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Research Progress on Graphene-Based Sensing Mechanism and Devices in Food Safety and Food Freshness

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Abstract: Food safety is a major basic guarantee for both public health and life safety in modern industrial society. The freshness and safety testing of food are like an indispensable protective wall. Traditional analysis methods such as chromatography, mass spectrometry are cumbersome to operate. There are also limitations such as high cost and time-consuming. This paper clarifies the adsorption mechanism of graphene-based on the relevant gases generated by food spoilage and the liquid sensing mechanism of additives that endanger food safety, summarizing different modification methods. It sorts out the sensor devices and specific applications adapted to food safety and food freshness, looking forward to the challenges and future development trends in this field.

Keywords: Graphene-based; Mechanism; Device; Food Safety.

1. Introduction

As a two-dimensional material composed of a single-layer carbon atom structure, graphene's huge surface area and excellent electrical properties enable it to convert gas molecular signals into electrical signals. These unique gas-sensitive properties show great application potential in the field of gas sensing and in meeting the urgent need for high-efficiency detection of food. The graphene base is a series of functional materials constructed by modification, compounding, doping and other methods on the basis of graphene, including but not limited to graphene oxide (GO), reduced graphene oxide (RGO), GO polymer [1]. Compared with graphene, it has stronger adsorption ability, more controllable stability and conductivity, and higher sensitivity of the corresponding gas, resulting in its stronger practical industrial application value.

In recent years, graphene and its composite materials have been widely used in the field of sensing. In terms of mechanism, devices and application, there have been in-depth research and analysis by scholars. In terms of mechanism, there are density functional theory [2] and first principle calculation [3]; resistance type [4], SERS type [1] and other different state sensors have been proposed on devices; in terms of application, sensors have shown research potential in corruption markers such as aquatic products and meat.

However, there is a lack of systematic review from mechanism to device to application at present. Therefore, this paper reviews the research progress of graphene-based sensing mechanism and device in food safety and food freshness from the above three dimensions to provide reference for follow-up research.

2. Graphene-based Sensing Mechanism

2.1. Gas Sensing Mechanism

Gas is a major factor in detecting whether food is corrupt. It is inextricably related to the freshness of food. The crystal structure and geometric stability of graphene make it exhibit unique electronic properties. As early as 2007, Schedin et al. [5] found that the resistivity of graphene has a sensitive response to its gas adsorption function and proved that electron molecules such as NO_2 can lead to an increase in the concentration of graphene carriers, which opened the trend of gas-sensitive research on graphene. However, this experimental finding is not enough to explain the microscopic principle of the gas-sensitive mechanism of graphene. Subsequently, Leenaerts and others [3] made up for this limitation through the first principle calculation. They concluded that NO_2 molecules have high electron affinity and show good adsorption energy on the graphene surface, which further confirmed the excellent experimental effect of Schedin and others [5]. Therefore, the above experiments and theories verify that charge transfer is the core mechanism of graphene gas sensing mechanism. Unfortunately, due to the zero-band gap structure of graphene, there is still room for improvement in its capture and adsorption distance to gas molecules. The researchers also made an in-depth analysis of the gas adsorption properties of composite graphene groups.

Wan Yuwei and others [6] used the first principle to study the adsorption properties of Ag and Cu-doxid graphene on NH_3. They proposed that the formation of chemical bonds between Ag atoms and N atoms increased the adsorption energy of oxygenated graphene after doping. In addition, Cu-doped graphene oxide produces stronger adsorption energy for NH_3.

Yue Yuanxia and others [2] calculated Cr and Mn respectively based on the first principle of density functional theory. The adsorption behaviour of Fe atom-modified graphene on H_2S gas shows that the surface of C atoms connected by these metal ions is protruding, which greatly increases the surface area of the graphene base and greatly increases the adsorption performance.

Species	D/Å	Q/e		E_{ads}/eV
		NH_3	Ag	
GO-O-NH_3	2.28 (H-O)	0.005	—	–0.11
AgGO-O-NH_3	2.29 (N-Ag)	0.171	–0.038	–1.25
GO-OH-NH_3	1.80 (N-H)	0.078	—	–0.60
AgGO-OH-NH_3	2.29 (N-Ag)	0.160	–0.033	–1.26
GO-COOH-NH_3	2.44 (H-O)	0.036	—	–0.17
AgGO-COOH-NH_3	2.29 (N-Ag)	0.170	–0.082	–1.39

