Preparation and Characterization of Gaphene-Doped Carbon-Aerogel Electrode

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Abstract. Carbon-aerogel is a kind of nano-porous carbon material with special three-dimensional network structure. Electrode materials with high specific surface area, high porosity, superior conductivity and low density were obtained by adding graphene to prepare graphene-doped carbon-aerogels.

1. Introduction

With the development of science and technology, people have been looking for nanomaterials with various application functions, and carbon aerogels have attracted wide attention from scholars all over the world because of their unique fiber structure, large specific surface area, high porosity, strong heat insulation, strong photoconductivity and low density. Now carbon aerogel materials have been widely used in our life, biomaterials, catalyst carriers, heat insulation materials, supercapacitors, sewage treatment and other fields. It can be seen that it has a broad application prospects. Therefore, it is of great and far-reaching significance to continue to study and explore carbon aerogel materials. Therefore, it is of great and profound significance to continue the research and exploration of carbon aerogel materials and further explore their value.

In this study, resorcinol and formaldehyde were mixed into a mixture. Then sodium carbonate is added to catalyze the reaction, then graphene and deionized water are added to mix in a certain proportion. Graphene-doped carbon aerogels were obtained by sol-gel, solvent replacement, drying and high temperature carbonization. Then carbon aerogel properties were characterized. The surface area and pore size distribution were measured by automatic surface area pore size analyzer and the cyclic voltammetry curves were measured by electrochemical workstation.

2. Experiment

2.1. Experimental Reagent and Instrument

The experimental reagents are shown in Table 1.
### Table 1. Experimental reagents

| Name of drug          | Molecular formula | Specifications | Manufacturer                                         |
|-----------------------|-------------------|----------------|------------------------------------------------------|
| Resorcin              | C₆H₆O₂            | AR             | Tianjin Damao Chemical Reagent Factory               |
| Methanal              | HCHO              | AR             | Shanghai Wokai Biotechnology Co., Ltd                |
| Anhydrous sodium carbonate | Na₂CO₃         | AR             | Chemical Reagent Co., Ltd                            |
| Acetone               | CH₃COCH₃         | AR             | Fine Chemical Plant of Laiyang Economic and Technological Development Zone |
| Monolayer graphene powder | C             | AR             | Jiangsu Xianfeng Nanomaterials Technology Co. Ltd    |

The experimental instruments are shown in Table 2.

### Table 2. Experimental instruments

| Name of instrument                  | Model       | Manufacturer                                      |
|-------------------------------------|-------------|---------------------------------------------------|
| Vacuum drying oven                  | DZF-6050    | Shanghai Boxun Industrial Co. Ltd                 |
| Thermostat water bath               | DF-101S     | Gongyi Yuhua Instrument Co. Ltd                   |
| Ultrasonic cleaning instrument      | KQ-300E     | Kunshan Ultrasonic Instrument Co. Ltd             |
| Vacuum tube furnace                 | OTF-1200X   | Hefei Kejing Material Technology Co., Ltd         |
| Specific surface area aperture analyzer | Kubo X1000 | Beijing Biode Technology Co. Ltd                  |
| Electrochemical Workstation         | CHI660E     | Shanghai Chenhua Instrument Co. Ltd               |

### 2.2. Experimental Steps and Methods

#### 2.2.1 Preparation of graphene doped carbon aerogel electrode

Graphene-formaldehyde-resorcinol was used to prepare graphene-doped carbon aerogel. The preparation process is shown in figure 1.

![Graphene doped carbon aerogel preparation process](image)

**Figure 1.** Flow chart of preparation of graphene doped carbon aerogels
Specific steps are as follows:

1) Resorcin, methanal, graphene powder, deionized water and Na₂CO₃ were mixed at a molar ratio of 1:2:1:16:0.008. After mixing, glass rods were used to stir and mix evenly.

2) Stir the configured solution for 10 minutes. After mixing evenly, inject the solution into a small beaker, seal it and put it into a vacuum drying box. Heat at 30°C for 24 hours, then at 50°C for 24 hours, and finally at 90°C for 72 hours. With the heating, the fluidity of the solution decreases gradually, and finally solidifies gradually to form gel. The color of the reactants changed gradually from colorless and transparent at first, first orange red, then dark red, and finally the gel turned black red.

