

Application of graphene in photocatalytic water treatment

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Abstract

This paper mainly explains the basic properties of graphene, and the preparation and specific functions of photocatalytic graphene materials. The advantages of photocatalytic graphene materials are introduced in detail. Emphasis is on the application of photocatalytic graphene materials in water purification. Finally, we write about the aspects that can be studied and the shortcomings that can also be improved.

Keywords

Graphene, photocatalysis, clean water purification.

1. Introduction

1.1 The structure and basic physicochemical properties of graphene

In graphene, carbon atoms pass through SP² hybridized to form C=C, and form positive hexagonal with other surrounding carbon atoms, eventually forming a two-dimensional honeycomb lattice structure[1]. Each positive hexagonal unit is actually similar to a benzene ring, and each carbon atom contributing an unbounded single electron on a 2p orbit, thus forming a pi bond structure in the entire graphene plane[2]. Researchers such as Andre Hem believe that two-dimensional monolayer graphene is stable because the graphene surface is not completely flat, but rather nanoscale fluctuations and fold at the microscopic scale[3]. The ideal graphene structure is composed of a flat hexagonal lattice and can be seen as a layer of peeling graphite molecules. Each carbon atom is SP² hybridized and contributes to the remaining electrons on the P orbit to form a large bond. Electrons can move freely, which gives graphene a good electrical conductivity. If there are pentagons and hexagonal in the structure, graphene defects will be formed, and the twelve pentagons will then form fullerene together.

Graphene photocatalytic technology is a new method to improve the self-purification capacity of water bodies. With the help of graphene photocatalytic network, under the sunlight, the toxic organic compounds in the water body can be decomposed, increase the dissolved oxygen content of the water body, gradually get rid of the anaerobic state of the black and smelly water body, activate the beneficial bacteria at the bottom of the river, and restore the purification ability of the water itself. The reaction conditions were mild during the whole process, and the later cleaning was relatively easy.

1.2 An introduction of photocatalytic materials for graphene

Photocatalysis is able to convert light energy into chemical energy, thus enabling purification of air and degradation of organic pollutants in wastewater. It is shown that graphene is combined with a semiconductor optical catalyst, and the normalized two-dimensional planar structure of graphene is used as the carrier of the optical catalyst. On the one hand, the dispersion degree of the catalyst can be improved, on the other hand, the rate of optical charge migration can be accelerated, and the photocatalytic activity of the composite material can be improved.

1.3 Development of photocatalytic technology

In 1976, John.H.Carey et al. found that at TiO₂ turbidity at a concentration of about 50g/L, the reactants for half an hour were completely dechlorinated, without biphenyl in the intermediates[4] . In 1989, Tanaka.K and other found that adding hydrogen peroxide to the photocatalytic system could improve the degradation effect, and studied that the degradation reaction was caused by photocatalysis[5] . This research laid the theoretical foundation for photocatalysis, and points out the direction of future reaction conditions, hydroxy radical is a material with strong oxidation ability with no selectivity for organic pollutants, which makes photocatalytic technology truly accepted by researchers.

2. Body

2.1 Specific functions of photocatalytic graphene materials

2.1.1 It can be used as the collector and transmitter of semiconductor excited electrons

When graphene is introduced into the photocatalytic system, Since many semiconductors have higher guide band levels than the Fermi level of graphene, Photoelectrons are easily transferred from semiconductor to graphene through the interface of semiconductor and graphene, The two-dimensional graphene plane structure consisting of a giant conjugate system can rapidly transfer the electrons into the target reactants with a carrier mobility of $1.5104\text{cm}^2/(\text{V s})$, Also extending the mean freedom range of photoraw electrons, Participating in the formation of a highly active Srilanka, For example, the hydroxy free radical and the hydrogen peroxide free radicals, When the guide band level of the semiconductor is below the Fermi level of graphene, Photoelectrons cannot be transferred from semiconductors to graphene. When the sensitizer is present in the system, the received photons are sensitized to produce electrons because the graphene conductivity exceeds the semiconductor, and the electrons can be transferred from the sensitizer to graphene and then to the semiconductor. The extremely fast conduction speed of graphene and the unique 2-dimensional plane structure can improve the rate of electron migration to semiconductors and then to the reactant surface, increasing the average free range of electrons, which can reduce the recombination of photoraw electrons and holes, and improve the quantum efficiency of photocatalysis.