Figure 1. Adsorption distance D, charge transfer Q, and adsorption energy Eads of AgGO and GO with different oxygen-containing groups adsorbing NH3.Wan Yuwei, Wang Rui, Zhou Wenquan, etc. [6] Research on the primary principle of Ag, Cu-doped graphene oxide adsorption of NH3 [J]. Physics Journal, 2025, 74 (07): 71-81

2.2. Liquid Sensing Mechanism

Although the freshness of food can be verified by gas, some bad merchants will illegally add prohibited drugs or excessively add restricted drugs to food, such as malachite green, crystalline purple, chloramphenicol or Sudan red I, which makes liquid detection of such drugs especially critical. Zhao Yan [1] combined with surface-enhanced Raman scattering (SERS) analysis and detection technology to detect three drugs: malachite green, crystalline purple and chloramphenicol. The synthesised Au NPs-GO substrate has a better detection effect on crystalline purple, and its standard solution can be measured up to 0.001 ng/mL, followed by malachite green, but the detection effect of chloramphenicol is not good. The liquid sensing mechanism of this metal-doped graphene oxide is to find that the target molecule is adsorbed on the surface of gold nanoparticles and laser excitation produces local surface plasma resonance (LSPR), which can produce a strong electromagnetic field effect. Combined with the charge transfer between the Au metal and the molecule, the Raman scattering of the visible target molecule is observed. The radiation signal is amplified several times, so the content of the substance to be tested in the liquid can be obtained. Yu Xiaona and others [7] studied the detection of Sudan Red I in paprika samples by the three-dimensional conductive system formed by one-dimensional carbon nanotubes and two-dimensional graphene composites through electrochemical principles. When Sudan red I molecules diffuse to the surface of the electrode, a redox reaction occurs to generate electrical signals. The combination of graphene and carbon nanotubes produces a catalytic effect, making the current response greater and the peak shape more obvious.

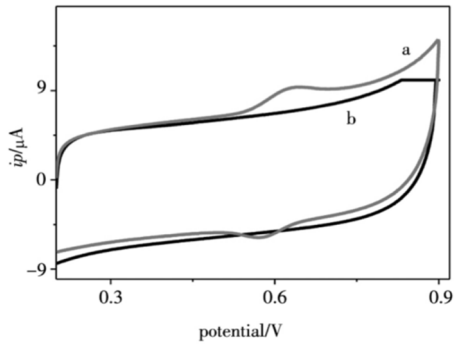


Figure 2. (a) Cyclic voltamme diagram of Sudan Red I on different electrodes. [7]

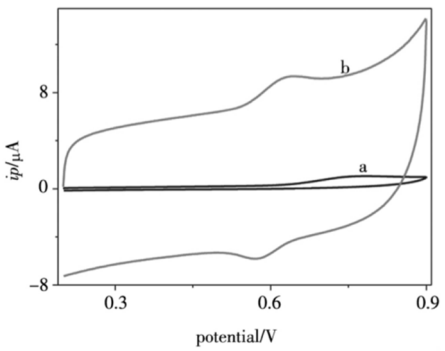


Figure 2. (b) CV curve of CNTs/graphene electrodes in PBS and Sudan red I solution. [7]

Similarly, nitrite and tea polyphenols proposed by Xu Feng [8] will undergo electrocatalytic oxidation on the surface of the electrode, and the size of the oxidation current reflects the content of the target substance.

3. Sensor Devices and Applications

3.1. Gas Sensing Devices and Applications

Regarding ammonia NH3, the iconic gas for measuring food freshness, can construct a flower-shaped h-MoO3 nanorod graphene composite gas-sensitive device [9] The device is composed of flower-shaped h-MoO3 nanorods prepared by graphene combined with chemical bath deposition after chemical vapour deposition. Under indoor temperature test, the device has a strong response to 1×10^{-6} ammonia, with a sensitivity of 1.13%, which is 20 times that of pure graphene. The GFET-GS prepared by Xu Tao adopts a back grid structure that can maximise the gas-sensitive properties of graphene [10]. Graphene modified by hydroxyl (-OH) can react chemically with ammonia to detect the ammonia content.

Mohame A A and others prepared MnO_2@GO composite materials into NO_2 detection devices. [4] The device loads sensitive materials on the ceramic substrate with gold electrodes by drop coating, and the working temperature is set to 150°C. The gas sensitivity test shows that its detection limit for NO2 can reach 200 ppb, and the response has a good linear relationship in the concentration range of 200-1000 ppb.

Selective tests show that the device's response to NO_2 is much higher than that to NH_3, CO, ethanol, benzene and H_2, reflecting the high identification spicability. The long-term stability test shows that the device still maintains a stable response after 8 months of continuous operation, providing key data support for it from the laboratory to the practical application scenario.

