adverse consequences at the contact site, including ulcers, nasal mucosal irritation, and nasal septum perforation. Ingestion of excessive doses of chromium can lead to kidney and liver damage, nausea, gastrointestinal irritation, gastric ulcers, spasms, and even death. Skin contact can cause ulcers or allergic reactions (hexavalent chromium is one of the most susceptible metals to allergies, second only to nickel). According to experimental studies, high-dose feeding of mice with hexavalent chromium can have an impact on their reproduction, resulting in a decrease in the number of offspring per litter and a decrease in fetal weight. The greatest harm is the risk of cancer when exposed to or inhaled for a long or short period of time.

Excessive (over 10ppm) hexavalent chromium has a lethal effect on aquatic organisms. Experiments have shown that hexavalent chromium in contaminated drinking water can cause cancer. Hexavalent chromium compounds are commonly used in electroplating and other applications. After animal’s drink water containing hexavalent chromium, hexavalent chromium is absorbed by cells in many tissues and organs in the body.

The residual hexavalent chromium in leather can be absorbed through the skin and respiratory tract, causing damage to gastrointestinal, liver, and kidney functions. It may also damage the eyes, causing retinal hemorrhage, optic nerve atrophy, and so on.

### 4. Research Status of Photocatalytic Technology for Wastewater Treatment

#### 4.1. Research Status of Photocatalytic Degradation of U (VI) by g-C₃N₄ and its Composites

Li et al. [7] used NH4Cl as a gas template to synthesize porous g-C₃N₄, which exhibited a high surface area (78.8 m²/g) and provided more sites for adsorbing U (VI). Under visible light irradiation, Li showed excellent photocatalytic reduction performance for U (VI). Lu et al. [8, 9] introduced B and S element doping into g-C₃N₄ and synthesized g-C₃N₄ doped with B element (B-g-C₃N₄) and g-C₃N₄ doped with S element (S-g-C₃N₄) for photocatalytic reduction of U (VI). Under visible light irradiation, methanol was used as the sacrificial agent, and B-g-C₃N₄ and S-g-C₃N₄ had good removal effect on U (VI) in the environment of nitrogen. On the basis of monomer modification, various g-C₃N₄ complexes are also widely used for photocatalytic reduction of U (VI). Dai et al.[10] synthesized S-type heterojunction ZnFe₂O₄/g-C₃N₄ (ZFOCN), which exhibits excellent adsorption and photoreduction properties for U (VI). At a pH of 5, its maximum Langmuir adsorption capacity (qmax) reached 699.3 mg/g, and the optimal removal amount of U (VI) by adsorption and photoreduction reached 1892.4 mg/g, with a removal rate of 94.62%. Moreover, after 5 cycles, the removal rate of U (VI) remained above 90%.

#### 4.2. Current Research Status of MOF Photocatalytic Materials Application

Wang et al.[11] prepared a series of MIL-125 (Ti) loaded metal sulfide photocatalytic materials, achieving the reduction and removal of Cr (VI) in wastewater under ultraviolet light; Jing et al.[12] prepared MIL-68 (Fe) by solvothermal synthesis method for photocatalytic reduction of Cr (VI) in wastewater. Under certain conditions, under visible light irradiation, the removal rate of Cr (VI) can reach almost 100%. At the same time, MIL-68 (Fe) has been proven to be an efficient photocatalyst that can be used to remove different pollutants such as malachite green (MG) in water; Sha et al.[13] prepared zirconium based MOF-UIO-66 for photocatalytic degradation of Rhodamine B. By preparing Ag₂CO₃ and UIO-66 into composite materials, their degradation rate of Rhodamine B was greatly improved. Matthew J. MacDonald et al.[14] prepared Fe/MIL-47MOF materials and added H₂O₂ as a co oxidant, achieving efficient photocatalytic degradation of methylene blue (MB) with a degradation rate of 98.2%; Chi et al.[15] prepared iron based MOF material MIL-101 (Fe) and its amino functionalized derivatives, and used them as water oxidation catalysts (WOCs) for oxygen evolution under visible light irradiation. The results showed that MIL-101 (Fe) had excellent visible light driven oxygen evolution activity.

#### 4.3. Application of SnS₂ in Photocatalysis

As a new type of solar driven photocatalyst, SnS₂ has relatively good photocatalytic stability and has been widely studied in the degradation of environmental pollutants.
According to reports, compared to CdS, SnS$_2$ nanoparticles exhibit higher photocatalytic activity and excellent corrosion resistance during the degradation of formic acid aqueous solutions[16]. Mondal et al.[17] successfully synthesized SnS$_2$ nanoflowers and SnS$_2$ nanowires, and found that SnS$_2$ nanoflowers have higher efficiency in photocatalytic reduction of Cr (VI) than SnS$_2$ nanowires. This is due to the differences in surface chemistry and morphology of SnS$_2$ nanoflowers, resulting in a larger specific surface area and a large number of active centers. Umar et al.[18] synthesized SnS$_2$ nanosheets that are easy to prepare on a large scale using low-temperature hydrothermal method, and found that the synthesized SnS$_2$ nanosheets can serve as high-efficiency photocatalysts for photocatalytic degradation and nitroaniline chemical sensors. Under visible light and sunlight irradiation, Meng et al.[19] synthesized BiOCl/SnS$_2$ hollow spheres through hydrothermal method with significantly higher photocatalytic activity for Rhodamine B than pure SnS$_2$ and BiOCl. SnS$_2$/TiO$_2$ composite materials exhibit higher photocatalytic activity for the reduction of Cr (VI) aqueous solution under visible light irradiation compared to TiO$_2$[20].

