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Application of graphene composites in photocatalysis

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Abstract:

Graphene composites have a wide range of energy and environmental applications due to their high adsorption capacity, high carrier mobility, and stability. Therefore, it is getting more and more attention from researchers. Furthermore, photocatalytic reaction compared with the traditional catalytic reaction has the characteristics of being green, clean and having mild conditions. The application of graphene composites in the field of photocatalysis can solve many environmental pollution problems and enhance the development and utilization of new energy sources. Graphene composites as photocatalysts can play important roles in photocatalytic reduction of carbon dioxide, photocatalytic hydrogen production from water splitting and photocatalytic degradation of organic pollutants. This paper describes the preparation and advantages of graphene composites. It also summarizes the research progress of graphene composites in photocatalytic applications. Afterwards, it analyzes the drawbacks of current graphene composites as photocatalysts involved in the reaction, and provides an outlook on future directions for improving performance and reducing costs.

Keywords: Graphene composites; photocatalytic reaction; carbon dioxide reduction; hydrogen production from water splitting; degradation of organic pollutants.

1. Introduction

In recent years, light energy has attracted much attention as a green, clean and easily accessible renewable energy source. More and more scientists have begun to pay attention to photocatalytic reaction, due to its simple operation, high selectivity, mild reaction conditions and green features[1]. However, previous photocatalysts suffer from a narrow light absorption range and low photogenerated charge separation efficiency. With the advent of graphene in 2004, new opportunities opened up in the field of photocatalytic reactions. Graphene is a two-dimensional carbon nanomaterial consisting of carbon atoms in sp^2 hybridized orbitals in a hexagonal honeycomb lattice. Scientists have discovered that graphene as a photocatalyst is characterized by high specific surface area, high electrical conductivity, and good mechanical strength[2]. However, the direct use of graphene as a catalyst for photoreactions still has some shortcom-

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ings. The number of highly active catalytic sites available for graphene is relatively small, making it difficult to improve catalytic performance. Secondly, the strong π - π interaction force between graphene nanosheets easily leads to their own agglomeration, which obscures a large number of active sites and reduces the effective specific surface area in contact with the reaction substrate. Furthermore, agglomeration also affects its dispersion and stability in catalytic systems. Therefore, graphene needs to be doped and composite processed into graphene composites to further enhance the catalytic performance and efficiency for photoreactions. Graphene shows dramatic performance improvement when compounded with photocatalytic materials. It can effectively adsorb reactants and has good structural stability. Furthermore, it can effectively transfer photogenerated charges to reduce the recombination of electrons and holes. Nowadays, graphene is gradually gaining status in photocatalytic reactions. Its composite materials are used in the environment for air purification, water pollution treatment. In terms of energy, its composite materials can break down water to make hydrogen, carbon dioxide reduction. Graphene composites are expected to be crucial materials in the field of photocatalytic reactions. This paper describes the preparation and advantages of graphene composites, and summarize the related research work of graphene composites in photocatalytic degradation of organic pollutants, photolysis of water to produce hydrogen and CO_2 reduction. In the end, this paper discusses the shortcomings and outlook of graphene composites in future development.

2. Preparation and Advantages of Graphene Composites

2.1 Preparation of Graphene Composites

Currently, graphene composites are prepared by hydrothermal or solvothermal methods, in-situ growth method, sol-gel method, thermal hydrolysis method, chemical vapor deposition method. This paper focuses on the hydrothermal method, thermal hydrolysis method, and sol-gel method.