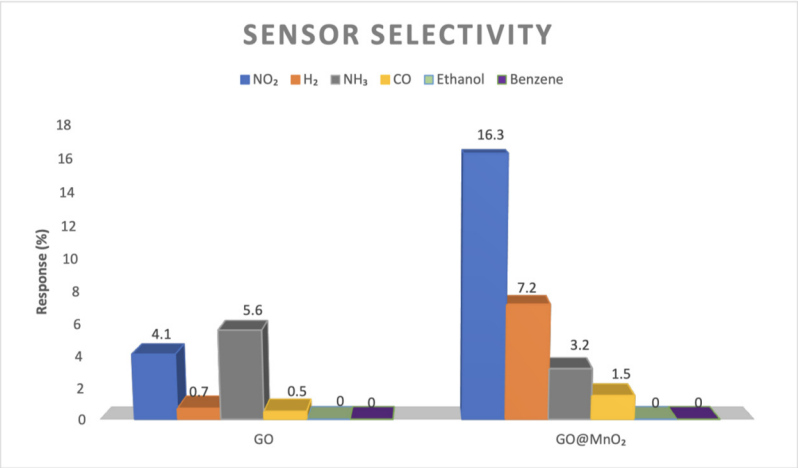


Figure 3. Comparison of the responses of the different sensors towards different gases under dry conditions to study the selectivity of the sensitive layer. [4] Mohame A A, Juan C, Santiago B M, et al. A NO_2 Sensitivity MnO_2/Graphene Oxide Composite Based Gas Sensor[J]. Chemosensors 2025,13,96

For people who find it difficult to judge whether food is fresh or not, being able to simply judge whether food is rotten or not has become a need for vegetable markets and kitchens. Different food corruption will produce organic volatile gases with different characteristics [11], such as fish corruption produces nitrogen, meat corruption produces hydrogen sulphide, and fruit corruption produces ester substances; these iconic gases can be used as a major detection object for gas sensor detection. The most common gas sensor is resistive [4], which uses gas adsorption to change the concentration of graphene-based carriers to cause changes in resistivity.

3.2. Liquid Sensing Devices and Applications

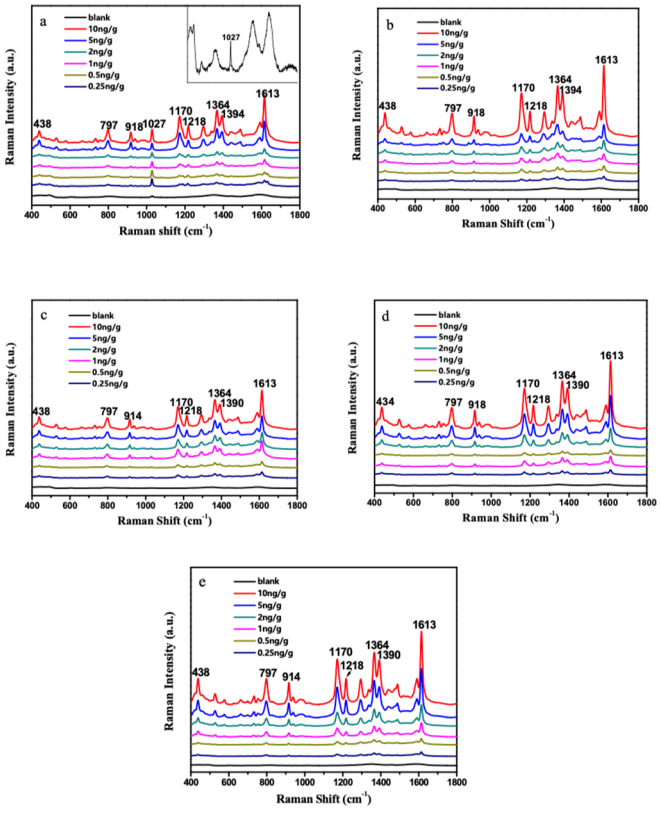


Figure 4. SERS spectra of MG-contaminated fish muscle extracts. (a) snakehead, (b) breamfish, (c) grass carp, (d) weever, and (e) catfish. [1] Zhao Yan. Preparation of graphene oxide composite substrate and its application in food safety testing [D]. Shanghai Ocean University, 2019. DOI: 10.27314/d.cnki.gsscu.2019.000377

