Preparation of porous composite materials with semi-coke based activated carbon doped with graphene oxide

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Abstract: In this paper, the waste semi-coke is used as the carbon precursor, doped with a certain amount of graphene oxide (GO), and activated by KOH to obtain graphene-doped activated carbon. The changes of morphology and structure were compared by SEM, the properties of specific surface area and pore structure were tested by nitrogen adsorption at low temperature, and the changes of iodine adsorption capacity of samples with different ratio were tested. Finally, the graphene-doped activated carbon with specific surface area of 1072.08 m²/g and iodine adsorption capacity of 1223.99 mg/g was obtained. The optimal ratio of semi-coke to graphene oxide was 300:1, KOH and the semi-coke ratio is 4:1, which provides an excellent adsorbent for the adsorption of methane and carbon dioxide.

1. Introduction
The demand for natural gas in national production and life is increasing, and it is still in a state of short supply. As a main component of coal bed methane, CH₄ mainly exists in the coal voids in free state. However, due to technical reasons, the utilization rate of methane is not high, so people pay more and more attention to its enrichment technology[1-2]. With the rapid development of modern industry, the global greenhouse effect is becoming more and more serious. The concentration of harmful gases in the atmosphere of CO₂ and methane, which are six kinds of greenhouse gases, is increasing, resulting in the formation of a large number of aerosols (PM > 2.5 micro particles), the harm to the ozone layer is more serious, and the global temperature is also increasing year by year. Therefore, carbon capture technology has extremely vital significance [3-5].

Semi-coke is obtained from the pyrolysis of low cohesive or non cohesive high volatile bituminous coal at medium and low temperature. It has the characteristics of high chemical activity, high fixed carbon content, developed pore structure, low ash content and low volatile content. Semi-coke is a new type of carbon material, which has a block structure and a particle size of about 10-60 mm and a light black appearance. However, semi-coke is often used as waste material to discharge directly, which causes environmental pollution[6-8]. Therefore, the reasonable use of semi-coke powder to prepare porous carbon for adsorption and separation is not only conducive to the development of carbon capture technology and concentration technology of low concentration coal bed methane, but also can effectively improve the classified utilization of coal, reduce environmental pollution, provide basic adsorption data for gas separation, promote the development of preparation technology, promote
the rapid development of waste gas treatment and other related fields. When semi-coke is used as carbon source, the cost of raw materials is reduced to a certain extent, which is conducive to promoting the transformation of the semi-coke industry to the direction of comprehensive utilization, low energy consumption, low pollution and low carbon, expanding the application field of semi-coke resources, extending the semi-coke industry chain, promoting the development of semi-coke industry, generating huge economic benefits, and realizing sustainable economic development and environmental protection significance. However, the effect of the activated carbon prepared by semi-coke on the enrichment of methane and the adsorption of carbon dioxide is not obvious.

The microstructure of graphene oxide (GO) is a kind of honeycomb lattice two-dimensional structure composed of carbon atoms and SP² hybrid orbital. Its surface has a large number of functional groups, excellent mechanical properties and chemical stability[9]. Therefore, it is interesting that the porous carbon materials based on graphene will not bring by-products to the reaction, but also can be used as carbon materials to adjust the pore structure, specific surface area and other properties of porous carbon, making it develop in a favorable direction[11].

Herein, semi-coke is used as carbon source and graphene oxide is doped to form a new type of composite. Porous structure is produced by alkali activation. The influence of different ratio of graphene oxide and semi-coke on the composite is explored. The addition of graphene oxide can not only improve the diffusion rate of the adsorbate, but also regulate the pore structure and specific surface area, and increase the utilization rate of the adsorption active site. What's exciting is that compared with the pure bulk activated carbon, the activated carbon doped with graphene oxide has a better structure, and there is no need to worry about the production of any intermediate products in the reaction process, which provides favorable conditions for the adsorption of methane, carbon dioxide and other substances.

2. Experiment

2.1. Preparation of graphene oxide (GO)

Graphene oxide was synthesized by graphite powder oxidation method with improved Hummers method. Concentrated H₂SO₄ (130 ml) was added into the mixture of graphite powder (5.0 g) and NaNO₃ (2.5 g), and the mixture was cooled to 0°C. Slowly add KMnO₄ (20 g) in batches to keep the reaction temperature below 5°C for 30 minutes. The reaction was heated to 40 °C and stirred for 1.5 h. at this time, water was added slowly (230 ml), resulting in a large exothermic temperature of 98 °C. Introduce external heating to maintain the reaction temperature at 98 °C for 20 minutes, then remove the heat and cool the reaction with a water bath for 10 minutes. Add additional water (700 ml) and 30% hydrogen peroxide (50 mL) to the suspension. Under the action of ultrasound, the suspension of go was repeatedly filtered with 5% HCl aqueous solution and water until the pH value of the solution became neutral without SO₄²⁻. Powder solid GO obtained by freeze-drying[10].

