

Structural characterizations of carbon aerogels and Resorcinol-Formaldehyde aerogels

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Carbon aerogels were prepared by carbonizing the organic resorcinol-formaldehyde (RF) aerogels at 700 °C for two hours in N₂ flow. The organic RF aerogels were supercritical dried materials of the wet gel, which were the condensation products of resorcinol with formaldehyde at 1:2 fix molar ratio, where distilled water served as solvent, and sodium carbonate as the base catalyst. Based on the results of Atomic Force Microscope (AFM) and Transmission Electrical Microscope (TEM), the surface profile of the samples was discussed. Compared with the results of N₂ adsorption and desorption, it can be revealed that the pore size distribution plot derived from the branch of N₂ adsorption isotherm is approximate to the true description of pore size distribution. The results of Fourier-Transform Infrared (FT-IR) spectra, Raman spectra and X-Ray Diffraction (XRD) showed that the three dimension network structure is mainly organized by carbon-carbon bands adjoined as aromatic strings in plane. There is no any stretch and bend in it after RF aerogel is carbonized at 700 °C for two hours in N₂ flow.

Key words: carbon aerogels, supercritical drying, nanostructure characterization, surface profile

1. INTRODUCTION

Carbon aerogels have been one of the most active materials for nearly two decades since R. W. Pekala successfully fabricated the organic aerogel [1]. Compared with many inorganic porosity solid aerogels, carbon aerogels are the unique kind of organic porosity materials, which can be converted by any organic aerogels, and still retain many properties of the organic aerogel, in addition to becoming electrically conductive. As a new kind of porosity carbon, the carbonized aerogels composed of pure carbon, with properties of the high surface area, low density and high porosity. Due to these properties, carbon aerogels have been used for various applications, such as electrode materials, catalyst supports, and thermal insulation materials [2-4]. However, few reports were found upon the successful practical applications of them. In the following, two examples were given to show that the reason lies in the difficulty in controllable fabricating the carbon aerogels with certain nanopore size and nanopore size distribution.

In first example, carbon aerogels were used as the support of noble metals Pt for the proton exchange membrane fuel cell (PEMFC) catalysts. The result had been reported that the PEMFC thus prepared with a low Pt particles loading (0.1 mg cm⁻³) had shown high power densities up to 0.8 mW cm⁻² [5]. In fact, the wide application of Pt catalyst fuel cell was still impeded for the sake of high cost. It is the adsorbing state of the noble metals on the surface of the amorphous support that correlated to the application efficiency of the fuel cell. Usually, multiply layers of the Pt particles were adsorbed on the surface of carbon electrodes, but only the first out layer was active for the fuel cell reaction. It

may be one of the solutions of this problem that to make the controlled single layer Pt particles adsorbed on the surface of the support.

In second example, carbon aerogels were used as the electrodes materials in Capacitive Deionization (CDI) for seawater ion removing, which greatly improved the quality of the cleared water for the sake of their high surface area [2]. However, it is still expensive for regeneration of the electrodes. Thereby this method has a long way to practical application.

It can be seen from what mentioned above, the adsorbing efficiency of both the metal catalyst particles and the waste heavy metal ions strongly depend on the nanostructure of the carbon aerogels. Therefore, it is indispensable to study the structure of the high porosity materials aiming to provide a practical instruction to the controllable fabrication.

This paper investigated the pore size distribution derived from two branches of N₂ isotherms by comparing the surface profile of AFM. One was from the N₂ adsorption isotherm and the other was from desorption isotherm. The true surface profile of the carbon aerogels was viewed by AFM. The nanostructure was observed by TEM. To study the nanostructure of adjoining type of carbon-carbon bands, FT-IR spectra of RF aerogel and carbon aerogel, Raman spectra of carbon aerogel, and XRD profile were analyzed.

2. EXPERIMENTAL

2.1 Sample preparation

The samples were prepared by the same method as reported previously [6-7]. Resorcinol and formaldehyde were mixed in a 1:2 molar ratio, where distilled water served as the solvent and sodium carbonate used as a

base catalyst. Stirring for two hours, the mixture solutions were transferred to glass molds. Then the samples were cured at 70 °C for about three days until they had slight shrink. The color of them changed from yellow to black red through orange. We called them wet gels. In order to supercritical dry the wet gel in liquid carbon dioxide, the water, filled in the intervals of nanoparticles, was washed by organic solvent for about 3-5 times, which depends on the shape and size of the samples. After that the solvent was substituted by liquid carbon dioxide at 8 MPa for 3-5 days. Finally supercritical drying was carried out at the condition of 8 MPa and 60 °C for 2 hours. RF aerogels were prepared by supercritical drying.

