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ADVANCEMENT IN THE APPLICATION OF GRAPHENE AND GRAPHENE OXIDE IN FLUORESCENCE MEASUREMENT TECHNIQUES

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Abstract: As a new type of nanomaterial, graphene has some unique physical and chemical properties such as large specific surface area, good chemical stability, good optical and electrical properties, and is widely used in many fields. This article mainly introduces the research and development of fluorescence measurement methods of graphene and graphene oxide in metal ions, drugs, environmental pollutants and other compounds, and also looks forward to their application prospects in the field of measurement.
Keywords: Graphene; Graphene oxide; Fluorescence; Measurement

1 APPLICATION IN DETERMINATION OF METAL IONS

Graphene (G) is a two-dimensional crystal material composed of carbon atoms connected together in a hexagonal honeycomb shape formed by sp2 hybridization. In 2004, Novoselov et al. [1], scientists at the University of Manchester in the United Kingdom, prepared graphene in the laboratory using the tape method. The hexagonal honeycomb structure formed by its six-membered rings forms a large-scale π-π delocalized structure between layers. The special structure gives it many unique properties, including excellent mechanical, optical, thermal and electrical properties. It also has the advantages of large specific surface area, simple synthesis method, low price of raw materials and easy modification. Graphene oxide (GO) is an important derivative of graphene, which is mainly produced by oxidative exfoliation of graphite. Graphene oxide (GO) is an ideal two-dimensional nanomaterial. Its huge honeycomb planar conjugated structure gives it excellent thermal properties, electrical properties, biocompatibility, and quite high specific surface area and mechanical strength [2]. At the same time, a large number of active oxygen-containing functional groups (such as -O-, -OH, etc.) are enriched on the surface of GO, making it easy to disperse in water or other highly polar solvents [3] and facilitate further reactions with other substances to achieve GO surface functionalization. Through non-covalent bond modification and covalent bond modification, various small molecules or polymers can be efficiently grafted on the surface of GO, thereby enriching and improving the performance of GO [4,5]. Due to their large-area conjugated structures, graphene and GO can serve as energy receptors to quench the fluorescence of a variety of organic dyes and quantum dots. They are widely applicable fluorescence quenchers. Compared with traditional quenchers , Graphene material has higher quenching efficiency [6]. In recent years, fluorescence has begun to be combined with graphene. Using the fluorescence quenching properties of graphene, researchers have prepared a series of GO-based fluorescence sensors [7,8]. At the same time, because the surface of GO contains a large number of hydrophilic groups and is a carbon-based material, it is non-toxic and harmless to organisms and environmentally friendly.

Li Zhengshun et al. [9] synthesized graphene oxide using an improved Hummer method, and used a time-resolved spectral detection system to explore in detail the fluorescence quenching physics of graphene oxide by Fe^{3+} (concentrations of 0.5, 1, and 2 mmol/L). mechanism. In the steady-state fluorescence emission spectrum, as the Fe^{3+} concentration increases, the fluorescence intensity of graphene oxide decreases sharply. Time-resolved fluorescence spectroscopy and femtosecond transient absorption spectroscopy studies have confirmed that there is basically no change in the kinetic decay curve of GO added with different concentrations of Fe^{3+}. The fluorescence quenching of graphene oxide by Fe^{3+} is mainly a static fluorescence quenching process.

Zhu Yufeng et al. [10] in alkaline medium, graphene oxide adsorbed acridine orange (AO), which can quench the fluorescence of AO. By adding an appropriate amount of cadmium (II) ions, the fluorescence of the system at 526nm was enhanced. , the ΔF value has a good linear relationship with the cadmium (II) ion concentration in the range of 2.97×10 ~4.40×10 -8 mol/L. The linear regression equation is ΔF = 5.318 c(10 mol/L) + 13.34, r = 0.9970, the detection limit is 8.90×10mol/L, and the relative standard deviation is 1.58%~2.52%.

In order to study the fluorescence method of rapid detection of mercury ions in water, Liu Le et al. [11] designed a ssDNA sequence with a 5'-end labeled fluorescent dye (FAM) that can specifically bind mercury ions, and used graphene oxide to detect ssDNA and T- The difference in the affinity of the Hg^{2+}-T complex and the efficient quenching of fluorescence signals by graphene oxide have established a fluorescence method that can quickly and sensitively detect mercury ions in water. Under optimized test conditions, the detection range of mercury ions in water by this method is 0.1-100 μg/L, and the detection limit is 0.3 μg/L. Moreover, this method is easy to operate and has good selectivity, and is expected to be used for rapid detection of mercury ions in water.