The hydrothermal method uses water as a solvent heated in a highly sealed reactor, where the water is vaporized by heat to generate pressure, thus creating a high-temperature, high-pressure reaction atmosphere. In this environment, substances that are not readily soluble in water at room temperature dissolve and recrystallize. In this process, the substances are more easily processed for material handling and inorganic synthesis. This preparation method has mild conditions, simple process, low requirements for equipment, and good dispersion of the product. Zhang's group reported a method to prepare TiO_2 /r-GO nanocomposites with different graphene loadings. In this method, TiF_4 solution was ultrasonically mixed with r-GO, and TiO_2 /r-GO composites were produced after drying. In the next step, they utilized a hydrothermal method to obtain the product by hydrothermal treatment of GO with TiO_2 nanoparticles in ethanol. The photocatalytic activity of this prepared material is greatly improved compared to TiO_2 photocatalytic activity[3].

Thermal hydrolysis is a type of hydrolysis method, using this method of materials can generally be hydrolyzed by simply adding water, and heating will accelerate hydrolysis. This method has the advantages of simple process, low cost and short time consuming. Xiao's group proposed a way to prepare ternary composites of diatomite/TiO_2 /GO using thermal hydrolysis. First, a certain mass of $TiOSO_4$ was added to distilled water and the solution was sonicated. Afterwards, the pH of the solution was adjusted to 2 and the solution was stirred in a water bath at 40 ^{o}C until clarified. Researchers put pretreated diatomite into the solution and reacted at 95 ^{o}C for 1~2 h, thus accelerating the hydrolysis of $TiOSO_4$. After waiting for the product to cool to room temperature, researchers washed it with distilled water. The product was dried at 60 ^{o}C for 8 h and then calcined in a muffle furnace at 400 ^{o}C for 2 h to obtain diatomite/TiO_2 binary composites. The diatomite/TiO_2 powder was added into distilled water, and different mass fractions of GO were added separately under stirring. The solution was ultrasonicated and dried to obtain the solid. Afterwards, the solid was calcined in a muffle furnace at 200 ^{o}C for 1 h to obtain the diatomite/TiO_2/GO ternary composites[4].

The sol-gel method first hydrolyzes and condenses metal organic or inorganic compounds to form a sol. After the sol gradually gels, it is then processed accordingly to obtain oxides or other solid compounds. The process of this method is simple and convenient, and the reaction is uniform, but there are problems of easy shrinkage and long preparation period. Li's group developed a method for the in situ synthesis of r-GO/TiO_2 composites using the solution gel method. They first weighed different masses of GO into the prepared TiO_2 precursor sol and ultrasonically oscillated for 2.5 h to make GO fully dispersed and undergo complexation reaction with citric acid. Then they dried and ground the sol and roasted it at 400 ^{o}C for 3 h to remove citric acid to obtain GO/TiO_2 powder. Afterwards, an appropriate amount of distilled water was added to the powder. Then the solution was dispersed uniformly by ultrasonication and reduced with sodium borohydride to obtain r-GO/TiO_2 composite photocatalysts[5].

2.2 Advantages of Graphene Composites

Graphene composites are more adsorptive compared to conventional catalysts because of the high specific surface area and special surface properties of graphene composites. Graphene is a two-dimensional planar structure having a huge specific surface area. It can adsorb a large number of reactant molecules, so that the reactants are enriched around the photocatalyst, increasing the local concentration, which is conducive to improving the photocatalytic reaction rate. The graphene composites after oxidative processing have residual oxygen-containing functional groups on their surfaces that can be combined with the reactants through a variety of interactions such as hydrogen bonding and electrostatic forces. Its conjugated benzene ring region after reduction on this basis can adsorb some aromatic compounds through π - π interactions[6].

Graphene has a high carrier mobility. It can rapidly transfer photogenerated electrons and reduce the recombination of photogenerated electrons with holes, thus enhancing catalytic efficiency. Therefore, it can significantly enhance the catalytic activity of catalysts when compounded with semiconductor catalysts[7]. In addition, graphene can change the band gap of semiconductor photocatalysts, thus increasing the efficiency of absorbing light. Many semiconductor photocatalytic materials absorb only a small amount of light of specific wavelengths, such as ultraviolet light, but when compounded with graphene, light absorption can be expanded to the visible and even near-infrared regions by forming structures such as heterojunctions. Moreover, due to graphene's own unique structure and electronic properties, compositing with photocatalysts can enhance the absorption of light[8].