3) Pour the acetone solution into the beaker, immerse the gel in it, then replace the acetone every 24 hours, and replace it three times.

4) The function of acetone replacement is to remove the residual water in the gel and the incomplete reaction catalyst, so that the gel can still retain the integrity of the structure during the drying process, and the structural network will not break due to the existence of surface tension. Effectively improve the efficiency of solvent replacement.

5) After the replacement gel beaker was placed in the ventilation cabinet and dried at room temperature and atmospheric pressure for three days. The dried gel column was obtained after the acetone volatilized cleanly.

6) High temperature carbonization.

The dark red organic aerogel was put into a vacuum tube carbonization furnace, vacuumed to -0.1 MPa, and then filled into a quartz tube with nitrogen as a protective gas at a rate of 50 ml/min. When the pressure in the pipe reaches 105 Pa, open the outlet valve, use the program to control the temperature and start carbonization. Set the final temperature of carbonization to 900°C. Set to use 2 hours to heat up to 250°C, maintain 2 hours at the temperature. Then set to use 1 hours to heat up to 400°C, maintain 2 hours at the temperature. then 2 hours to 900°C and maintain 4 hours. After the temperature control is finished, wait until the temperature drops to 300°C, turn off the vacuum tube furnace, after natural cooling and cooling for about 3 hours, open the tube furnace and get the black carbon gas gel column.

2.2.2 Characterization of carbon aerogel materials

2.2.2.1 Surface area and pore size analysis. The structure analysis of carbon aerogels is using automatic surface area and pore size analyzer. The sample is ground to powder, then poured into test tube, and the sample is degassed.N2 was used as the medium [30] adsorbent, and at the temperature of -196°C, nitrogen was and desorption measurements were carried out. The adsorption and desorption isotherms of carbon aerogel materials were obtained by measuring the relationship between the adsorption amount and pressure of carbon aerogel.

Set relative pressure 0-0.98, keep degassing temperature at 90°C for 1 hour and 250°C for 6 hours. The specific surface area of carbon aerogel is calculated by BET method, the pore size distribution of carbon aerogel is calculated by BJH method, and the pore volume of carbon aerogel is calculated by t-plot method.

2.2.2.2 Analysis of cyclic voltammetry curves. The electrochemical characteristics of carbon aerogels were investigated by cyclic voltammetry(CV).The cyclic voltammetry curve was determined by electrochemical workstation. Determination by Standard Three Electrode Method. The platinum electrode as reverse electrode, the saturated Ag /AgCl electrode as reference electrode, the carbon aerogel sheet as working electrode and anhydrous sodium sulfate solution as electrolyte were used. The chemical characteristics of carbon aerogel were analyzed by cyclic voltammetry curve.
3. Result and Discussion

3.1 Macro-analysis
The photo of columnar graphene-doped carbon aerogels is shown in figure 2. Through direct observation, it can be found that the carbon aerogels after carbonization are dark brown solid, and the hardness is very high, especially the carbon aerogels in block shape. The volume size is almost unaffected by applying a certain amount of pressure to them by hand. Take the gel sheet carefully and see some tiny pores visible to the naked eye. But whether it is block or thin, their density is relatively small, between 0.06-1.0 g/cm³, it is very suitable for use as composite materials, such as electrodes.

![Figure 2. Columnar graphene-doped carbon aerogels](image)

![Figure 3. N₂ desorption isotherms of sample No.1](image)

3.2 Specific Surface Area and Pore Size Analysis
The specific surface area of carbon aerogels is shown in Table 3.

| Sample | Specific surface area (m²/g) |
|--------|------------------------------|
| 1      | 578.42                       |
| 2      | 612.53                       |
| 3      | 602.71                       |

After calculating the average specific surface area of the three samples is 597.89 m²/g, it can be seen that the carbon aerogel has a large specific surface area relative to other materials.

The adsorption and desorption isotherms of graphene carbon aerogel were selected as sample 1, as shown in figure 3. The relative pressure is used as the x axis and the nitrogen adsorption capacity is the y axis in figure 3. The relative pressure range is divided into 0-0.1 low pressure range, 0.2-0.8 medium pressure range, 0.9-1.0 high pressure range. It can be seen that the isotherm changes rapidly in the low pressure range, showing a straight upward trend. With the increase of pressure, it tends to be gentle and almost unchanged.

