

Review of the development of graphene and application in photocatalyst

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Abstract. Graphene was originally found as a thin sheet structure. Researchers have expanded their studies to include this 2D carbon structure in recent years. The paper aims to give a review of the development of graphene and its application in photocatalysts based on existing research literature and data. The result shows that, currently, graphene-based nanomaterials for medical applications are a popular research topic. In this paper, the structure, characteristics, synthesis and surface modification of graphene is classified into covalent and non-covalent approaches.

Keywords: graphene, new material, catalyst, nano material, preparation.

1. Introduction

Graphene is a sheet of carbon — a material used in pencil leads. These two-dimensional carbon layers are potential to form various forms(e.g. quantum dots, nanoflakes, and nanoparticles). These materials can be sliced to enable new products[1]. The same atoms are present in graphite, which is a ligand of carbon, but they are organized differently, giving the substance various properties. For instance, despite the fact that both diamond and graphite are carbon compounds, their characteristics are significantly dissimilar. Diamond has amazing strength, while graphite is fragile. The atoms of graphene are arranged into hexagons. With multiple excellent properties and important prospects in science and industry, graphene is considered to be a revolutionary material of the future[2]. Based on the data and research literature already available, the paper aims to provide an overview of the creation of graphene and its use in photocatalysts. The significance of studying graphene is to replace traditional materials to improve the efficiency of industrial processing.

2. Preparation

Physicists Andre Geim and Konstantin Novoselov at the University of Manchester, UK, have successfully isolated graphene from graphite for the first time using micromechanical stripping. With the further study of graphene, the researchers have come up with a variety of practical graphene preparation methods.

2.1. Method of chemical vapor deposition(CVD)

The CVD method refers to the chemical reaction of the reaction under gas conditions, followed by the production of solid material on the surface of the heated matrix to achieve solid material technology. Currently, the CVD approach is used to produce graphene by introducing hydrocarbons and other

carbon-containing gases into a simple tubular deposition furnace. Graphene is formed by splitting carbon atoms into carbon atoms and depositing them on the surface of nickel, which is then chemically etched to separate the nickel leaves from the graphene sheet. The conductivity of the film is as high as $1.1 \times 10^6 \text{ S/m}$ when the light transmittance is 80%. Large areas of high-quality graphene can be prepared by the CVD method, but single crystals of nickel are very expensive. This method can meet the requirements for high quality and scale-like graphene preparation, but the complexity and high cost of the process limits the widespread use of the method[3].

2.2. Solvent stripping procedure

Low concentration dispersion is produced by dispersing a small amount of graphite in a solvent, and then destroying the VDW forces between the graphite layers by ultrasound. The solvent can be successfully introduced into the graphite layers and then shed layer by layer. High quality graphite can be obtained by separating the solvent without damaging the surface of the graphene. It allows the wide use of graphene in microelectronics, multifunctional composites and many other fields[4].

2.3. Oxidation-reduction method

The so-called oxidation-reduction method, the essence of which is to make natural graphite, strong acid and strong oxidizing substances react and generate graphite oxide, and then ultrasonic dispersion can complete the preparation of graphene oxide. Graphene is created by first preparing GO, adding a reducing agent to remove it, and then reducing and removing oxygen-containing compounds from its surface, such as carboxyl groups and epoxy groups. Since this method was proposed, it is simple and easy to make. The preparation process has become the most common and easiest method for preparing graphene in the laboratory. However, this method also has drawbacks. For example, if the topology of seven-membered ring and five-membered ring is defective, or the OH group structure is defective, the electrical properties of graphene will be damaged, which limits its application[5].

2.4. Electrochemical reaction

By using two methods parallel to the high-purity graphite rod, insert it into the ionic liquid solution, and control the electric potential between 10V and 20V. After thirty minutes, the anode rod is in corrosion, and the cations in the solution are eliminated to form radicals. These free radicals are combined with the existing electronic graphene film, and the ionic liquid formed by graphene is functionalized. The sediment in the electrolytic cell is then washed with absolute ethanol and then put under 60 degrees Celsius for 2 hours to gain graphene. However, the graphene prepared by this method has a thicker sheet than the single atomic layer[6].

