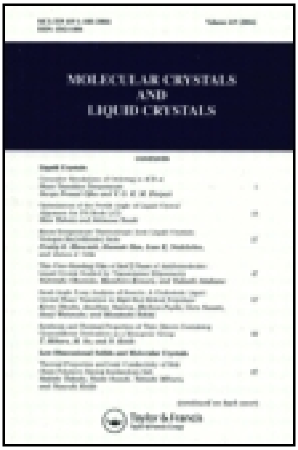


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Nanofibrillar carbon from native cellulose

Shigenori Kuga [a] , Dae-Young Kim [a] , Yoshiharu Nishiyama [a] & R. Malcolm Brown [b]

[a] Graduate School of Agricultural and Life Sciences, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, 113-8657, Japan

[b] Section of Molecular Genetics and Microbiology, The University of Texas, Austin, Austin, Texas, 78712-1095, USA

To cite this article: Shigenori Kuga, Dae-Young Kim, Yoshiharu Nishiyama & R. Malcolm Brown (2002): Nanofibrillar carbon from native cellulose, Molecular Crystals and Liquid Crystals, 387:1, 13-19

To link to this article: http://dx.doi.org/10.1080/713738864

Mol. Cryst. Liq. Cryst., Vol. 387, pp. [237]/13–[243]/19
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113510

NANOFIBRILLAR CARBON FROM NATIVE CELLULOSE

Shigenori Kuga, Dae-Young Kim, and Yoshiharu Nishiyama
Graduate School of Agricultural and Life Sciences,
The University of Tokyo, Yayoi, Bunkyo-ku,
Tokyo 113-8657, Japan

R. Malcolm Brown Jr.
Section of Molecular Genetics and Microbiology,
The University of Texas at Austin, Austin,
Texas 78712-1095, USA

Native cellulose samples with high crystallinity were pyrolyzed up to above 2000 C and the resulting carbon structures were examined. The drying method for water-swollen or water-suspended cellulose prior to pryrolysis was found to significantly affect preservation of the large surface areas of the original cellulose; i.e., solvent exchange drying (water-ethanol-t-butyl alcohol) of hydrogels and rapid-freeze drying of water suspended particles by spraying onto a cooled copper plate gave surface area of cellulose of 60–120 m^2/g, about twice of those by ordinary freeze dyring. The carbons derived from these materials had nearly the same surface area as the starting cellulose and maintained the nanofibrillar morphology.

Keywords: cellulose; nanofibrillar carbon; surface area

INTRODUCTION

Cellulose is an important source of pyrolytic carbon, but its use as a graphite precursor has been limited to regenerated fibers (rayon) [1,2]. Since the molecular organization of the starting material is known to strongly affect the structure of pyrolytic carbon, the highly crystalline cellulose materials attract our attention as possible sources of novel carbon materials. We present here some features of pyrolytic carbon from cellulose microfibril/microcrystal (actually having nanometer scale lateral sizes) derived from bacteria, a tunicate (sea animal), and cotton. We found that

This work was partly supported by Welch Foundation Grant 1217 to RMB.

the drying method of water-swollen or water-suspended cellulose prior to pyrolysis strongly affects the resulting carbon structure, and conclude that the carbon prepared via careful drying of native cellulose might be useful with its unique nanofibrillar structures.

EXPERIMENTAL

Cellulose

(a) Bacterial cellulose: Cellulose produced by *Acetobacter xylinum* (JCM10150) in static liquid culture (4% sucrose and 4% corn steep liquor). The resulting gel-like pellicle was washed with distilled water and treated with 1% NaOH at 80°C for 1 h, followed by rinsing. (b) Tunicate cellulose: The mantle of the tunicate was collected and purified [3]. (c) Whatman CF11 Cellulose Powder (cotton origin) was hydrolyzed with 60% H_2SO_4 at

