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The research progress on photocatalytic performance of graphene-based nanocomposites

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Abstract: As soon as nanomaterials were discovered, they attracted a lot of attention because of their unique and excellent properties and became major hot research. They are regarded as the most promising materials in the 21st century. With the growth of industrial production, photocatalytic technology has been pursued as an efficient, green, and economical way of industrial production and treatment of pollution. However, the low light energy utilization of traditional semiconductor materials is a drawback that cannot be ignored. Graphene, as one of the most common and widely used 2D nanomaterials, has a special structure and characteristics that can effectively solve this problem. The paper briefly introduces the structure, properties, preparation method, and basic principle of photocatalysis of graphene. At the same time, a review is provided on the application of graphene-based composite materials in the field of photocatalysis, including dye degradation, photocatalytic treatment of other emerging pollutants, photocatalytic treatment of air pollutants, and water decomposition. By summarizing and integrating the photocatalytic properties of several graphene-based composites, this article lays the foundation and helps to discover new graphene composites.

Keywords: Graphene-based composites, Photocatalysis, Dye degradation, Dydrolysis

1. Introduction

In the rapidly developing 21st century of science and technology, as well as the economy and society, people's living standards have significantly improved. However, the rapid development of industry has also led to serious environmental pollution and the depletion of fossil fuel resources. They are two major thorny problems that affect human life. Therefore, it is of great practical significance to seek for sustainable renewable energy sources to mitigate and eliminate the damage caused by industrial pollutants to the ecological environment. Based on these two serious problems, consideration was given to utilizing the inexhaustible light energy from the sun. However, the conversion efficiency of light energy is too low and is time-limited by over-dependence on the intervals of sunlight. In 1972, when Fujishima and Honda first discovered that TiO_2 could be used as a photocatalyst to decompose water to prepare hydrogen [1], many scientists explored and investigated TiO_2 as a photocatalyst for the degradation of dyes and the treatment of pollutants. Since then, photocatalysts have been explored and researched by many scientists in the fields of photocatalytic dye degradation, photocatalytic treatment of emerging pollutants, photocatalytic treatment of air pollutants, and photocatalytic water decomposition. Although the mechanism of photocatalysis varies in terms of reaction details, it can

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basically be described through four important steps. First, electron-hole pairs are produced by light absorption. Excitons split apart from one another second. Third, the transmission of electrons to the photocatalyst's surface pores. Fourth, surfaces are the site of redox processes. By storing solar energy in the form of chemical bonds and using photon energy to drive beneficial chemical processes, photocatalytic reactions enable flexibility for a range of potential end uses. Meanwhile, researchers have discovered that photocatalytic technology offers several benefits over conventional solar energy utilization systems. These benefits include the ability to directly harvest solar energy, turn it into heat, store it, and supply heat for locals. Even additional types of energy may be created off of electricity [2]. As the investigation developed, researchers focused on nanocomposites as a means of increasing the photocatalytic reaction's efficiency. A single sheet of closely spaced carbon atoms in a two-dimensional honeycomb crystal structure makes up graphene, a nanomaterial with exceptional rigidity and thermal and electrical conductivity. Furthermore, graphene has exceptional optical characteristics. Thus, one excellent alternative to increase the effectiveness of photocatalytic processes is to seek for graphene-based composites. Utilizing carbon nanomaterials to create high-performance composites, such as carbon nanotubes and fullerenes, has gained popularity recently. This is due to the fact that these carbon allotropes' off-domain conjugated β-systems may be employed as electron reservoirs to quickly receive and shuttle photogenerated electrons for charge transfer and separation. They also aid in expanding the photocatalysts' catalytic activity sites and improving their adsorption capabilities. The peeling of graphene was invented by Novoselov and Geim [3]. Electrons of a micrometer size can normally conduct across its orbital configuration. This indicates that, at room temperature, electrons may conduct at very high mobility with very minimal dispersion. As a result, graphene is a prime contender for high-performance electron transport or absorption media [4]. In addition, they can be used as part of composite materials because their properties can be highly modified and their surface properties can be artificially and favorably adjusted and modified by chemical methods. This paper collects a large amount of relevant literature to understand and summarize the preparation and properties of emerging high-quality graphene composites and summarizes the progress of photocatalytic dye degradation, pollutant treatment, photocatalytic carbon dioxide reduction, and photocatalytic water decomposition in photocatalysis.