3. Application of graphene — photocatalyst mechanism

Semiconductor materials are extensively utilized in photocatalysis on account of their special electronic structure. In simple terms, the electrons in a semiconductor fill a number of lower energy bands called full bands, with the highest energy full band is called the valence band(VB). Above the VB there is a series of empty bands, and the lowest energy empty band is called the conduction band (CB). A gap exists between the VB and the CB. The width of the band gap(E_g), represents the energy gap between the peak of the VB and the bottom of the CB, i.e. the minimum energy required for an electron in the VB to jump out of a covalent bond into the CB. When a semiconductor material is exposed to light with an energy greater than or equal to E_g , a few electrons in the VB are activated to the higher energy CB, and this electron leap causes the CB to contain electrons(e^-), while the relative holes(h^+) appear in VB, thus forming an electron-hole pair that can participate in conducting electricity under the action of an external electric field.

The electron-hole pairs formed by the electron leap are able to migrate to the surface of the semiconductor under the action of the space charge layer. The electrons will react with O_2 etc. to produce various reactive oxides, while the holes may react with OH^- or H_2O on the surface to produce the strongly oxidizing $\cdot OH$, and a series of redox reactions will then occur, driving the entire photocatalytic

reaction, as shown in processes (1) to (5) in Figure 1. However, the electrons and holes generated by photoexcitation may recombine inside or on the surface of the semiconductor, as shown in processes (6) and (7) in Figure 1, and the energy is released in the form of light or heat, resulting in a reduction in photocatalytic efficiency.

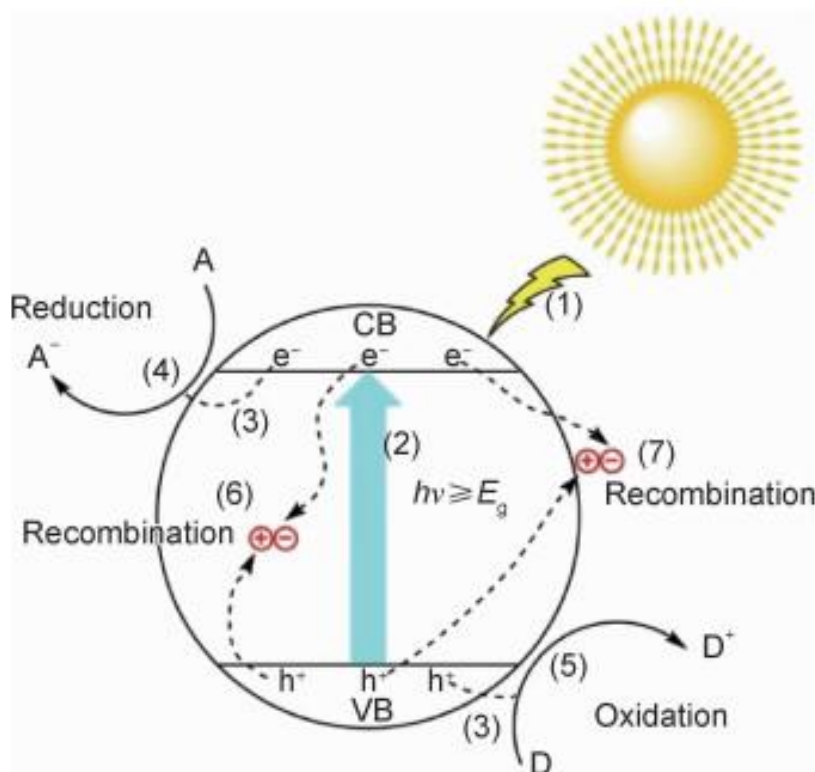


Figure 1. Photocatalysis mechanism[7].

To drive the photocatalytic reaction, not only does the light energy needs to be greater than or equal to the band gap width E_g of the semiconductor, but also the position of the CB and VB of the semiconductor material needs to match the electrode potential of the specific REDOX reaction. Specifically, the material whose oxidation potential is above the semiconductor VB position can be oxidized by H^+ . The reduction potential below the semiconductor CB can be reduced by E^- . Figure 2 shows the band positions of several common semiconductor materials. Among them, TiO_2 , Bi_2O_3 , ZnO and WO_3 all have positive VB potentials, indicating that their photogenerated holes have strong oxidation capacity and can even oxidize H_2O to OH .

On the contrary, their photogenerated electrons have a weak reduction capacity. On the other hand, CdS and $g-C_3N_4$ have relatively negative conduction potential, which indicates that they have strong photogenerated electron reduction ability, can reduce CO_2 to CO , CH_3OH and other organic substances, and can also generate superoxide radical with oxygen, but their photogenerated hole oxidation ability is weak. The most studied photocatalytic reactions are the catalytic cracking of water to produce H_2 or O_3 , the degradation and mineralization of pollutants, and the reduction of CO_2 to produce organic matter. In practical applications, the corresponding semiconductor catalytic materials can be selected according to the electrode potential of the desired reaction.