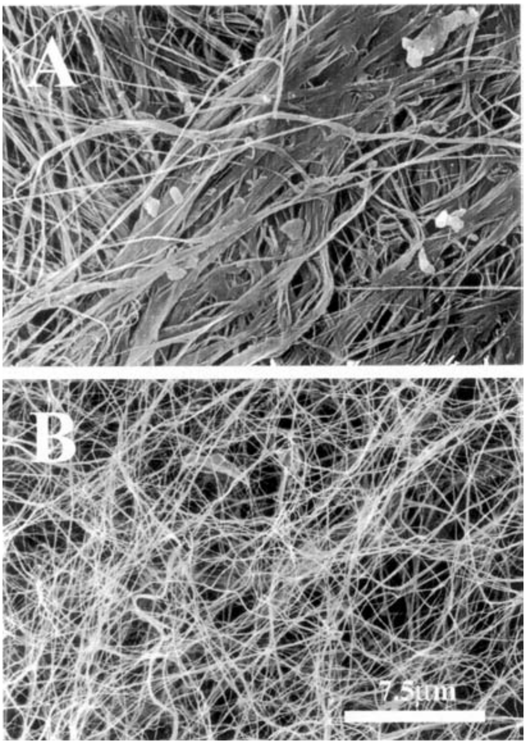


FIGURE 1 SEM image of (A) freeze-dried and (B) solvent-exchange-dried bacterial cellulose.

60°C for 4 h and resultant microcrystalline particles, typically 7 nm wide and 100–300 nm long, were collected as a water suspension.

Drying Method

The hydrogels of cellulose (bacterial and tunicate) was subjected to solvent exchange (water-ethanol-*t*-butyl alcohol) and freeze-dried. The microcrystalline suspension obtained by acid-hydrolysis was rapidly frozen by spraying it onto a liquid nitrogen-cooled copper plate. The resulting snow-like mass was freeze-dried.

Pyrolysis and High-temperature treatment

The dried cellulose samples were subjected to carbonization at 600°C and subsequently to high-temperature treatment at above 2000°C under a nitrogen or argon atmosphere.

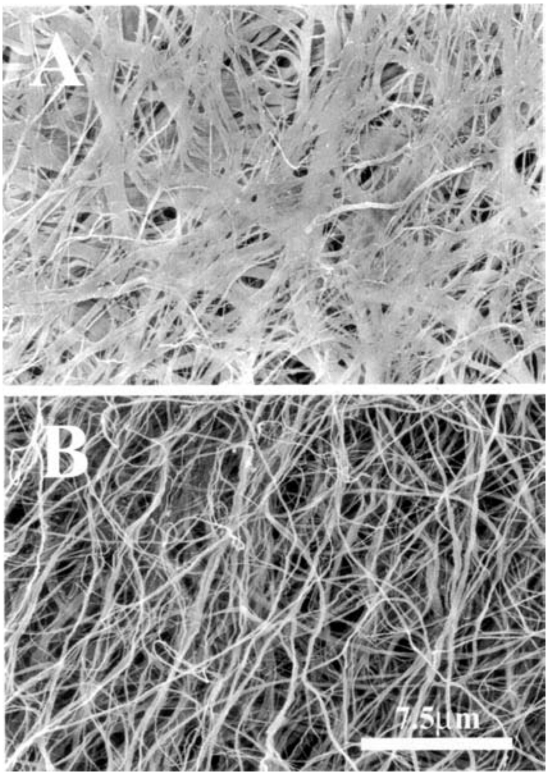
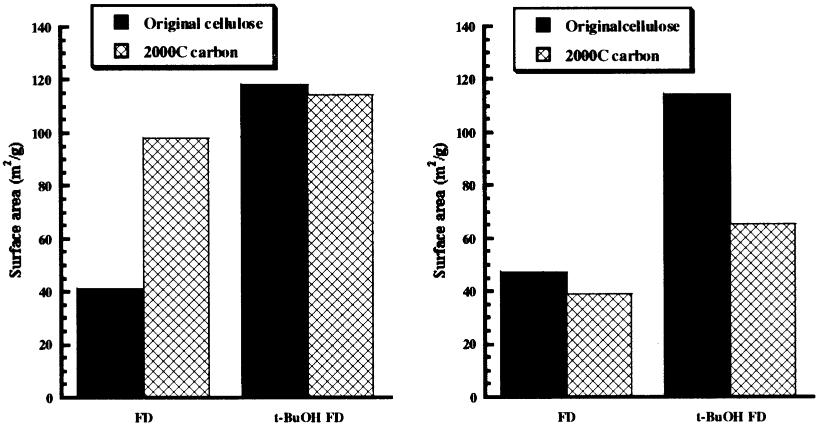


