

Monolithic Macroporous Carbon Cryogel Prepared from Natural Polymers

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(Received 30 January 2010)

In this study, monolithic macroporous carbon cryogels with a surface area of 117.1 m²/g, a sheet resistance of 23 Ω/□ and a contact angle of 140° were prepared from a bacterial cellulose membrane. The microscopic morphology of the cryogels contained a macroporous networking structure with a large number of micropores. Before polytetrafluoroethylene treatment, the carbon cryogels were very hydrophobic because of the large number of micropores on the surfaces of the cryogels. Therefore, the carbon cryogels exhibited great potential for applications as a gas diffusion layer in fuel cells because of their high electrical conductivity, macroporous structure and hydrophobicity.

PACS numbers: 81.05.Rm, 81.05.Lg

Keywords: Carbon cryogel, Macroporous, Monolith, Bacterial cellulose

DOI: 10.3938/jkps.57.1950

I. INTRODUCTION

Carbon aerogels are a special class of carbon materials with high porosity and high surface area [1]. Normally, these aerogels are synthesized through the sol-gel polycondensation of organic precursors, such as resorcinol-formaldehyde; then, they are supercritically dried and pyrolyzed in an inert atmosphere [2]. Carbon aerogels can be used in a wide variety of applications ranging from absorbents to anodes in lithium ion batteries or electrodes for supercapacitors and fuel cells because they are electrically conductive and have typical aerogel properties such as a low density, an open mesoporosity and a high surface area [3–6]. However, although carbon aerogels possess superior porous properties, the supercritical drying method requires expensive high-pressure equipment, which leads to a high processing cost. Therefore, a more economical, practical and relatively mild drying method, freeze-drying, is used to prepare porous materials. Porous solid that are prepared using the freeze-drying method are called “cryogels”. Carbon cryogels also have a low density, a high porosity and a high surface area [7].

Bacterial cellulose is a sustainable natural polymer that belongs to the polysaccharide family and is produced by acetic bacteria, *e.g.*, *Acetobacter xylinum*. This material has a unique structure and unique properties compared to other types of cellulose in terms of its high purity, crystallinity and mechanical strength. Above all, bacterial cellulose membranes (BCMs) have a monolithic macroporous 3D-network structure which is preserved during the carbonization process [8,9]. Therefore, af-

ter the carbonization process, a monolithic macroporous carbon cryogel (MMCC) can be obtained from a BCM.

In this study, MMCCs were prepared from a BCM. These cryogels were prepared using an easy process, which included solvent exchange, drying and carbonization, not sol-gel chemistry. The morphology and the pore characteristics of the cryogels were investigated using scanning electron microscopy (SEM) and nitrogen adsorption-desorption isotherms. These carbon cryogels can potentially be used as gas diffusion layers in fuel cells because of their high electrical conductivity, macroporous structure and hydrophobicity.

II. EXPERIMENTS AND DISCUSSION

Gluconacetobacter xylinum BRC-5 was cultured in a Hestrin and Schramm (HS) medium, which was composed of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.5% (w/v) bacto-peptone, 0.27% (w/v) disodium phosphate, and 0.115% (w/v) citric acid. The cells were precultured in a test tube for 3 days and then inoculated into a 60 × 15 mm Petri dish containing 10 mL of a HS medium. The cells were statically incubated in the Petri dish at 30 °C for 7 days. Then, the BCMS were purified in a 0.25-M NaOH solution for 48 h at room temperature in order to eliminate the cells and the components of the culture liquid. The pH of the BCM was lowered to 7.0 through repeated washing with distilled water. The BCM with distilled water was added to tert-butanol and then placed in an oven at 55 °C for 24 hour to replace the distilled water with tert-butanol. The BCM with tert-butanol was refrigerated at -30 °C for 6 hours and then freeze-dried. The freeze-dried bacterial cellulose cryogel

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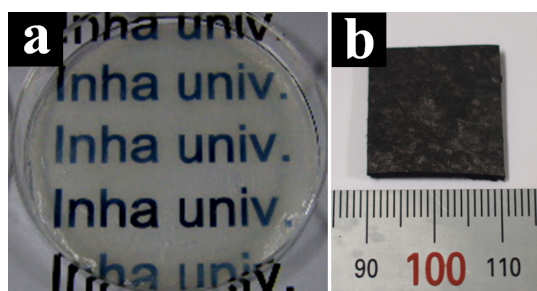


Fig. 1. Photo images of (a) the pristine bacterial cellulose membrane and (b) the carbon cryogel that was synthesized from the bacterial cellulose membrane.