2. Preparation of graphene-based photocatalytic materials

Graphene-based photocatalytic composites can combine the excellent properties of graphene with some of the properties of common photocatalytic materials, which in turn improves the performance of the composites in photocatalysis and the degree of practical application. The preparation methods of graphene-based photocatalytic composite materials mainly include in situ growth method [5], hydrothermal or solvothermal method [6], and solution mixing method [7].

In situ growth is a common method for preparing graphene-based composites. Usually, graphene oxide (GO) and metal salts are selected as precursors, and the metal compound nuclei are grown on graphene by controlling the reaction conditions, and GO is reduced to rGO. Lambert T N et al. [5] added TiF_4 to the GO solution and utilized the hydrolysis of TiF_4 to generate flower-like anatase phase TiO_2 on the surface of GO.

Hydrothermal or solvent-thermal methods are one of the traditional methods for the preparation of semiconductor nanomaterials. This method allows semiconductor nanoparticles or precursors to be uniformly loaded on graphene. The method is now widely used in the preparation of graphene-based composites. Zhu J et al. [6] prepared ZnFe-layered double hydroxides/reduced graphene oxide (ZnFe-CLDH/RGO) composite materials by hydrothermal method and studied the effect of different graphene loading amounts on the photocatalytic performance of ZnFe-CLDH.

The mixed solution method refers to the preparation of composite materials by simply mixing a graphene suspension with a metal salt solution containing semiconductors or precursors, followed by simple drying and roasting. This method is simple and mild, but it is difficult to form chemical bonds between graphene and semiconductors. Urtiaga et al. [7] added commercial TiO_2 to GO suspension, ultrasonically mixed and hydrothermally reacted at 120 °C for 3 hours to prepare TiO_2/GO composite

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materials, and studied the effect of different GO doping amounts on photocatalytic degradation of perfluorooctanoic acid (PFOA).

3. Research progress in graphene-based photocatalytic composite materials

3.1. Photocatalytic degradation of dyes

The most commonly used organic substance in the textile, printing, and food production industries is dye, and its wastewater contains a large amount of non-degradable harmful substances. The rapid development of the dye and textile industries in the past decades has resulted in the release of large quantities of dyes into the aquatic environment, posing potential hazards to the aquatic environment and human health. For example, dyes such as methyl orange, rhodamine B, and methylene blue (MB) are seriously damaging to human health and have carcinogenic effects. It was shown that graphene-based composites have good degradation effects on dyes. Piyawan Nuengmatcha et al. [8] explored the creation and use of ternary zinc oxide/graphene/iron oxide (ZGF) catalysts for visible light-driven photocatalysis. They were motivated by zinc oxide-based catalysts, certain magnetic nanoparticles, and graphene derivatives. They used four procedures to prepare the ZGF catalyst [9]. In order to conduct comparative analyses, an analogous approach was utilized to synthesize zinc oxide (ZnO; Z), graphene (G), and iron oxide (Fe_2O_3; F). Additionally, the factors that influenced this experiment were investigated. The photocatalyst dose, solution pH, irradiation period, and intensity all had an impact on the photocatalytic efficiency, according to an analysis of the experiment's data. When the photocatalytic performance of the ZGF catalyst was compared to that of other catalysts (Z, F, and G catalysts) with the same influencing parameters, the best MB degradation was discovered. The first 90 minutes of irradiation caused MB to degrade quickly, and after that time, the degree of MB explanation stayed constant. The rate at which MB degraded went from 38% to 91% when the irradiation intensity was progressively raised to 100 W. Nonetheless, the deterioration rate dropped as the irradiation intensity increased more. The rate of MB degradation rose from 0% to 90% when the dose of ZGF catalyst was progressively raised to 0.03 g/L. The degradation rate of MB rose from 34.06% to 94.14% when the pH of the solution increased from 2.0 to 8.0. However, as the pH of the solution was raised further, the rate at which MB degraded dropped to 90.96%. In the end, it was determined that ZGF's photocatalytic performance outperformed that of the other catalysts employed in the experiment, and that it was highly stable and reusable. The synthesized ZGF catalyst has a strong catalytic potential for the effective treatment of organic dyes in wastewater and works well as a catalyst for the photocatalytic process.