The carbonization of the RF aerogels was performed in N₂ flow (at the flow rate of 100 ml min⁻¹) by heating up to 700 °C (with a heating rate of 2 °C min⁻¹) and soaked for 2 hours.

2.2 Structure characterization

In this paper, the prepared carbon aerogel, with ratio of R/C=1/25 (R/C, the molar ratio of resorcinol to catalyst), and carbonized in N₂ at 700 °C for 2 hours is selected as the typical sample for discussion.

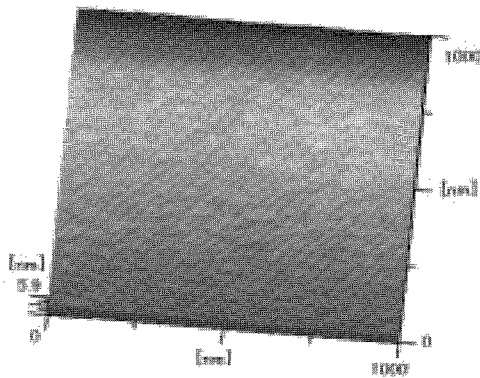
The sample was characterized by methods of AFM, TEM, FT-IR, Raman spectrum, XRD and N₂ adsorption and desorption experiment.

3. RESULTS AND DISCUSSION

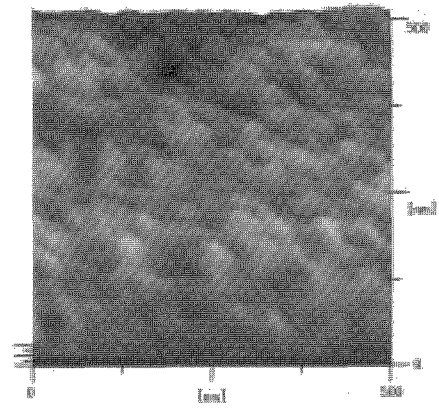
3.1 Three dimension cross-linked network structure of carbon aerogels

The true surface profile of the carbon aerogels was viewed by AFM, showed in Figs.1 (a) and (b). At the same time, the morphology microstructure of the sample was observed by TEM. The microstructure at scale bar of 5 nm was showed in Fig.2.

From Figs.1 and Fig. 2, it can be seen that the carbon aerogels on three scale bars, 5nm, 500 nm and 1000 nm, all of them have the same structure shapes of cross-linked network. It provides a hint that the pore size was determined at the stage of the formation of the RF particle strings. It is a possible strategy to widen or lengthen the strings of RF particles for the aim of increasing the pore size.



(a) Three dimension show of surface profile (with image size of 1000*1000 nm²)



(b) Three dimension show of surface profile (with image size of 500*500 nm²)

Fig.1 3-D display of the surface profile of carbon aerogel, observed by AFM

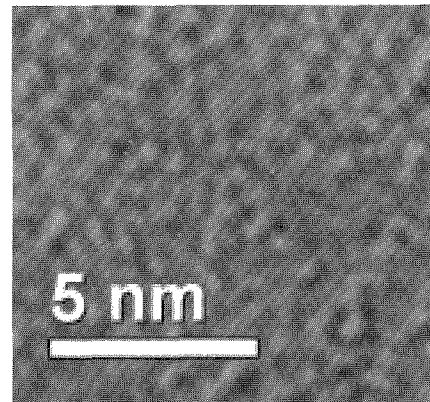
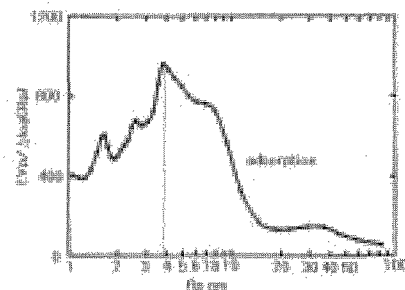