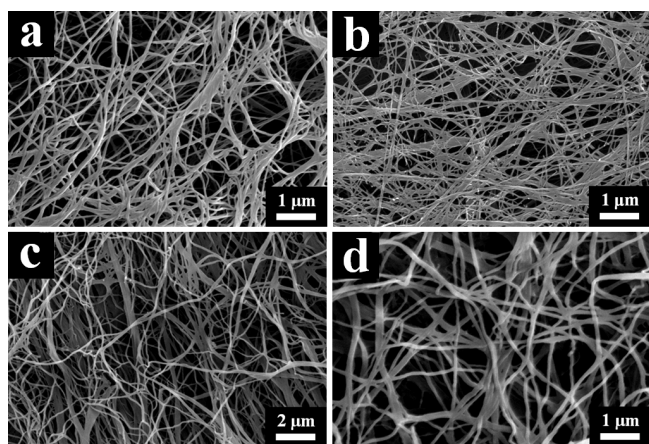


Fig. 2. SEM images of (a) a nano-sized fibril of the bacterial cellulose cryogel that was swelled in water, (b) a nano-sized fibril of the bacterial cellulose cryogel that was swelled in tert-butanol and (c), (d) the carbon cryogel that was synthesized from the bacterial cellulose membrane.

was carbonized at a heating rate of 5 °C/min to 800 °C with a nitrogen flow.

The morphology of the MMCCs was observed using SEM (S-4300, Hitachi, Japan) at an accelerating voltage of 15 kV after the sample had been precoated with a homogenous Pt layer through ion sputtering (E-1030, Hitachi, Japan). The porous properties of the MMCCs were analyzed using nitrogen adsorption-desorption isotherms that were obtained using the surface area and a porosimetry analyzer (ASAP 2020, Micromeritics, USA) at -196 °C. The BET surface areas (S_{BET}) were calculated according to the Brunauer-Emmett-Teller (BET) theory. The micropore surface area (S_{mic}) and the micropore volume (V_{mic}) were obtained using t-plot theory whereas the mesopore surface area (S_{meso}) and the mesopore volume (V_{meso}) were calculated according to the Barrett-Johner-Halendar (BJH) theory. The electrical conductivity of the MMCCs was measured using the four-probe method with an electrical conductivity meter (Hiresta-UP MCP-HT450, Mitsubishi Chemical, Japan). The contact angle was measured using an image analysis, where a water droplet was placed on the carbon cryogels and images were taken from the side. The size of the wa-

Table 1. Pore characteristics of the carbon cryogel synthesized from bacterial cellulose.

Sample Name	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{meso} (m^2/g)	V_{mic} (cm^3/g)	V_{meso} (cm^3/g)
Carbon cryogel	117.1	114.9	2.2	0.0603	0.2976

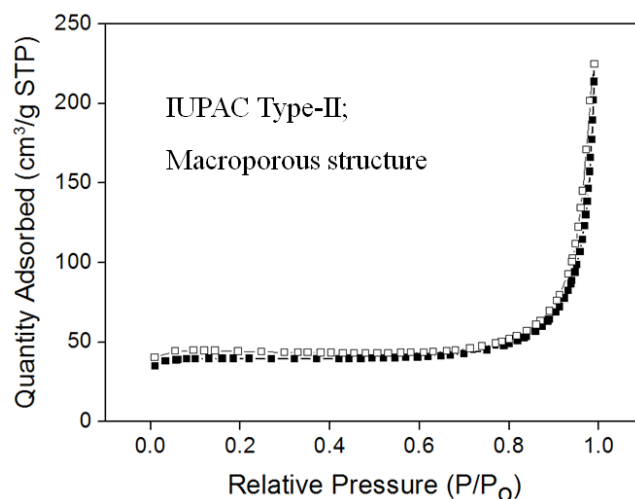


Fig. 3. Nitrogen adsorption-desorption isotherm of the carbon cryogel that was prepared from the bacterial cellulose membrane.

ter droplet was reduced to minimize the effect of gravity before the contact angle tests were carried out.