On the basis of the classification of IPUAC (Applied Chemistry), it can be judged that this curve belongs to I type isotherms. I isotherms are generally a sign of adsorption of some microporous gel materials. As the pressure range is 0-0.1, the isotherm always rises close to the y axis, indicating the interaction between nitrogen as adsorbent and carbon aerogel adsorbent. According to the definition of IPUAC, the appearance of I kinds of isotherms proves that the material is a microporous structure, while graphene carbon aerogel is a nanoscale porous material, which accords with the experimental results. The change process of isotherm at low pressure is due to the filling of the volume of microporous structure. The outer surface area of the sample is small than the inner surface area, and the adsorption amount depends on the volume of micropore. The isotherm showed a clear turning point before 0-0.1 because the micropores of the carbon aerogel were filled with the condensate. When this type of material is close to saturated vapor pressure, the isotherm will rise sharply because of the
existence of micropores, which will be similar to macroporous adsorption. Although the pressure is still increased, the adsorption is close to saturation, so there will be no great change.

The pore size distribution of sample No. 1 is shown in figure 4.

Figure 4. Distribution of pore size of graphene carbon aerogels

The physical meaning of the graph is the change rate of hole area with pore size. The x axis is aperture and the y axis is hole area. It is found by figure 3-3 that there is no curve before the aperture is 0.5 nm. The curve changes greatly between 0.5-0.6 nm, there is a protruding peak, at 0.547 is the maximum, from the curve to the highest point of the curve this stage, has been rising, and the rise is very large, almost straight rise. From the highest point to 0.8 nm, the curve has been decreasing and the decline is very large. Between 0.8-1.7 nm, the curve decreases slowly until the curve disappears. From the figure, we can see that the pore size of carbon aerogel is relatively concentrated. The presence of the peaks indicates the presence of mesopores. The pore size distribution is between 0.5-0.6 nm, which indicates that the pore size distribution is very narrow, which is conducive to the formation of a higher specific surface area. This is consistent with the large specific surface area of carbon aerogel materials.

3.3 Analysis of Cyclic Voltammetry Curves
The cyclic voltammetry (CV) method can be used to test the change of current with charge and discharge voltage during charge and discharge of carbon aerogel material. In this study, the electrochemical workstation was used to test the No. 1 sample. The cyclic voltammetry curve is obtained by changing the range of voltage and scanning speed. The voltage variation range of the sample at -0.5~0.5 v is tested first. The scanning speed is 0.1 v/s, the number of scanning cycles is 6 cycles, and the cyclic voltammetry curve shown in figure 5 is obtained.

After that, keep the range of voltage change unchanged, change the scanning speed to 0.05 v/s, the number of scanning circles to 10 circles. The cyclic voltammetry curve is obtained as shown in figure 6.

Figure 5. Cyclic voltammetry curves

Figure 6. Cyclic voltammetry curves

Figure 7. Cyclic voltammetry curves
Then change the condition again, set the voltage change range between -1~1v, the scanning speed becomes -0.1 v/s, and the number of scanning circles is still 10 circles. The cyclic voltammetry curve is obtained as shown in figure 7.

By observing the above three curves, it can be found that under different conditions, the general trend of the curves is basically unchanged, all of which are closed curves, although some curves fail to coincide with the increase of voltage in figure 3-6. This is because cyclic voltammetry curves often appear polarization, which does not affect the characterization of carbon aerogel properties.

It can be seen from the image that there is no redox peak in the three curves, and the shape of each curve is the same, which belongs to the behavior of capacitor, which indicates that the material is very suitable for use as capacitor. The curve has always been smooth, indicating that the material performance is stable and has good stability. The closed state of the curve proves that the cycle performance of the sample is good. All of these can indicate that graphene carbon aerogel materials have excellent electrochemical properties.

4. Conclusions
In this study, graphene doped carbon aerogels were prepared by sol-gel, solvent replacement and atmospheric drying. The results were as follows: Graphene doped carbon aerogels are light in weight, smooth in surface, hard in appearance and fine pores in surface. It is proved that graphene carbon aerogel material is a porous network structure with large specific surface area, high porosity, outstanding conductivity and good stability. It is suitable for sewage treatment electrode material, catalyst carrier, capacitor material and so on.

5. References
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