Graphene composites have better stability. In the composite structure, graphene can play a certain supporting role for the photocatalyst, preventing the photocatalyst nanoparticles from agglomerating and maintaining their structural stability. It can withstand long-term light exposure and maintain its catalytic activity, showing good photochemical stability and resistance to photodegradation[9].

3. Current Applications of Photocatalytic Reactions in Graphene Composites

Graphene composites use graphene as a carrier, which greatly improves the photocatalytic performance compared with conventional photocatalysts. When the photocatalyst is exposed to light, graphene's superior conductivity accelerates the transport of photogenerated electrons and reduces energy loss. At the same time, graphene's huge specific surface area and functionalized surface effectively adsorb the reactants, thus promoting the photoreaction to take place. Therefore, graphene composites have been widely used in several fields of photocatalytic reactions. For example, it can effectively catalyze the hydrogen production from water splitting and reduction of CO_2, and also effectively degrade organic pollutants.

3.1 Photocatalytic Reduction of Carbon Dioxide

In 1978, Halmann had used GaP as a photocatalyst to reduce CO_2 to energy storage compounds such as CH_3OH, HCOOH, and HCHO by photocatalytic reaction[10]. As a result, photocatalytic reduction of CO_2 has received much attention. At first, light excitation of the photocatalyst produces electrons and holes. Then, the electrons and holes migrate to the surface of the photocatalyst. They react with CO_2 to form reactive intermediates such as $\cdot OCH_3$ and $\cdot CH_3$. In the end, reactive intermediates are further converted into valuable hydrocarbon organic compounds.

Tu's group utilized TiO_2-GR sandwich-like composites prepared by in situ hydrolysis technology as photocatalysts for CO_2 reduction reaction. In the end, they obtained much higher yields of CH_4 and C_2H_6 than the yields when pure TiO_2 was used as a catalyst. The material retains the two-dimensional sheet structure of graphene. Furthermore, graphene has a longer average electron lifetime and free path. These allow the electrons to cover a larger surface area of graphene, increasing the possibility of reaction with surface adsorbates. In addition, this composite has more adsorption sites and reaction centers compared to TiO_2, thus accelerating the efficiency of the photocatalytic reaction. Moreover, it contains many Ti^{3+} on its surface, which can synergize with graphene. It favors electron transfer to CO_2, and reduces the likelihood of the recombination of photogenerated electrons with holes. Therefore, TiO_2-GR sandwich-like composite is a photocatalyst that can efficiently reduce CO_2[11]. The application of this composite material allows for the production of high value-added chemicals for use as fuels. This reaction also mitigates carbon dioxide emissions, thus reducing the greenhouse effect. Therefore, this application contributes to solving environmental problems and energy crisis.

3.2 Photocatalytic Hydrogen Production from Water Splitting

The first step in photocatalytic hydrogen production from water splitting is the rapid migration of electrons and holes generated by photoexcitation to the surface of the photocatalyst. Afterwards, the electrons will combine with H^+ in water to produce H_2. However, the holes attached to the metal oxides are then consumed by reaction with

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sacrificial agents in water or combine with OH^- to produce O_2. After effective doping or composite of graphene and semiconductor photocatalysts, the photogenerated charge migration rate can be accelerated due to the conductivity of graphene, which reduces the probability of carrier recombination, thus effectively improving the photocatalytic activity of the composites. Chang's group has prepared many groups of composites using graphene for photocatalytic hydrogen production from water splitting. It was found that MoS_2-GR-CdS composite had the highest catalytic activity. This is due to the high activity of H^+ adsorbed by S atoms with unsaturated activity at the bare edges of MoS_2, and the photogenerated electrons can react with H^+ to form H_2 either directly or through graphene. The introduction of graphene enhances the photogenerated charge transfer and inhibits electron-hole pair recombination, thus improving the efficiency of photocatalytic hydrogen production from water splitting[12]. Photocatalytic hydrogen production from water splitting using graphene composites can effectively stimulate the potential of hydrogen production from water splitting to enhance the energy reuse. It can be widely used in the hydrogen energy industry, providing a source of clean fuel and effectively reducing carbon emissions.