4.4. Research Status of Bismuth based Photocatalytic Materials

BiFeO$_3$ has the characteristics of perovskite structure, narrow bandgap width, and ability to respond to visible light. It is also one of the few materials with both ferromagnetism and ferroelectricity, which is expected to solve the problem of difficult photocatalyst recovery. BiVO$_4$, as a photocatalytic material, has also received increasing attention in recent years. The monoclinic scheelite type BiVO$_4$ has a bandgap width similar to BiFeO$_3$, belonging to the narrow bandgap semiconductor that has a good response range to visible light. It has high ability in catalytic degradation of organic pollutants and heavy metals in water, and has good application prospects. For BiFeO$_3$, XiongWang et al.[21] added a certain proportion of bismuth nitrate ($\text{Bi(NO}_3)_3\cdot 5\text{H}_2\text{O}$) and iron nitrate ($\text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O}$) and fully dissolved them in ethylene glycol to obtain a reddish brown solution. The solution was then dried in an oven to obtain a dry sol powder, and then calcined at 500 $^\circ$C to obtain a bismuth ferrite sample. Experimental results have shown that the catalytic reduction of Rhodamine B by the prepared sample under acidic conditions is nearly 100 times higher than that of bismuth ferrite prepared by other methods. Zhu et al.[22] prepared spherical perovskite type bismuth ferrite nanoparticles at 10-50 nm and soft bismuth type hexagonal nanoparticles at 18-33 nm through microwave hydrothermal method. Through experiments, it was found that the photocatalytic effect of soft bismuth ore is higher than that of perovskite. In 2010, Liu Zhike et al.[23] prepared bismuth ferrite particles with a particle size of approximately 15nm using a chemical co precipitation method. The experimental results showed that bismuth ferrite had a degradation rate of 92% for methyl orange under visible light irradiation. Xian Tao et al.[24] prepared BiFeO$_3$ particles by increasing the dosage of PAM, and demonstrated through experiments that increasing the dosage of PAM can reduce the size of the catalyst material and improve the catalytic activity of the photocatalyst under UV and visible light; For BiVO$_4$, Ravidas et al.[25] prepared monoclinic BiVO$_4$ using a co precipitation method and found that the catalyst prepared at a calcination temperature of 450 $^\circ$C had the highest photocatalytic performance. Han et al.[26] synthesized octahedral bismuth vanadate material using hydrothermal method with the assistance of sodium dodecylbenzene sulfonate. Through experiments, it was found that the degradation efficiency of Rhodamine B by this material was greatly enhanced under visible light. Wang et al.[27] used the sol gel method, $\text{CdH}_2\text{N}_2$ as the ammonia source, and sodium citrate as the complexing agent to prepare N doped BiVO$_4$ materials. The results show that N doping makes the light absorption edge of the materials red shift, and the calcined materials show more excellent photocatalytic activity. Zhang et al.[28] obtained tetragonal BiVO$_4$ nanorods using bismuth nitrate and ammonium metavanadate as raw materials by uniform solution precipitation at room temperature, which exhibited good responsiveness under visible light.

5. Conclusion and Outlook

The studies in the above papers all demonstrate the broad application prospects and good effects of photocatalytic technology, especially in the treatment of printing and dyeing wastewater and radioactive wastewater containing U (VI). However, the actual composition of radioactive wastewater is complex, with not only $^{238}\text{U}$, $^{90}\text{Sr}$, $^{137}\text{Cs}$ and other radioactive nuclides, but also generally characterized by strong radiation, high salt content, and high acid content. This poses strict requirements for the irradiation and high acid resistance of two-dimensional semiconductor materials used in photocatalytic reduction treatment of uranium containing radioactive wastewater. Therefore, starting from practical applications, the radiation stability, high acid and high salt stability of materials should be considered in the material stability testing process; At the same time, there are also waste organic liquids in these radioactive waste liquids, mainly including radioactive waste oils, waste organic solvents, waste organic scintillation liquids, and decontamination liquids. Photocatalytic treatment technology can provide reference for the treatment of organic wastewater in other fields. At present, most of the research on photocatalytic removal of pollutants from water is still in the laboratory research stage, with relatively weak theoretical support. The establishment of effective theoretical models is still being explored, and there is still a long way to go in practical applications. In addition, in-depth exploration of how semiconductors are coupled, how heterogeneous interfaces are formed, and how material morphology is controlled has always been a key and difficult point that needs to be continuously explored and overcome in the field of materials research.

References


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