Figure 1 shows photo images of the pristine BCM and the carbon cryogel that was synthesized from the BCM. The pristine BCM was transparent and jelly-like. Additionally, the BCM exhibited good mechanical properties with both high toughness and flexibility (Fig. 1(a)). The carbon cryogels had a monolithic structure (Fig. 1(b)).

The microscopic morphologies of the bacterial cellulose cryogel and the carbon cryogel were investigated using SEM (Fig. 2). The nano-sized fibrils of the pristine BCM were three dimensionally inter-connected, and the structure was macroporous (Fig. 2(a)). The solvent exchange from distilled water to tert-butanol did not damage the macroporous 3D network structure of the BCM except for some shrinkage (Fig. 2(b)). The surface morphologies of the carbon cryogels that were synthesized from the BCM are shown in Figs. 2(c) and (d). The macroporous inter-connected structure was preserved after the carbonization process. However, the morphology of the carbonized bacterial cellulose membrane slightly differed from the pre-carbonized BCM, and its morphology was loose compared to the BCM that was swelled in water or tert-butanol.

The nitrogen adsorption-desorption isotherm showed the pore characteristics of the carbonized BCM (Fig. 3). This isotherm was similar to the IUPAC type II, which indicated that the BCM had a macroporous structure. Additionally, the isotherms at relatively low pressures

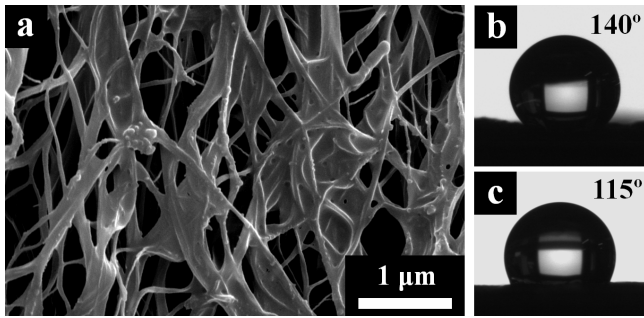


Fig. 4. SEM images of (a) a nano-sized fibril of the PTFE-treated carbon cryogel prepared from the bacterial cellulose membrane and contact angles of (b) the carbon cryogel, and (c) the PTFE-treated carbon cryogel.

showed that a large number of micropores existed in the carbon cryogel. The pore characteristics of the carbon cryogel are depicted in Table 1.

Figures 4(a) - (c) show the microscopic morphology of the PTFE-coated carbon cryogel, the contact angles of both the carbon cryogel and the PTFE-coated carbon cryogel, respectively. The contact angle of the carbon cryogel was 140° , corresponding to a very hydrophobic surface, which was caused by the large number of micropores on the surface of the cryogel. On the other hand, the contact angle of the PTFE-coated carbon cryogel was only 115° because most of the micropores on the surface of the carbon cryogel were covered with PTFE, and the surface was smoother. The sheet resistance of the carbon cryogel was $23 \Omega/\square$ which was slightly higher than the value of $38 \Omega/\square$ for the PTFE-coated carbon cryogel.

III. CONCLUSION

MMCCs were prepared from a BCM by using an easy process that included solvent exchange, freeze-drying and carbonization. The MMCCs contained a macropo-

rous structure with a large number of micropores, and the surface area of the MMCCs was $117.1 \text{ m}^2/\text{g}$. The sheet resistances of the carbon cryogel and the PTFE-treated carbon cryogel were 23 and $38 \Omega/\square$ respectively. Before PTFE treatment, the carbon cryogels were more hydrophobic because of the large number of micropores on the surface of the cryogel. The carbon cryogels that were synthesized from a bacterial cellulose membrane had a high electrical conductivity, a macroporous structure and hydrophobicity, making them a potentially good candidate for a gas diffusion layer in a fuel cell.

ACKNOWLEDGMENTS

This work was supported by the grant from the Industrial technology development program of the Ministry of Knowledge Economy (MKE) of Korea.

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