2.1.2 Light absorption range and intensity can be expanded

When graphene is compound with the semiconductor, under favorable reaction conditions, the semiconductor may occur some degree of chemical interaction with graphene, forming a M-C or M-o-C (M means metal) doping chemical bond even at a certain depth, which is similar to the carbon doping of the semiconductor, forming the doping level, narrowing the bandwidth of the semiconductor, occurring a certain degree of redshift, expanding the response to visible light.

2.1.3 It can enhance the adsorption capacity of the reactants

A large number of electrons of graphene and its unique two-dimensional single atomic layer structure can interact with pollutant molecules, improve the adsorption performance of pollutants on the composite photocatalyst, and thus improve the efficiency of photocatalytic degradation. In addition, compared to the carbon nanomaterials of other geometric structures (graphite, carbon black, activated carbon, carbon fiber, carbon nanotubes, fullerene, etc.), the two-dimensional plane structure of graphene has the largest specific surface area, can provide additional space for the reaction, and is also very beneficial to the dispersion of semiconductor materials, such as reducing reunion and increasing the contact between semiconductor and pollutants.

2.1.4 Some other roles

In addition to the above actions, graphene can also be used as a photosensitizer, photostabilizer, support carrier, etc., to improve the synthesis of photocatalytic materials

2.2 Preparation of graphene-semiconductor composite photocatalytic materials

In-situ growth preparation is usually the mixture of substances such as graphene oxide with the semiconductor precursor in a liquid phase solvent, and then converting the semiconductor precursor into a target semiconductor product through chemical treatment or heat treatment, to grow on graphene, forming a good interface contact.

When GO is used as a precursor to graphene, GO nanosheets can be used because the GO surface contains rich oxygen-containing functional groups and a large number of defects. It provides a shaped nucleation point for the growth of the semiconductor catalyst and regulates the size, morphology, and crystallinity of the semiconductor elements. During in situ preparation, the GO can be reduced to RGO, by chemical, thermal, and light treatment to form a graphene semiconductor composite photocatalytic material. Similarly, when organic compounds are used in a graphene precursor, they can also be mixed with the precursor of the semiconductor to form a uniform structure. After chemical and heat treatment, the organic compounds react, and the semiconductor precursor is converted into a target product, forming a semiconductor composite photocatalytic material of graphene with good interface contact. In the preparation of graphene semiconductor composites in situ with GO and organic matter as the graphene precursor, additional catalyst and adhesive are usually not required, so the experimental preparation step is relatively simple, which ensures that a clean interface contact forms between the graphene component and the semiconductor component. Unlike GO and organic precursors, SEG usually requires modification to increase the number of its surface functional groups, which overcomes the disadvantage that SEG does not easily disperse and reunite in water and organic solvents and improves its processing performance. Moreover, the uniform functional group on the SEG surface can also regulate the growth of the semiconductor elements and enhance the interaction between graphene and the semiconductor.

2.3 Application of graphene photocatalytic materials in water treatment

2.3.1 Purse the pollutants in the water

Organic pollutants in water mainly include dyes, pesticides, phenols, halide, adipose hydrocarbons, polycyclic aromatic hydrocarbons, nitroaromatic hydrocarbons, polycyclic compounds, hydrocarbons, surfactants, etc. Phenols, organic chlorine and aromatic organic compounds are considered to be the most toxic to the most environmental hazards, with strong toxicity, wide distribution, long environmental retention time, and difficult to deal with other methods[6]. However, semiconductor materials by light can produce holes with superoxidation capabilities, degrade many organic pollutants by photocatalytic oxidation and convert them completely into non-toxic simple inorganic substances such as CO₂ and H₂O [7]. Therefore, there are broad prospects for treating organic pollutants using semiconductor photocatalytic technology. For example, Wang Xinchun, a professor of Fuzhou University, developed Zn-Ge-nitrogen oxide catalyst, and Zhu Yongfa of Tsinghua University developed F doped Zn WO₄ catalytic materials to achieve good degradation of chlorophen (4CP) [8].

2.3.2 Purse the industrial wastewater

With the development of industry, industrial wastewater also brings many problems to people's lives, and the pollution brought by industrial wastewater seriously endangers human health and ecosystem. Compared with conventional materials, the advantages of photocatalytic graphene materials are degradation, mineralized pollutants.

