Nitrogen-modified Graphene Synthesis and Modification of H₂S Removal Efficiency Comparison

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Abstract. In this paper, multilayer graphene is used as the raw material, graphene oxide is prepared by Hummers’ improved method, and Nitrogen-modified Graphene is prepared by solvothermal method. It uses SEM, XRD, XPS, Ramman to characterize the sample morphology, internal composition, internal structure and element content, analyze its chaos and functional group change trend, and get: graphene to graphene oxide to Nitrogen-modified Graphene, graphene oxide The replacement of C atoms by O atoms increases surface wrinkles and increases defects and confusion. Nitrogen-modified Graphene is reduced due to the oxygen-containing functional groups of graphene oxide, reducing functional groups and reducing interlayer materials, resulting in a clean surface and reduced defects. The layer spacing is reduced. Then through a fixed bed reactor, using graphene, graphene oxide, and Nitrogen-modified Graphene as experimental samples, the adsorption of hydrogen sulfide gas was tested and researched: the original graphene and graphene oxide had similar adsorption capacities for hydrogen sulfide gas. Nitrogen-modified Graphene is about 3 times that of the first two experimental samples.

1. Introduction

In recent years, with the growth of the national economy, the demand for coal resources has become stronger, the mining area has expanded and the depth has increased, and accidents of hydrogen sulfide gushing out of mines have occurred from time to time. When the volume fraction of H₂S in the downhole air flow is only 50ppm~100ppm, it has a strong harm to the human body. Therefore, there is an urgent need to study practical materials for the prevention and treatment of the hydrogen sulfide pollution in the working face.

Graphene is a hexagonal honeycomb-shaped monoatomic layer material composed of SP² hybrid carbon atoms. It has special optical, electrical, mechanical, and thermal properties, and also has certain characteristics of biocompatibility, transparency, conductivity, elasticity, etc[1-2].Because of its porous structure with a large specific surface area and rich in active genes on the surface, it can be used for the removal of harmful substances. When the original graphene is used for high-concentration fine desulfurization without processing, the sulfur capacity is not as good as expected, the material consumption is large, and the desulfurization efficiency is difficult to meet the ideal requirements that people expect, so the graphene is modified. Increasing its sulfur capacity is one of the key steps.Mastalir first used graphene to support Pd nanoparticles, and used experimental methods to explore the performance of the catalyst. The experiment proved that using graphene to support Pd nanoparticles can greatly improve the catalytic activity of Pd[3]. Graphene is prepared to generate Nitrogen-modified Graphene, firstly, raw graphene is prepared into graphene oxide, and then graphene...
oxide is prepared into Nitrogen-modified Graphene. Graphene oxide has strong adsorption due to its special internal pore structure. Through hydrothermal synthesis, nitrogen can be uniformly doped inside graphene oxide, changing its internal chemical bonds and functional groups, and promoting H2S in which absorption is removed. Compared with graphene oxide, nitrogen doping can not only accelerate the reaction, but also increase the removal rate of H2S gas flow. In this study, graphene was used as the original material, nitrogen-doped, and Nitrogen-modified Graphene was prepared, and the structure characterization and desulfurization performance experiment were carried out.

2. Sample preparation

The Hummers modified method is used to prepare graphene oxide, and the solvothermal method, that is, the hydrothermal synthesis method, is used to prepare Nitrogen-modified graphene.

2.1. Preparation of graphene oxide

Graphite oxide is a precursor for the preparation of graphene oxide, and graphene oxide can be obtained by peeling off graphite oxide. Under the action of strong acid, graphite can be treated with strong oxidant to obtain graphite oxide. The specific experimental methods are as follows:

1) Weigh 500 mg graphite powder (98% purity, Suzhou Tanfeng Graphene Technology Co., Ltd.), 3g KMnO4 (Analytically pure), measure 60ml concentrated H2SO4 (98% purity), 6.6ml concentrated H3PO4 (98% purity), add them to a 150ml round-bottom flask in turn, and stir for 12h in an oil bath at 50°C. Fill the beaker with 40-60ml of ice water, and pour the prepared reactants into the ice water under continuous stirring;

2) Measure 3ml of H2O2 (30%) and slowly add it to the above reaction under strong stirring until no bubbles are generated to react the excess raw material KMnO4, at this time the solution turns from earthy gray to bright yellow, Centrifuge the suspension solution to remove the supernatant, wash the solids in the lower layer with 100ml of dilute HCl (10%) once and wash twice with deionized water;

3) Disperse the cleaned graphite oxide into a little deionized water, and peel it off in an ultrasonic cleaner (VGT-1000B, Shenzhen Keweixin Co., Ltd.) for 3 hours (120W, 40Hz) to obtain the graphite oxide solution. The obtained graphene oxide solution was put into a dialysis bag for dialysis for one week, and finally centrifuged (TG16-II, Changsha Xiangping Co., Ltd.), dried (drying box for PCR experiment, Beijing Fuyilian Equipment Co.), and set aside.