3.3 Photocatalytic Degradation of Organic Pollutants

In the process of photocatalytic degradation of organic pollutants, the first step is to excite the photocatalysts. When the photocatalyst absorbs light energy greater than or equal to the band gap energy of the catalyst, the electrons in the valence band of the catalyst jump to the conduction band, thus generating photogenerated holes in the valence band with strong oxidative properties. Then the next step is the formation of free radicals. The electrons that jump to the conduction band react with O_2 to form $\cdot O^{2-}$, and the photogenerated holes can produce ·OH with water molecules. The final step is the degradation of organic pollutants. $\cdot O^{2-}$ and ·OH are both strong oxydative radical groups, which are capable of oxidizing and degrading organic pollutants to form H_2O and CO_2. Whereas graphene has a high carrier mobility and can rapidly transport photogenerated electrons to the catalyst. This can greatly extend the lifetime of photogenerated carriers and reduce the rate of electron-hole pair recombination. Meanwhile, graphene can also inhibit the agglomeration effect of semiconductor catalyst nanostructures, which is conducive to increasing the specific surface area of the catalyst and improving its photocatalytic activity. Therefore, graphene composites can also be widely used in the field of photocatalytic degradation of organic pollutants.

Graphene composites can be used for both wastewater treatment and air purification. Du's group prepares TiO_2-graphene films and uses them to degrade methylene blue solution. Since graphene can act as an acceptor for the photogenerated electrons produced by TiO_2, inhibiting electron-hole pair recombination, this film has more photogenerated holes involved in the degradation of methylene blue compared to those generated by pure TiO_2 as a catalyst, and the photocatalytic efficiency is greatly improved[13]. Ling's team successfully prepared a ternary composite photocatalyst consisting of BiOBr, RGO and diatomite using the solvothermal method. This photocatalyst can be applied to the degradation of formaldehyde, and the degradation rate could reach 89.6% at 3 h. Moreover, the composite catalyst can be recycled with no significant decrease in catalytic efficiency[14].

These graphene composites, which are catalytic for the degradation of organic pollutants, are conducive to playing an important role in environmental governance. They can effectively promote the purification of industrial wastewater, the degradation of harmful gases, and provide a guarantee for sustainable development.

4. Conclusion

Graphene composites can be prepared by the hydrothermal method, thermal hydrolysis method, and sol-gel method. They are simple, efficient and practical, and are a few of the most common ways to prepare graphene composites. Graphene composites also have higher catalytic efficiency and stability compared with traditional photocatalysts, and they also make up for the problem that graphene as a catalyst has fewer highly active sites and is prone to agglomeration.In the field of photocatalysis, graphene composites can efficiently catalyze the hydrogen production from water splitting and CO_2 reduction, as well as the degradation of organic pollutants, due to the unique advantages of graphene composites. This paper reviews the preparation methods and advantages of graphene composites, as well as the current status of their application in the field of photocatalysis, which can provide certain theoretical references for future research related to graphene composites.

Currently, graphene composites have many excellent properties as photocatalysts in the photocatalytic field, but there are still problems such as low catalytic efficiency and high production cost. Future research needs to focus more on the mechanism of the photocatalytic reaction to investigate more efficient pathways for hydrogen production, CO_2 reduction, and organic pollutant degradation. It is also possible to add nanomodified graphene, doped or composite graphene materials in order to explore superior structures. In addition, graphene composites are recycled through different deposition rates of photocatalysts and reactants as well as products. Alternatively, production costs can be reduced by enhancing the stability of the catalyst, allowing it to be separated more easily for recycling.

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