Zhai Qiuge et al. [12] In aqueous solution, graphene oxide (GO) can quench the fluorescence of methylene blue (CMB). Adding an appropriate amount of Bi^{3+} can enhance the fluorescence of the system. The degree of fluorescence recovery increases with the increase in the amount of Bi^{3+}. Based on this, a new method for the determination of Bi^{3+} using graphene oxide-methylene blue fluorescence photometry was established. The effects of the concentration of methylene blue, graphene oxide, acidity and the order of adding reagents on the fluorescence recovery of the system were investigated. The excitation wavelength of the complex system is 667 nm and the emission wavelength is 690 nm. Under optimized conditions, the concentration of Bi^{3+} is between 0.5 and 100 There is a good linear relationship with fluorescence intensity within the range of μmol·L-1, and the correlation coefficient is 0.9955. The detection limit of the method is 1.0×10-8 mol·L-1 (S/N =3). The new method has the advantages of high sensitivity, rapidity, and low cost. The proposed method was used for the analysis of environmental water samples, and the recovery rate was 93.4%~105.2%.

2 APPLICATION IN DRUG DETERMINATION

Ma Cuiping et al. [13] found that graphene oxide quenched the fluorescence of acridine orange in an acidic medium. Adding an appropriate amount of dopamine at this time resulted in an enhancement of the fluorescence intensity of the system, and the degree of enhancement was proportional to the amount of dopamine added. Based on this, a method for the determination of dopamine by acridine orange-graphene oxide fluorescence photometry was established. The mass concentration of dopamine is linear in the range of 0.05~12.0 μmol/L. The linear equation is ΔIF= 3.9 +57.8c(μmol/L), the correlation coefficient r= 0.9933; the detection limit is 2.9 nmol/L. This method has good selectivity and was applied to the determination of actual samples with satisfactory results.

Guo Ying et al. [14] used graphene oxide as a single carbon source and prepared graphene quantum dots (GQDs) with uniform morphology, good monodispersity and a size of about 5 nm through a simple ultrasonic-hydrothermal method. The prepared GQDs not only possess strong blue fluorescence emission but also have excitation wavelength-dependent fluorescence. Using GQD as the energy donor and vitamin B2 (VB2) as the energy acceptor, a fluorescence energy transfer system was established to detect VB2 content. Under optimized conditions, the detection range of this method is 1.0 × 10-6 ~ 3.0 ×10-5 mol·L-1, the correlation coefficient is 0.9978, and the detection limit is 3.3×10-7 mol·L-1.

Liao Juan et al. [15] used fluorescence spectroscopy to study the mechanism of action of graphene oxide nanoparticles (NGO) on bovine serum albumin (BSA). The results show that the fluorescence quenching type of BSA by NGO is mainly dynamic quenching and static and dynamic mixed quenching. At T= 283, 298, and 310 K, the minimum binding constants of the two are 6.7× 109, 9.5× 107, and 2.1× 106 L mol-1 respectively. The numbers of binding sites are 2.12, 1.32, and 0.87 respectively. The type of interaction between NGO and BSA is determined by thermodynamic parameters to be hydrogen bonding and van der Waals force. NGO quenches the fluorescence of tryptophan residues in BSA without changing the fluorescence emission intensity of tyrosine residues, but reduces the hydrophobicity of its environment.

Wei Hailang et al. [16] used new nanomaterials combined with fluorescence methods to achieve simple and rapid detection of pyrogallic acid in water samples. Graphene with fluorescent properties was prepared through a simple method of high-temperature pyrolysis of citric acid. Experiments found that horseradish peroxidase was used as a catalyst to catalyze the reaction of pyrogallic acid, and the changes in the fluorescence properties of graphene were used to focus on pyrogallic acid. Acid was quantitatively determined. In a phosphate buffer solution with pH=7.8, pyrogallic acid reacts under the action of a catalytic enzyme to form a colored substance, quinone, which can quickly quench the fluorescence intensity of graphene. Based on this, a pyrogallic acid fluorescence quenching detection method was designed. The experiment found that with the continuous addition of pyrogallic acid, the fluorescence quenching phenomenon gradually increased and showed good linearity.

Gong Qiaojuan et al. [17] used an improved Hummers method to prepare graphene oxide, and used infrared, Raman spectroscopy, and scanning electron microscopy to characterize the structure and morphology of graphene oxide, and investigated the effects of different solvents on L-tryptophan. Effect of fluorescence spectrum; L-tryptophan and graphene oxide were used as fluorescent agent and fluorescence quencher respectively, and the fluorescence quenching effect of graphene oxide on L-tryptophan was studied with the help of fluorescence spectroscopy. According to the ultraviolet absorption spectrum, Stern-Volmer equation and Lineeweawer-Burk double reciprocal curve equation, parameters such as graphene oxide's fluorescence quenching type of L-tryptophan, quenching rate constant (kq) and binding constant (K) were obtained . The results show that graphene oxide has a strong quenching effect on the fluorescence of L-tryptophan, and its fluorescence quenching mechanism is the static quenching of the complex formed by graphene oxide and L-tryptophan.