2.2. Nitrogen-modified Graphene

The solvothermal method (hydrothermal synthesis method) is used to prepare Nitrogen-modified Graphene. The specific steps are as follows:

1) Take 15ml of graphene oxide solution (5mg/ml), add 15ml of distilled water, mix with 1.8g of urea (98% purity), magnetically stir (HJ-3, Great Wall Technology, Industry and Trade Company) for 30 minutes and mix well;

2) Transfer the mixture into a polytetrafluoroethylene autoclave (SX2-6-13, Shanghai Shijia Instrument Co., Ltd.), react at 160°C for 3 hours and then cool down naturally; Take out the solution obtained after cooling, mix and stir for 0.5h with 3 times the amount of acetone (Analytically pure), and then centrifuge the final mixture for several times in a centrifuge (TG16-II, Changsha Xiangping Co., Ltd.);

3) After centrifugation with ethanol (99.8% purity), it was dried in a vacuum drying oven (DZF-6020, Hangzhou Kexiao Chemical Instrument Co., Ltd.) at 60°C for 12 hours to obtain Nitrogen-modified Graphene. The prepared Nitrogen-modified Graphene was recorded as NG-1.8. Graphene oxide doped with nitrogen is referred to as NG-0.

3. Material characterization

3.1. SEM characterization of samples

SEM (Hitachi SU8100-Cold Field Scanning Electron Microscope) was used to test the morphology of
the sample. The sputtering current was 10mA, the sputtering time was 90s, and the observation magnification was 80,000.

![Graphene](image1) ![Graphene oxide (NG-0)](image2) ![Nitrogen-modified Graphene (NG-1.8)](image3)

Figure 1. Scanning electron micrograph

Comparison Figure 1 Compared with the original graphene, the surface structure of graphene oxide (NG-0) is much more complicated and chaotic, and the wrinkles are significantly increased. This is because the surface of the original graphene is damaged during the preparation of graphene oxide. C atoms are replaced by O atoms [4]. Compared with graphene oxide (NG-0), Nitrogen-modified Graphene (NG-1.8) has a much cleaner surface. The reason for this phenomenon is nitrogen-doped In the process, the oxygen-containing functional groups of graphene oxide are reduced, the functional groups are reduced, and the interlayer material is reduced.

3.2. XRD analysis of samples

Measured with Rigaku SMARTLAB 9KWX X-ray diffractometer, the sample test range is 10°~90°, the scan rate is 10°/min, the voltage used is 45kV, the current is 40mA, CuKα radiation is used, and the X-ray wavelength $\lambda=1.5406\text{Å}$. The XRD characterization diagram of the experimental sample is shown in Figure 2.

![Graphene](image4) ![Graphene oxide (NG-0)](image5) ![Nitrogen-modified Graphene (NG-1.8)](image6)

Figure 2. XRD spectrum

Through the analysis of JADE software, the original graphene curve has a C peak at the position of
\[ \theta = 25.64^\circ \], which is brought into the calculation by the Bragg formula \( 2d \sin(\theta) = k \lambda \) (\( k = 1, \lambda = 0.15406\text{nm} \)), and the original graphene curve can be obtained. The interlayer spacing \( d = 0.347\text{nm} \), and the interlayer spacing of graphene oxide (NG-0) and nitrogen-doped graphene (NG-1.8) are \( d = 0.225\text{nm} \) and \( d = 0.213\text{nm} \), respectively. The comparison shows that from graphene to graphene oxide (NG-0) to nitrogen-doped graphene (NG-1.8), the interlayer spacing gradually decreases, and graphene oxide (NG-0) and nitrogen-doped graphene (NG-1.8) have layer spacing not much different. And it can be seen from the analysis in Figure 2 that with the doping of nitrogen, the \( 2 \theta \) value of the peak position increases slightly, which is caused by the decrease of the functional groups between the nitrogen-doped graphene layers with the doping of nitrogen. The result is consistent with the SEM characterization.