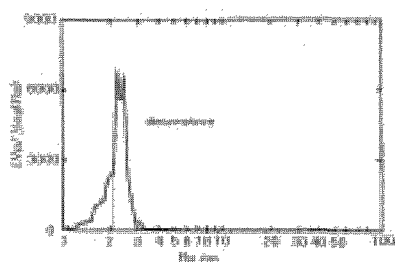
Fig.2 TEM result of structure morphology of carbon aerogel

3.2 Pore size investigation

The pore size and pore size distribution estimated by applying the Dollimore-Heal method [8] to the original data of N₂ adsorption and desorption isotherms. The distribution curves were viewed in Figs.3 (a) and (b). The surface single profile analysis result of carbon aerogel is shown in Fig.4, including the surface single profile image and the corresponding surface height difference curve of the selected line.



(a) Pore size distribution plot of carbon aerogel (calculated by D-H method, from adsorption branch)



(b) Pore size distribution plot of carbon aerogel (calculated by D-H method, from desorption branch)

Fig. 3 Pore size distribution plots derived from adsorption (a) and desorption (b) branch, respectively

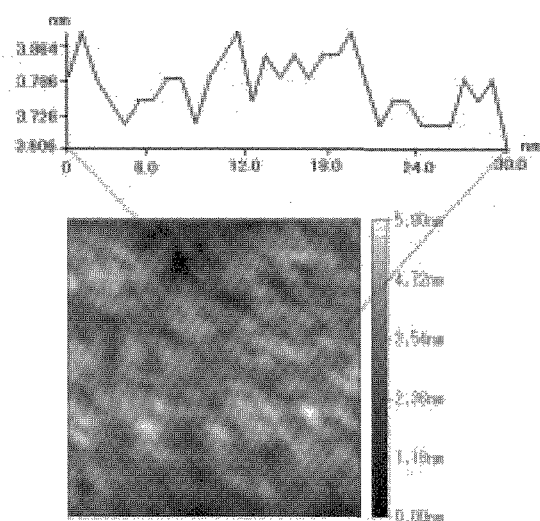


Fig. 4 The result of surface single profile analysis of carbon aerogel by AFM measurement

From N_2 adsorption and desorption isotherms, the two curves of pore size and pore size distribution had been calculated: the adsorption curve and the desorption one. Which one can describe the true state of pore size? To study this problem, we compared the two kinds of pore size distributions with the analysis result of the AFM image of the same carbon aerogel. The pore size distribution calculated based on the adsorption isotherm, is mainly occupied the range of 1-10 nm, the corresponding R_p is near 3.8 nm (Fig.3 (a)). The pore size distribution calculated from the desorption isotherm, is mainly occupied the range of 1.5-3 nm, the corresponding R_p is near 2.5 nm (Fig.3 (b)). The maximum surface height difference is 5.90 nm (Fig.4). The maximum surface height difference of the selected line, with length of 30 nm on the surface, is 3.864 nm (Fig.4). Obviously, compared with the true three dimension surface profile image of AFM result, the pore size distribution derived from the adsorption isotherm is relatively approximate to the true value.

3.3 FT-IR results of carbon aerogels before and after being carbonized

The FT-IR measurements of the RF aerogels and carbon aerogels (the spectra are shown in Fig.5)

were performed with IR spectroscope, to study the changes of structure and components during the sample being carbonized.

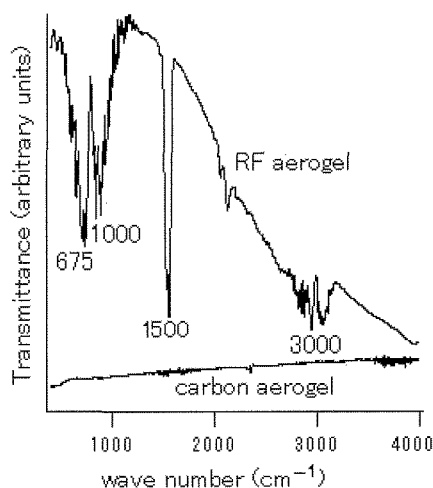


Fig. 5 FT-IR spectra of carbon aerogel and its corresponding organic RF precursor

The spectrum of RF aerogel has few strong bands (Fig. 5). The main bands are several strong carbon-carbon stretch bonds in the aromatic ring at about 1500 cm^{-1} . The aromatic carbon-hydrogen stretch bands appear at near 3000 cm^{-1} . Some other bands in the range from $1000 - 675\text{ cm}^{-1}$ are for the out of plane carbon-hydrogen bending. It revealed that the dried organic aerogels mainly organized by aromatic strings, derived from the reactant of resorcinol. The spectrum of the corresponding carbon aerogel does not have any adsorbing peak in the curve obviously. It tested that the carbonized derivative is a material composed of pure carbon. Carbon-carbon bands linked with each other and no any stretch and bend after being carbonized at $700\text{ }^\circ\text{C}$ for 2 hours.