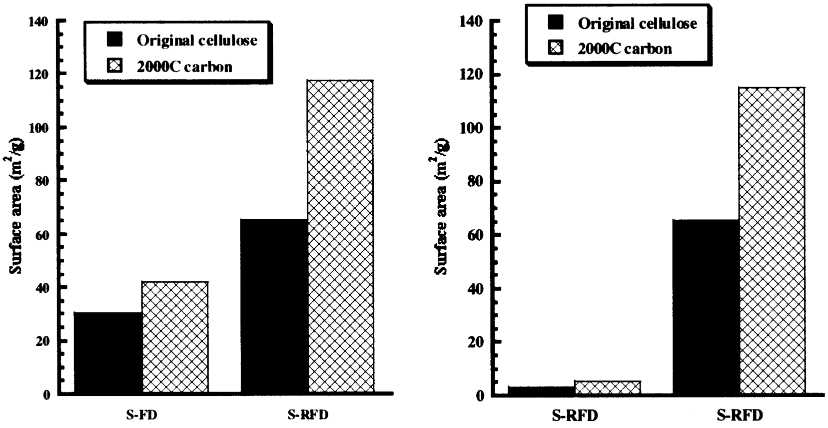
FIGURE 2 SEM image of (A) freeze-dried and (B) solvent-exchange-dried tunicate cellulose.

Characterization

The carbon samples were analyzed by X-ray diffraction, transmission and scanning electron microscopy (TEM: Philips EM420 with a Gatan 622 YAG crystal camera; SEM: Hitachi S4000 with field emission source), and nitrogen adsorption analysis (Coultar Omnisorp 100).



(A) Bacterial cellulose gel **(B) Tunicate cellulose gel**



(C) Bacterial cellulose suspension **(D) Whatman CF11 microcrystal suspension**

FIGURE 3 Surface area of original cellulose and corresponding 2000°C-treated carbon. Note the effect of drying methods: ordinary freeze drying (FD), solvent exchange-freeze (t-BuOH FD), and rapid feeze drying (RFD).

RESULTS AND DISCUSSION

The SEM observation revealed a striking influence of the drying method on the nanoscopic morphology of dried cellulose. While the ordinary freeze-dried materials were composed of many coalesced microfibrils forming wide bundles, the solvent exchange-dried samples were composed of finely divided fibrils apparently maintaining the original morphologies (Figs. 1 and 2). Correspondingly, the former gave specific surface areas of 30–40 m^2/g, against 100–150 m^2/g of the latter (Fig. 3(A)–(C), solid bars). Since the microfibril widths of 50–20 nm of bacterial and tunicate cellulose correspond to specific surface areas of 140–200 m^2/g, the actual values of 100–150 m^2/g indicate that the solvent exchange drying could mostly preserve the original separated microfibrils during the drying. The effect of rapid freeze drying of the microcrystal suspension derived from Whatman CF11 was more remarkable (Fig. 3, (d)).

The specific surface area of the carbon samples derived from these cellulose materials also reflected the influence of the drying method (Fig. 3, hatched bars). While the carbon samples carbonized at 600°C had surface areas of 500–600 m^2/g (data not shown), those of the high temperature-treated samples (2000°C and above) were close to those of corresponding cellulose. This indicates that the large surface area of 600°C carbon represents the inner surfaces of micropores and mesopores, which must have been lost by high temperature treatment. These features of the high temperature-treated samples were also manifested by electron microscopy (Figs. 4 and 5). The SEM images show that the microfibrillar morphologies are highly preserved after the high-temperature treatment, and therefore the surface areas described above are considered to represent the outer surfaces of microfibrils. The high-resolution TEM images (Figs. 4B and 5B) show the 002 lattice fringes of carbon crystallites, which are not typically