3 APPLICATION IN DETERMINATION OF ENVIRONMENTAL POLLUTANTS

Ye Qing et al. [18] synthesized magnetic graphene through hydrothermal reaction, used magnetic graphene as magnetic solid phase extraction material, and established a new method for the determination of trace amounts of bisphenol A in water combined with fluorescence photometry. The effects of parameters such as the amount of magnetic graphene, the type and volume of eluent, and the time of extraction and elution were investigated. Under the optimized experimental conditions, the detection limit of the method was 3.3 ng/L, the linear range was 0.01-0.5 μg/L, the correlation coefficient was 0.9995, and the relative standard deviation was 4.1%. The method was applied to the analysis of the dissolution of bisphenol A in disposable water cups, and the recovery rate of standard addition was between 96% and 105%.

Zhang Tairan et al. [19] used a two-step reduction method to reduce graphene oxide (GO), and during the reduction process, the graphene surface was sulfonated through a diazonium salt reaction, which improved the solubility of graphene in water. Atomic force microscopy (AFM), ultraviolet-visible absorption spectroscopy (UV-vis), Raman spectroscopy (Raman) and X-ray photoelectron spectroscopy (XPS) were used to study the morphology of graphene and the composition and structure changes during the reduction process. Characterized. After reduction and sulfonation of graphene, a large number of oxygen-containing functional groups on the carbon atom plane disappear. The size of the obtained graphene sheet is about 1 μm, the number of layers is roughly double layer, and it can be evenly and stably dispersed in water. On this basis, the behavior of graphene as a fluorescence quenching substrate in quenching the high quantum efficiency fluorescent dye rhodamine B solution was studied, confirming that graphene is a good fluorescence quencher. This lays the foundation for its applications in fluorescence detection and biomolecule sensing.

Liu Zhongde et al. [20] used graphene oxide as the precursor and gallic acid as the reducing agent and stabilizer to synthesize reduced graphene oxide in one step through a simple water bath heating method. A series of analysis and characterization of the product were carried out using UV-visible absorption spectrum, Fourier transform infrared spectrum, Raman spectrum, X-ray diffraction and scanning electron microscope. The results show that gallic acid can reduce graphene oxide to graphene. In addition, the effect of the prepared reduced graphene oxide on the fluorescence intensity of anionic and cationic fluorescent functional groups was also investigated. The results show that reduced graphene oxide synthesized through gallic acid-mediated synthesis can effectively quench the fluorescence of cationic functional groups such as rhodamine and enhance the fluorescence of anionic functional groups such as fluorescein, so that fluorescent functional groups can be selectively identified.

Wang Shuhui et al. [21] successfully synthesized β-cyclodextrin (β-CD) modified graphene (β-CD-GNs) using a wet chemical method, and discussed its effect on α-naphthol and β-naphthol in aqueous solution. identification function. The results show that graphene-functionalized β-CD can recognize α-naphthol and β-naphthol at the same time, causing their fluorescence to be quenched; the quenching of α-naphthol by β-CD-GNs includes the entry of α-naphthol into β-naphthol. The quenching caused by the inner cavity of -CD and the π-π interaction between graphene and α-naphthol, while the quenching of β-naphthol by β-CD-GNs is mainly due to the interaction between graphene and β-naphthol. Due to π-π interactions between phenols.

4 CONCLUSION

As a well-known natural phenomenon with a long history, cathode fluorescence of graphene has been fully and extensively studied in theory and application. Graphene has a unique structure, stable physical and chemical properties, good biocompatibility and excellent electrical, thermal, mechanical and other properties. Graphene has very attractive applications in the determination of metal ions, drugs and environmental pollutants. prospect. Since graphene has a fixed structure and properties, its development and application are also subject to corresponding restrictions. Introducing specific functional groups on the surface of graphene can greatly expand the application range of graphene, endow graphene with various new functions, and improve the compatibility of graphene with other matrices. At the same time, almost any active group loaded onto graphene, a surface with a huge specific surface area, can actively demonstrate its application performance. Functionalized modified graphene has become a hot research topic today. A large number of novel graphene-based Functional hybrid materials have been reported one after another. However, in the fluorescence sensing process, the role of functionalized graphene is mostly to quench fluorescence rather than to generate fluorescence. It is hoped that in future research on graphene fluorescence sensors, functionalized graphene materials that can generate fluorescent signals will be developed to improve the sensitivity and accuracy of detection methods. In short, the application of graphene-based optical sensors is an emerging field that deserves great attention.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

REFERENCES

[1] KS Novoselov, AK Geim, SV Morozov. Electric field effect in atomically thin carbon films. Science, 2004, 306(96): 666-669.