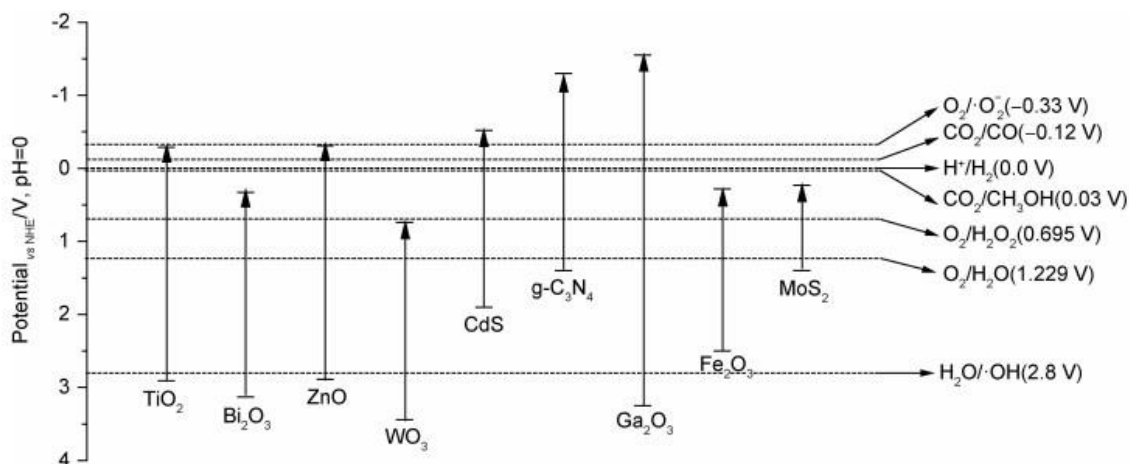


Figure 2. Electron energy band[8].

It should be noted that a single semiconductor photocatalytic material cannot have strong REDOX capacity and a wide light absorption range at the same time. Although Ga_2O_3 has strong reduction and oxidation capacity of photogenerated electrons and holes, it can only absorb short-wave ultraviolet light due to its large bandgap width. In addition, the high recombination rate of photogenerated electron-hole pair, poor absorbability, easy agglomeration, and easy photo corrosion are common problems of semiconductor photocatalytic materials. Therefore, it is necessary to modify a single semiconductor material to improve the photocatalytic ability.

With its excellent performance, graphene can make up for many of the shortcomings of photocatalytic materials. Its high room temperature carrier migration rate can accelerate the separation of photogenerated electron-hole pairs and reduce the probability of recombination. Huge specific surface area can be fast adsorption of reactants to the surface of a catalytic material, accelerate photocatalytic oxidation reduction reaction, as to support the carrier can make the photocatalyst dispersed uniformly, effectively restrain the reunion, as light stabilizer light catalyst light corrosion inhibition, and graphene in the photocatalytic materials are widely used due to its unique structure[9]. (as shown in Figure 3).

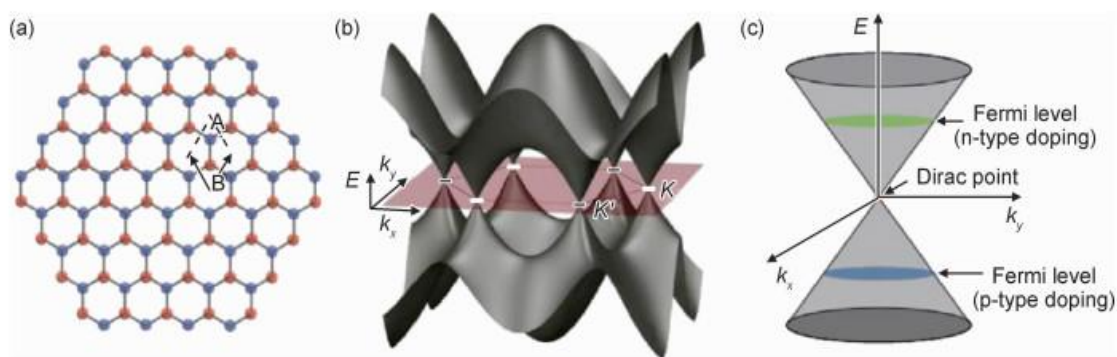


Figure 3. Structure of graphene[10].