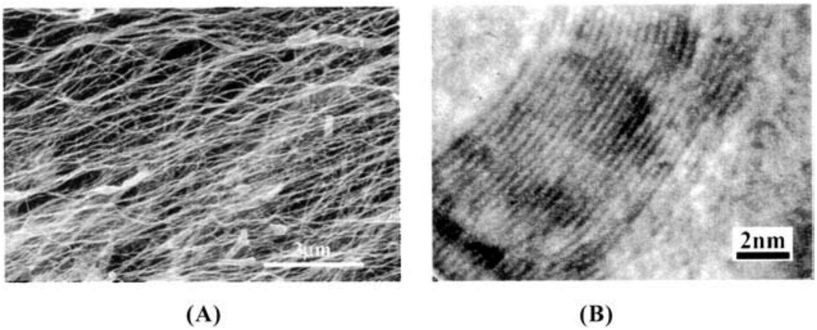


FIGURE 4 SEM (A) and TEM (B) images of high temperature-treated carbon from solvent exchange-dried bacterial cellulose.

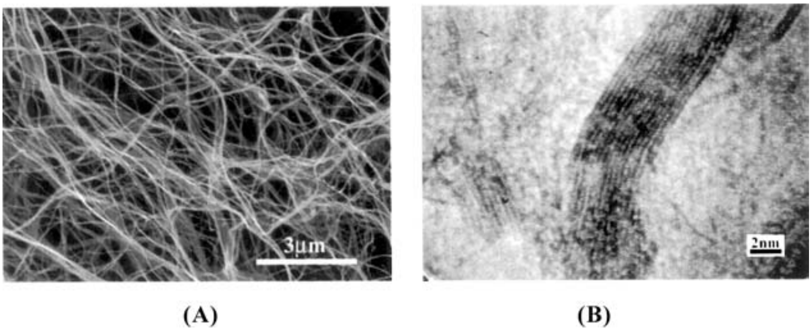


FIGURE 5 SEM (A) and TEM (B) images of high temperature-treated carbon from solvent exchange-dried tunicate cellulose.

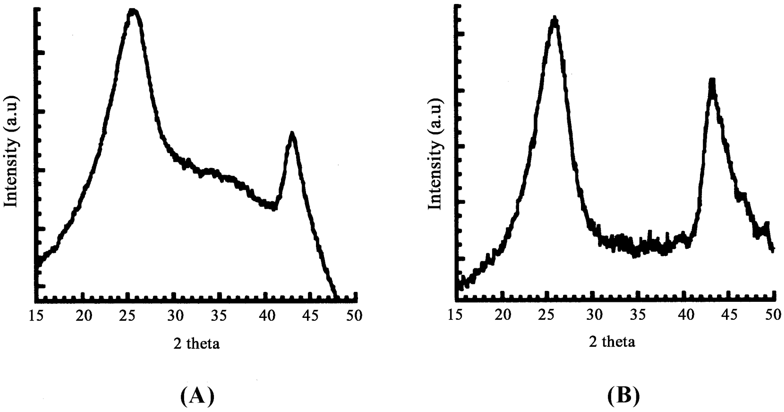


FIGURE 6 X-ray diffraction profiles of high temperature-treated carbon from solvent exchange-dried (A) bacterial cellulose and (B) tunicate cellulose.

seen in high temperature-treated carbon samples from the ordinary freezed-dried materials (data not shown).

Our high-temperature treatment did not cause full graphitization because of limitations in temperature; still they produce well defined X-ray diffraction patterns (Fig. 6), giving graphene spacings of 0.345 nm (bacterial cellulose) and 0.344 cm (tunicate cellulose). The broadness of the peaks does not necessarily mean poor crystalline orders, since the lateral sizes of crystallites are typically less than 10 nm; Such graphite crystallites have not been known previously and may provide a new class of carbon material.

REFERENCES

[1] Peebles, L. H. (1994). *Carbon fibers.* CRC Press.
[2] Pierson, H. O. (1993). *Handbook of carbon, graphite, diamond and fullerenes*, Noyes Publications, pp. 166–197.
[3] Wada, M., Sugiyama, J., & Okano, T. (1993). *J. Appl. Polym. Sci., 49*, 1491–1496.