2.2. Preparation of graphene oxide based semi-coke activated carbon composite

Firstly, KOH, semi-coke and graphene oxide are weighed in proportion, and a small amount of deionized water is added to graphene oxide to make it completely dissolved, and ultrasound is used to make it evenly dispersed in deionized water for two hours. At the same time, add a certain amount of deionized water to KOH, stir it fully to make it just completely dissolved, then add a certain mass ratio of semi coke powder and dissolved graphite oxide, stir it for 2 h under 70 °C magnetic force to make it viscous, then pour the viscous liquid into the porcelain boat, put it into the tubular furnace, and raise the temperature at the temperature rate of 5 °C/min at the starting temperature of 25 °C with the protective gas of N₂. After heating to 800 °C and keeping for 60 min, cooling to room temperature in nitrogen atmosphere, filter the sample repeatedly with 5% HCl aqueous solution and water to make it neutral, and dry in vacuum at 105 °C for 2 h to obtain the composite.
2.3. Low temperature nitrogen adsorption test
The specific surface area and pore structure of the test samples were tested by ASAP2020 physical adsorption instrument of Micromeritics Company. The adsorption-desorption isotherm curve of nitrogen at 77 K was measured by static capacity method. The total pore volume was calculated by the adsorption capacity of adsorption isotherm at 0.99 relative pressures. $S_{BET}$ was calculated by BET method from the adsorption capacity data. The pore size distribution was calculated by t-plot method, and then the pore size distribution was calculated by density pan function theory.

2.4. Scanning electron microscopy
The scanning electron microscope (SEM) of phenom Pro type is used to detect the micro morphology of the test sample: the magnification is 80-150000, the resolution is 8 nm, and the acceleration voltage is 5-15 kv, which is mainly used to characterize the microstructure characteristics of the sample, such as particle size, morphology, etc.

2.5. Determination of iodine adsorption value
Iodine adsorption value is mainly used as the adsorption test of coal based activated carbon. Its main principle is to determine the residual iodine concentration by titration with sodium thiosulfate standard solution after the quantitative sample and iodine standard solution are fully shaken under specific conditions, so as to determine the iodine adsorption amount.

Iodine adsorption value can be used as a qualitative indicator of microporous structure of activated carbon. Iodine adsorption value is determined according to GB/T 7702.7-2008.

3. Results and discussion

3.1. Surface topography
The micro surfaces of semi-coke and activated carbon were observed by SEM. Figure 1 shows semi-coke and graphene doped semi-coke porous carbon (semi-coke: GO = 300:1). Figure 1(a) shows that the surface of semi-coke is not completely smooth and the whole is relatively dense, with very few pores and very few pore structures.

Figure 1. (a) Scanning electron micrograph of semi-coke sample, (b) scanning electron micrograph of composite carbon with ratio of semi-coke to graphene oxide of 300:1.

In Figure 1(b), it can be seen that the activated semi-coke compared with semi-coke, the activated semi-coke has obviously generated small new pores, and there are some small particles, the pores are relatively developed, the structure is loose and porous. This should be because the disordered carbon structure in the semi-coke is activated by KOH at high temperature and etched into pores. These abundant pore structures also promote the increase of the specific surface area of the activated carbon and provide a favorable environment for the separation and adsorption of the activated carbon.
3.2. Texture characteristics

Figure 2 shows the adsorption-desorption isotherms of 100:1, 200:1, 300:1, 400:1 and pore size distribution of graphene based semi-coke porous carbon.

![Figure 2](image)

Figure 2. (a) Nitrogen adsorption-desorption curve of composite porous carbon with different proportion of graphene oxide and (b) pore size distribution diagram.

Through the nitrogen adsorption test at low temperature, it can be seen from the adsorption and desorption curve in Figure 2(a) and the pore structure distribution in Figure 2(b), the adsorption and desorption curves of 200:1 and 400:1 are partially inconsistent under the condition of high pressure. Compared with the changes of pore structure of semi-coke based composite porous carbon under different ratios, the pore development degree of graphene based composite porous carbon varies with the amount of go added. The increasing trend of the composite porous carbon is first increasing and then decreasing, which is consistent with its pore size distribution. With the addition of go, the adsorption isotherm of the composite porous carbon gradually presents a hysteresis loop, and the hysteresis loop type is H4, indicating that the composite material has a large number of mesoporous structures, which is the typical micro mesoporous structure with narrow fracture pores. This is related to the pore size distribution and the average pore size.

![Figure 3](image)

Figure 3. (a) Iodine adsorption capacity and (b) specific surface area of composite porous carbon with different proportion of semi-coke graphene oxide.

Figure 3 shows the iodine adsorption value and BET surface area of graphene based semi-coke porous carbon with different proportions of semi-coke and go. Through the test of iodine adsorption, it is found that the laws of iodine adsorption capacity and specific surface area of semi-coke and graphite oxide with mass ratio of 100:1, 200:1, 300:1 and 400:1 are consistent. When the mass ratio of semi-coke to graphite oxide is 300:1, the specific surface area and iodine adsorption amount reach the maximum.
4. Conclusion
The composite carbon material was prepared by tube furnace chemical activation method with semi-coke as carbon precursor and graphite oxide prepared by graphite powder in different mass ratio. The activation reagent was KOH, the activation temperature was 800 °C, and the activation time was 60 minutes. The results show that when the mass ratio of semi-coke to graphite oxide is 300:1, the ratio of alkali to carbon is 4:1, the iodine adsorption value is 1223.99 mg/g, the specific surface area is 1072.08 m²/g, the iodine adsorption value and the specific surface area are the best, the pore structure is also greatly improved, and the prediction has a good effect on the gas adsorption.

Acknowledgments
This study is supported by the Natural Science Foundation of China (No.41772166, 21706206), Shaanxi Key Industry Chain Innovation Project (2017ZDCXL-GY-10-01-02, 2018GY-076), Major Project from Key Laboratory of Coal Resources Exploration and Comprehensive Utilization, Ministry of Land and Resources (SMDZ-2019ZD-2) and Xi'an Science and Technology Innovation Guidance Project (201805036YD14CG20(6)).

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