[2] Zhang Hao, Cui Hua. Graphene oxide fluorescence sensor. Advances in Chemistry, 2012, 24, (8): 1554-1559.

[3] Han X, Fang X, ShiA. An electrochemical DNA biosensor based on gold nanorods decorated graphene oxide sheets for sensing platform. Analytical biochemistry, 2013, 443(2): 117-123.

[4] Lin Yuanwei, Guo Xuefeng. Chemical modification of graphene surface interface and its functional regulation. Acta Chemica Sinica, 2014, 72(3): 277-288.

[5] Yang Cheng, Chen Yubin, Tian Junpeng. Research progress on the preparation and application of functionalized graphene, Journal of Aeronautical Materials, 2016, 36 (3): 40-56.

[6] Gao Yuan, Li Yan, Su Xingguang. Research progress on graphene-based optical biosensors, Analytical Chemistry, 2013, 41(2): 174-180.

[7] Gao Yuan, Li Yan, Su Xingguang. DNA sensor based on graphene oxide quenching effect for specific detection of melamine, Nuclear Technology, 2012, 35(5): 386-389.

[8] Li Wei, Liu Zheng, Wei Xi. Application study on rapid detection of tartrazine content based on indigo double Schiff base graphene oxide fluorescence sensor, Chinese Food Additives, 2014, 25(9): 195-200.
[9] Li Zhengshun, Wang Yan, Wang Lei. Study on the fluorescence quenching mechanism of graphene oxide by Fe3+, China Optics, 2016, 9(5): 569-578.
[10] Zhu Yufeng, Peng Lilan, Wang Yongsheng. Determination of cadmium (II) ions by graphene oxide-acridine orange fluorescence photometry, Applied Chemical Engineering, 2016, 45(7): 1379-1381
[11] Liu Le, Wu Yuangen, Zhan Shenshan. Graphene oxide high-efficiency quenching fluorescence method for rapid detection of mercury ions in water, Journal of Shanghai Jiao Tong University (Agricultural Science Edition), 2014, 32(6): 1-6.
[12] Zhai Qiuge, Guo Peng, Zhou Lin. Sensitive determination of bismuth (III) ions by fluorescence photometry of graphene oxide-methylene blue system, Spectroscopy and Spectral Analysis, 2014, 34(8): 2152-2156.
[13] Ma Cuiping. Determination of dopamine by acridine orange-graphene oxide fluorescence quenching method, Journal of Analytical Testing, 2011, 30(3): 340-343.
[14] Guo Ying, Liu Yang, Zhao Qin. Graphene quantum dots-VB2 determination of VB2 by fluorescence energy transfer method, Guangzhou Chemical Industry, 2014, 42(23): 138-139, 173.
[15] Liao Juan, Zhang Yanhua, Ye Xiaozhou. Interaction between graphene oxide nanoparticles and bovine serum albumin, Spectroscopy Laboratory, 2013, 30(5): 2235-2241.
[16] Wei Hailang, Cao Liming. Experimental study on the detection of pyrogallic acid by fluorescence quenching method, Journal of Shanxi University (Natural Science Edition), 2015, 38(4): 670-674.
[17] Gong Qiaojuan, Wang Yongdong, Yang Haiying. Study on the fluorescence quenching of L-tryptophan by graphene oxide and its mechanism, New Carbon Materials, 2016, 31(6): 639-645.
[18] Ye Qing, Liu Xiaofei, Hong Liming. Magnetic graphene solid-phase extraction fluorescence photometry to determine the dissolution of bisphenol A in disposable water cups, Analytical Laboratory, 2016, 35(7): 806-808.
[19] Zhang Tairan, Sun Luwei, He Haiping. Chemical preparation of water-soluble graphene and its fluorescence quenching application, Journal of Materials Science and Engineering, 2013, 31(4): 484-488.
[20] Liu Zhongde, Liu Chunfang, Yang Hui. Selective recognition of fluorescent functional groups by gallic acid-mediated synthesis of reduced graphene oxide, Science China: Chemistry, 2014, 44(3): 358-365.
[21] Wang Shuhui, Huang Yuming. Fluorescence method to study the recognition effect of β-cyclodextrin modified graphene on α-naphthol and β-naphthol, Journal of Southwest University (Natural Science Edition), 2015, 37(7): 129-132.