### 3.3 XPS analysis

The Thermo Fisher EscaLab 250Xi X-ray photoelectron spectrometer produced by Thermo Fisher, USA was used for the test. The test conditions are: use Al K\( \alpha \) ray excitation source, energy of 1486.8eV, test spot area: 30-500um, test tube voltage: 15kv, tube current 10mA, background vacuum of analysis chamber: \( 2 \times 10^{-9}\text{mbar} \). The XPS characterization results of three different graphenes are shown in Figure 5 below:

![XPS spectrum](image)

From the analysis in Figure 3, it can be seen that the original graphene contains two elements, C and O, at 284.78eV and 535.78eV, respectively. The graphite oxide series (NG-0) contains two elements, C and O, with positions at 287.13 eV and 532.63 eV respectively. Nitrogen-modified Graphene contains three elements: C, N, and O, with positions at 286.33 eV, 401.53 eV, and 533.78 eV, respectively. The original graphene, graphene oxide NG-0, and Nitrogen-modified Graphene NG-1.8 have N content of 0\%, 0\%, 1.78\%, O content of 8.42\%, 32.15\%, and 29.64\%, and C content of 91.58\%, 67.85\%, 68.58\%. It can be seen that from graphene to graphene oxide (NG-0), the C element content decreases, and the corresponding O atom content increases, indicating that graphene oxide will cause the C element content to decrease. From graphene oxide (NG-0) to Nitrogen-modified Graphene (NG-1.8), the O atom content decreases, and the corresponding N
element content increases, indicating that the doping of nitrogen will cause the O element content to decrease.

4. Adsorption performance test
The adsorption and removal of H2S performance of three different experimental samples, graphene, graphene oxide and nitrogen-doped graphene were tested by the adsorption reaction fixed bed experimental device. The adsorption rate was the amount of H2S adsorbed by the experimental sample/the amount of initial H2S.

The H2S adsorption experiment temperature is 30℃, relative humidity is 20%, the initial H2S concentration is 100ppm (151.8mg/m3, N2 preparation), the flow rate is 50ml/min, the adsorption time is 150min, and the sampling bag is used to collect the exhaust gas every 10 minutes. After the experiment is completed, the H2S in the sampling bag is detected with a hydrogen sulfide detection tube (Shanghai Yichang Industrial Co., Ltd., detection accuracy ±1ppm). The adsorption rate of the experimental sample changes with the adsorption time as shown in Figure 4.

![Figure 4. The adsorption of H2S on the experimental sample changes with time](image)

In the same adsorption time, the adsorption rate of the three experimental samples increased with the increase of adsorption time, and reached the peak of adsorption at 90 min. The adsorption rates were 35.93%, 14%, and 13.72%. The adsorption rate basically does not change, and the adsorption has reached saturation at this time. Compared with the other two types, the adsorption rate of Nitrogen-modified Graphene increased by 21.92% and 22.21%. It can be seen that Nitrogen-modified Graphene has a significant desulfurization effect.

5. Conclusions
(1) Compared with original graphene, graphene oxide has increased surface disorder and wrinkles due to the substitution of C atoms by O atoms. Nitrogen-modified Graphene is compared with graphene oxide. The nitrogen doping process reduces the oxygen-containing functional groups of graphene oxide, reduces functional groups, reduces interlayer materials, and reduces the surface disorder of Nitrogen-modified Graphene.

(2) The interlayer spacing of original graphene, graphene oxide and nitrogen-doped graphene are 0.347nm, 0.225nm, and 0.213nm respectively. From graphene to graphene oxide and then to nitrogen-doped graphene, the interlayer spacing gradually decreases, and nitrogen-doped graphene The distance from the graphene oxide layer is slightly reduced.

(3) The N element content of original graphene, graphene oxide, and Nitrogen-modified Graphene are 0%, 0%, and 1.78%, respectively, the O element content is 8.42%, 32.15%, and 29.64%, and the C element content is 91.58%, 67.85%, and 68.58%. From graphene to graphene oxide (NG-0), the content of C element decreases, and the corresponding O element content increases. From graphene oxide to
Nitrogen-modified Graphene, the content of O element decreases, and the corresponding N element content increases. The increase indicates that the doping of nitrogen will cause the relative content of O element to decrease.

(4) Under the basic working conditions, when the three experimental samples did not reach the adsorption saturation, the adsorption rate increased with the increase of the adsorption time. The adsorption time reached the adsorption peak at 90 min. After reaching the adsorption saturation, the adsorption rate did not change. The adsorption time changes. The adsorption rates of Nitrogen-modified Graphene, graphene oxide, and original graphene are 35.93%, 14%, and 13.72%, respectively, and Nitrogen-modified Graphene has a more significant adsorption effect.

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