In addition to the gas that can be used as a standard for detecting food, attention should also be paid to the safety from the source of food production. At present, liquid-phase graphene-based sensors can be more maturely used to detect

multiple food safety indicators such as illegal additives and pigments. Zhao Yan proposed that Au NPs-GO composite substrate is a liquid-phase SERS sensing [1]. In the experiment, quartz sheets with positive charges are used as the base and negatively charged gold nanoions and graphene oxide are adsorbed on the body surface through positive and negative charge attraction to obtain Au NPs-GO composite substrate with a sensitive response to crystalline purple. The preparation of this device comes from the basic electromagnetic self-assembly method. The experiment found that the configuration of 1 mol/L of NaOH alcohol solution and two self-assembled laps is the optimal sensitivity. In actual fish samples such as black fish, grass fish, perch, etc., the detection results of malachite green can reach 0.25ng/g.

In terms of azo pigment detection, CNTs/graphene suspension is obtained by placing the thermal reduction graphene and quantitative carbon nanotubes synthesised by high-temperature annealing technology in DMF solution. Graphene/carbon nanotube composite materials are obtained by polishing, cleaning bare glass carbon electrodes and then applying CNTs/graphene suspension and other operations, so as to produce an electrooxidation reaction in Sudan Red I in specific chilli powder [7]. Sudan Red I, as an illegal additive, can be detected by thermally reduced graphene carbon nanotube composite modified glass carbon electrode through electrocatalytic effect [7]. Similarly, in terms of illegal additives, glass-carbon electrodes modified with nano-gold graphene composite materials can be prepared, involving cleaning, ultrasound, drip coating and other preparation methods [8]. Additionally, graphene-modified electrodes combined with immuno-recognition technology can build electrochemical immune sensors [12]. For example, graphene-chitosan complex-modified glass carbon electrodes can be constructed by using graphene and chitosan complexes and melamine small molecules to modify on glass-carbon electrodes. K3Fe (CN)6 is used as a probe to detect melamine in sample milk with the detection limit 0.2ng/mL.

4. Conclusion

In conclusion, this article studies, summarizes the selected literature and then sum up the research progress of graphene-based sensing mechanism and devices in food safety and food freshness. Focussing on the logical main line of gas/liquid dual phase, the following conclusions can be summarized.

Graphene materials have unique advantages such as good electrical conductivity and high specific surface area. Through metal oxide compounding, atomic doping and other means that it can effectively make up for the problems of limited adsorption capacity and lack of responsiveness of pure graphene. Combined with device design methods such as resistive gas-phase sensing and electrochemical liquid-phase sensing, it can be applied to special gas and liquid detection to provide a visual path for food safety supervision. However, if we want to solve the food safety dilemma of the masses, graphene-based sensing technology is needed to go from the laboratory to the mall. Judging from the current situation of overall research, the current graphene-based sensing technology is still in the transitional stage from laboratory research to actual industrialization. It is also a problem that cannot be ignored to reduce volume and reduce costs for the convenience and practicality of commercialization.

In terms of application, first of all, most of the existing research focuses on single substance detection. The two technologies of gas and liquid are completely independent, and the two types of detection systems are not compatible, making it difficult to adapt to real and complex food environments. Secondly, the current research is mostly focussed on short-term experimental performance tests and a closer exploration is needed to whether the materials can work continuously and operate normally within the fluctuation range of ambient temperature. Therefore, the single function and service life of graphene-based sensors and whether they are applicable in real scenarios have become difficult problems that need to be overcome at this stage.

Based on the advantages and exposed shortcomings of the current research, combined with the actual development needs of the food testing industry in the future, in response to the above challenges, the future research direction can seek breakthroughs from the following directions. First, develop a gas-liquid dual-phase integrated sensing system to overcome the limitation that only one class of substances can be detected separately, it can also adapt to the comprehensive detection needs of multiple scenarios. Second, build a long-term practical test for graphene-based sensors, detect the long-term ageing degree of the sensor through spectral analysis, electronic tracking, etc., so as to clarify the performance decay mechanism of graphene-based sensitive materials after high environmental changes and high-intensity operation, and optimise the loss resistance of materials and devices. Third, promote the miniaturization and convenience of graphene-based sensors. In the future, mass production costs can be reduced by simplifying the preparation process and optimizing the material ratio. It can be used to develop flexible sensing patch equipment to realise visual detection on food packaging. Fourth, strengthen the combination of graphene-based sensing technology and intelligent technology and combine it with data collection and intelligent analysis. Real-time recording of sensing data can provide risk prediction of whether food will rot and deteriorate in order to promote the intelligent development of graphene-based sensing technology.

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