Sixvalent chromium is a carcinogenic heavy metal environmental pollutant. Due to its good water soluble, it is easy to adsorb on the surface of other substances, thus polluting a variety of water sources. On the other hand, trivalent chromium is a non-toxic heavy metal oxidation state, poor mobility, easy precipitation separation. Therefore, reducing hexavalent chromium to trivalent chromium has become a more common means of governance.

Kumordzi et al. combined with the hydrothermal method of the TiO₂-GR composite photocatalyst to reduce the common 2 + photocatalyst in Zn to Zn[9] . The results showed that the photocatalytic

reduction rate for Zn²⁺ was increased by% (20.30.04) when compared to the TiO₂ without GR. This is because the composite photocatalyst has more adsorption sites, and the presence of GR reduces the band gap of TiO₂ and facilitates the effective separation of photocarriers.

AgBiO₃/GO/NCDs ternary composite photocatalytic material was prepared in situ on the go/NCDs (N-point) doped carbon agbio₃, matrix using Yue et al. The degradation activity of organic pollutants such as tetracycline, phenol, and tetracycline was significantly enhanced[10]. GO promotes the rapid transfer of photoraw electrons and the formation of active oxides, improving the photocatalytic activity of the material. In addition, NCDs as an active reaction site also promotes the photocatalytic reaction. Therefore, it can be argued that the degradation properties of a single semiconductor material can be significantly improved by the construction of a suitable multi-component system.

3. Conclusion

From the current research, the main breakthrough in graphene application in the field of water treatment lies in the cross-study of materials, chemistry, and environmental treatment. The study of graphene composites is mainly based on the pollutant removal properties of the material itself and enhances the adsorption, electron transfer and reduction capabilities by combining with graphene carbon materials. The mechanism of pollutant removal of graphene and its composites is unclear. Based on the mechanism, there is a lot of room for exploring the removal of heavy metal, inorganic substances and pollutants in the water, especially the new non-biodegradable pollutants. Moreover, the stability of graphene and its composites needs to be improved. Large-scale preparation of stable graphene composites is also a difficult problem for the widespread application of graphene in water treatment. The application of easily separable and environment-friendly magnetic graphene composite in water treatment has broad development prospects, but it still takes time in water treatment engineering.

References

- [1] Zh. YW, Murali. S, Cai. W. W, et. al. Graphene. and graphene oxide: synthesis, properties, and applications [J]. Adv. Mater, 2010, 22(35): 3906-3924.
- [2] Mishchenko E G. Effect of electron-electron interactions on the conductivity of clean graphene [J]. Phys. Rev. Lett, 2007, 98(21): 216801.
- [3] Meyer J C, Geim A K, Katsnelson M I, et al. The structure of suspended graphene sheets [J]. Nature, 2007, 446(7131): 60-63.
- [4] Carey J H, Lawrence J, Tosine H M. Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions [J]. Bulletin of Environmental Contamination & Toxicology, 1976, 16(6): 697-701.
- [5] Tanaka K, Hisanaga T, Harada K. ChemInform Abstract: Photocatalytic Degradation of Organohalide Compounds in Semiconductor Suspension with Added Hydrogen Peroxide [J]. Cheminform, 1989, 20(28): no-no.
- [6] Rubio, V, Valverde, M, Rojas, E. Effects of atmospheric pollutants on the survival pathway. [J] Environmental Science and Pollution Research. 2010, 17, 369-382.
- [7] Heathwaite, A. L. Multiple stressors on water availability at global to catchment scales: understanding human impact on nutrient cycles to protect water quality and water availability in the long term. [J] Freshwater Biology. 2010, 55, 241-257.
- [8] Zhang Yaozhong, Kong Xin, Zhou Yuexi, Study of Photocatalytic Degradation of Organic Industrial Waste Water [J]. Water Supply and Drainage in China, 2003, 19, 5-8
- [9] K UMORDZI G, MAEK SHOAR G, YANFUL E K, et al. So-lar photocatalytic degradation of Zn²⁺ using graphene based TiO₂ [J]. Separation and Purification Technology, 2016, 168: 294-301.
- [10] YUEX. MIAOX. SHENX. et al. Flower like silver bismuthate supported on nitrogen doped carbon dots modified graphene oxide sheets with excellent degradation activity for organic pollutants [J]. Journal of Colloid and Interface Science. 2019, 540: 167-176.