Because graphene effectively promotes charge separation and transport, the P25-GR composite created by Zhang et al. shows outstanding visible light catalytic activity in the degradation of methylene blue [11]. The electrons excited in the TiO_2 CB are transferred to graphene through percolation, and the excellent conductivity of graphene accelerates the transport of charge carriers, thus fostering the effective division of photocatalytic electron-hole pairs and restraining their reorganization [12]. Ren et al. used a hydrothermal method to composite an efficient CDS-GR photocatalytic material, which can alternatively oxidize benzyl alcohol to benzaldehyde under visible light exposure and mild conditions [13]. The increased conductivity and improved light absorption of graphene are primarily responsible

for the increase in photocatalytic efficiency. When exposed to visible light, electrons in the CdS VB go to the conduction band. The lifespan of photogenerated electron-hole pairs is extended and the photocatalytic effectiveness is increased as a result of electrons being transported from the conduction band to graphene due to its superior conductivity and close contact with CdS.

4. Conclusion

This paper summarizes the preparation of graphene at present and the basic role of graphene in photocatalytic materials, and introduces the types and preparation methods of graphene photocatalytic materials. The enhancement mechanism of graphene on photocatalysis also needs to be further studied. Nowadays, various electrochemical detection methods and in situ monitoring technology are developing rapidly. Only by designing multi-level verification experiments to further understand its internal mechanism can we better guide the synthesis of materials. Research on graphene materials is still going on, and its great advantages in the field of environmental purification have been recognized by the public. It is believed that with the continuous deepening of research, it will be able to complete industrial production one day, which will benefit the ecological environment and human life. At present, the preparation of graphene still has disadvantages of the complicated production process and low yield. My future research direction will mainly focus on the preparation method optimization of graphene and other nanomaterials.

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References

- [1] Yifan Ren, Fei Yu, Xin-Gui Li, Jie Ma, 2021, Recent progress on adsorption and membrane separation for organic contaminants on multi-dimensional graphene, *Materials Today Chemistry*, Volume 22, 100603, ISSN 2468-5194.
- [2] Tian Tian, Lu Min, Tian Yang, Sun Yanhong, Li Xiaoxia, & Fan Chunhai, et al. (2014). Research progress on biosafety of graphene. *Chinese Science Bulletin* (20), 10.
- [3] Li, X.S., Cai, W.W., Colombo, L. and Ruoff, R.S. (2009). Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling. *Nano Letters*, 9, 4268-4272.
- [4] Han B. 2019. Liquid phase stripping, surface modification of graphene and its application in PDMS composite modification[D]. Zhejiang University of Technology.
- [5] Zhou Feng, Wan Xin, Fu Yingqing. 2011. Preparation and adsorption properties of graphene by graphite oxide reduction method[J]. *Journal of Shenzhen University: Science & Technology*, 28(5):4.
- [6] Li Zaijun, Zhou Linting, Niu Yulian, et al. 2012. Electrochemical preparation of graphene/manganese dioxide composites and its application, CN102568847A[P].
- [7] YANG Cheng, SHI Shuang-qiang, HAO Si-jia, CHU Hai-rong, DAI Sheng-long. 2020, Research progress in graphene based photocatalytic materials and applications in environmental purification. *Journal of Materials Engineering*, 48(7): 1-13.
- [8] YANG X, CUI H, LI Y, et al. 2013. Fabrication of Ag₃PO₄-graphene composites with highly efficient and stable visible light photocatalytic performance[J]. *ACS Catalysis*, 3(3): 363-369.
- [9] VOIRY D, SHIN H S, LOH K P, et al. 2018. Low-dimensional catalysts for hydrogen evolution and CO₂ reduction[J]. *Nature Reviews Chemistry*, 2(1): 0105.
- [10] ZHANG H, LV X J, LI Y M, et al. 2010. P25-graphene composite as a high performance photocatalyst[J]. *ACS Nano*, 4(1): 380-386.
- [11] ONG W J, TAN L L, CHAI S P, et al. 2015. Surface charge modification via protonation of graphitic carbon nitride (g-C₃N₄) for electrostatic self-assembly construction of 2D/2D

- reduced graphene oxide (rGO)/g-C₃N₄ nanostructures toward enhanced photocatalytic reduction of carbon dioxide to methane[J]. Nano Energy, 13: 757-770.
- [12] AVOURIS P. 2010. Graphene:electronic and photonic properties and devices[J]. Nano Letters, 10(11): 4285-4294.
- [13] REN Z, ZHANG J, XIAO F X, et al. 2014. Revisiting the construction of graphene-CdS nanocomposites as efficient visible-light-driven photocatalysts for selective organic transformation[J]. Journal of Materials Chemistry A, 2(15): 5330-5339.