Perfluorooctanoic acid (PFOA) is a common ingredient in surfactants, firefighting foams, polymer additives, and other products because it is stable and difficult for the environment to break down. PFOA can build up and have negative consequences on human health. PFOA can build up in the body and have negative effects; photocatalytic degradation of PFOA is a technology that can be used. Shang E et al. [10] used the hydrothermal approach to manufacture a Pb-$BiFeO_3$/rGO composite catalyst and investigated the degrading effect of perfluorooctanoic acid under UV light irradiation, taking into account factors such as catalyst dose, solution pH value, initial pollutant concentration, and quantity of GO doping. The outcomes showed that the composite catalyst doped with 5% rGO eliminated 28.0% of toxic organic compound (TOC), decomposed 69.6% of 50 mgL^{-1} perfluorooctanoic acid (PFOA), and fluorinated 37.6% of PFOA at pH 2. Commercial TiO_2 and GO suspension were ultrasonically mixed by Gomez Ruiz B et al. [11] and then hydrothermally treated at 120 °C for three hours to produce TiO_2/GO composite materials. They evaluated how perfluorooctanoic acid degraded in response to UV exposure when commercial TiO_2 and produced composite materials were used. The outcomes showed that the produced composites could degrade PFOA by 93.7 percent and remove TOC by 60.0% in 12 hours. The efficiency of deterioration was four times greater than that of commercial TiO_2.

The use of antibiotics in agriculture, animal husbandry, and human health is widespread, but they also release a lot of antibiotics into the environment, endangering both the environment and human health. Photocatalytic technology is a great option for antibiotic degradation because existing biological methods have a low removal rate for antibiotics. In order to create g-C_3N_4(CN)/Ag_2CO_3(AC)/GO, Liu

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H et al. a dual Z-type heterojunction mechanism and provided a workable technique for the degradation of contaminants [12]. ternary catalyst at room temperature utilizing a straightforward chemical co-precipitation process. Tetracycline is used as a target pollutant for measuring the photocatalytic activity of CN/AC/GO in the visible light spectrum. Tetracycline was degraded by CN/AC/GO at an 81.6% rate after 60 minutes. The tetracycline breakdown rate reached 97.6% when the irradiation period was increased to 100 minutes. Investigated were the catalyst's effects on the degradation of levofloxacin and hygromycin hydrochloride. Levofloxacin and hygromycin hydrochloride both had CN/AC/GO degradation rates of 71.8% and 76.3%, respectively. After multiple cycle testing, the catalyst's stability was outstanding and its catalytic activity did not alter noticeably.

3.2. photocatalytic treatment of air pollutants

NO is a hazardous gas that damages the human respiratory system and endangers the soil, atmospheric, and aquatic environments. It is colorless, odorless, water-insoluble, and toxic. Zhu G et al. [13] produced the Bi-BiOI/GO composite material using an ethanol-assisted solvothermal technique. The material has a diameter of (2-4 m) and is microspherical in form. Graphene flakes are generated on the surface of the Bi-BiOI microspheres. The catalysts' catalytic effects on NO were outstanding. In 30 minutes, 51% of NO may be converted to stable nitrate when exposed to visible light. It was discovered that holes and superoxide radicals are key players in the oxidation of NO.