3.4 Raman spectra of carbon aerogels

Room-temperature Raman spectroscopy measurements were carried out. The Raman spectra of two kinds of carbon aerogels, fabricated with R/C ratio are 25 and 50, are shown in Fig. 6.

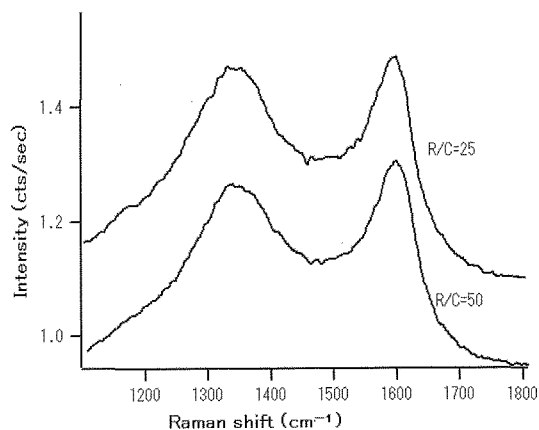


Fig. 6 Raman spectra of carbon aerogels, with the ratios of R/C are 25 and 50, respectively.

Two distinct peaks are observed in the two spectra. One lies near 1580 cm, designated as G band associated with a Raman-allowed E_{2g2} mode [9]. The other is located near 1360 cm, referred as D band associated with in-plane disorder [9]. Comparing the two curves, the positions of the peaks show no obvious difference, and so the height of them does. So at the same carbonization condition, the content of catalyst has not direct effect on the nanostructure.

3.5 XRD result

The X-ray diffraction (XRD) technique was adopted for identifying the crystalline phases in powder carbon aerogels of which the nanostructure properties have been analysed. The XRD pattern of carbon aerogel is shown in Fig.7.

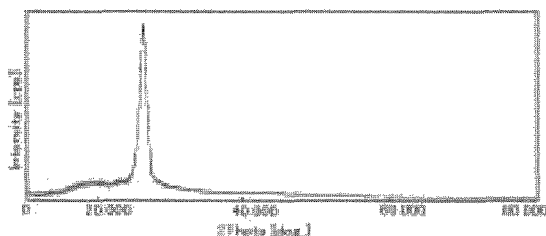


Fig. 7 XRD pattern of the carbon aerogels

The peak positions of the curve are in good agreement with those of PDF table No. 03-065-6212 [10]. According to Trucano's description of the pattern [11], the structure of graphite consists of a layer of linked hexagons of carbon atoms. The layer are linked in a ...ABAB...sequence, so that half the atoms in the layer are directly above and below carbon atoms in the adjoining layers, and half are directly above and below centers of the hexagons. The hexagonal unit cell contains atoms at the (0, 0, 1/4), (1/3, 2/3, 1/4), (0, 0, -1/4) and (2/3, 1/3, -1/4) positions. All in plane carbon-carbon distances have the same value $1.422 \pm 0.001 \text{ \AA}$ [11].

4. CONCLUSIONS

This research focused on investigating the microstructure of the carbon aerogel, to make an instruction for optimizing the practical applications of carbon aerogels. FT-IR and Raman spectrum analyses coupled with the result of XRD were carried out. To make a practical understanding to the pore size and pore size distribution, the true surface profile was observed by AFM.

The carbon aerogel thus prepared is composed of pure carbon; carbon-carbon bands adjoined together forming a three inter-cross linked network structure. The carbon-carbon has not any other stretch and bend. The nanostructure of RF aerogel has not obviously been destructed after the carbonization at $700 \text{ }^\circ\text{C}$ for 2 hours. The pore size distribution plot derived from adsorption isotherm is approximate to the true pore size.

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