An extremely promising strategy for resolving the present energy and environmental issues is the conversion of CO_2 to fuel. In order to reduce CO_2, C-O bonds must be broken and C-H bonds must be formed, both of which are challenging tasks in mild environments. On the other hand, CO_2 reduction can be accelerated by semiconductor photocatalysts, which also have the ability to lower the activation barrier for CO_2 reduction by converting light energy into chemical energy. Ag_2CrO_4/g-C_3N_4/GO ternary composites were made by Xu D et al. [14] using the self-assembly precipitation process. When CO_2 is exposed to simulated sunlight, it can be converted to CH_4 and CH_3OH. Comparing the composites to C_3N_4 and C_3N_4/Ag_2CrO_4, the maximum CO_2 conversion was 1.03 $\mu mol \cdot g^{-1} \cdot 0.30\ h^{-1}$, indicating a considerable increase in CO_2 reduction efficiency. In addition to acting as an electron acceptor to facilitate charge separation, the GO in the composites supplied enough active sites for the CO_2 reduction process that occurs through photocatalysis. (Pt/TiO_2) rGO composite catalysts coated with rGO and Pt/TiO_2 were created by Zhao Y et al. [15]. The octahedral anatase TiO_2 surface was found to have folded rGO wrapped around it, as revealed by scanning electron microscopy (SEM). Using a catalyst, CO_2, and H_2O, photocatalytic reduction of CO_2 was performed in a closed reactor fitted with a 300 W Xe lamp. The prepared (Pt/TiO_2) rGO-2 can selectively reduce 99.1% of CO_2 to CH_4 with a methane production rate of 41.3 μmol $(g\cdot h)^{-1}$, and the CO production rate was very small, only 0.4 μmol $(g\cdot h)^{-1}$, which was 31 times higher than that of commercial TiO_2.

3.3. Photocatalytic water decomposition

Because of its special carrier mobility, huge specific surface area, and chemical stability, graphene is frequently utilized as a co-catalyst in catalysts for the synthesis of hydrogen. Additionally, it can be used as a transporter or mediator of electrons to prevent photogenerated electron-hole pairs from compounding on the semiconductor surface. Using hydrothermal and electrostatic self-assembly techniques, Boppella R et al. [16] produced rGO/$La_2Ti_2O_7$/NiFe LDH heterojunction catalysts by layering layered double hydroxides (NiFe-LDH) and rGO on the surface of lanthanum titanate in succession. Under ideal circumstances, the hydrogen release rate was 532.2 $\mu mol\cdot(g\cdot h)^{-1}$, which was nine times higher than that of lanthanum titanate alone. The photocatalytic hydrogen precipitation experiment was conducted in simulated sunshine with 10% triethanolamine as the cavity cleanser. The combination of rGO and NiFe-LDH greatly increased the absorption of lanthanum titanate in the visible area, according to the UV diffuse reflectance study. Tests using electrochemical impedance spectroscopy (EIS) demonstrated that the overall charge transfer resistance at the electrode/electrolyte interface was significantly decreased upon the addition of rGO nanosheets and NiFe-LDH. It illustrates how the addition of rGO and NiFe-LDH encourages photogenerated electron-hole pair separation. The produced heterojunction catalysts exhibit outstanding stability in hydrogen generation, and the results of four successive sets of hydrogen production studies showed little variation in hydrogen production efficiency.

4. Conclusion

In recent years, graphene-based composite photocatalytic materials have achieved excellent results in their preparation and application, but their application in photocatalysis, which has great potential, has not yet been widely utilized due to some obstacles in their practical application. Graphene composites have similar limitations in dye degradation, emerging pollutant treatment, atmospheric pollutant treatment, and catalyzed water decomposition. First, the preparation cost of graphene is so high that large-scale production is difficult. Second, its photocatalytic efficiency needs to be improved, and in some applications, the catalytic efficiency of graphene composites is not as good as that of traditional photocatalytic materials. Third, in practical applications, graphene composites are difficult to separate and recycle, which may cause pollution to the environment and require reasonable treatment and disposal. In exploring solutions to the above problems, future research directions include optimizing the composition and structure of graphene composites and exploring multifunctional graphene composites. By optimizing the composition and structure of graphene composites, the photocatalytic efficiency can be improved and the cost can be reduced. For example, the introduction of metal ions or non-metal elements into graphene composites can improve their light absorption capacity and electron transport properties. The study of multifunctional graphene composites will help to expand their application fields and increase their practical application value.

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