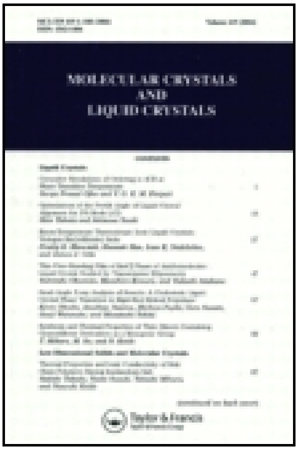

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Tem Observation of Metal-Loaded Carbon Aerogels Prepared by an Ion-Exchange Method

Noriko Yoshizawa [a] , Mildred S. Dresselhaus [b] , Ruowen Fu [c] , Joe Satcher [d] & Ted Boumann [d]

[a] National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, 305-8569, Japan

[b] Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA, 02139, USA

[c] PCFM Laboratory, Zhongshan University, Guangzhou, 510275, China

[d] Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, 94551, USA

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TEM OBSERVATION OF METAL-LOADED CARBON AEROGELS PREPARED BY AN ION-EXCHANGE METHOD

Noriko Yoshizawa
National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba 305-8569 Japan

Mildred S. Dresselhaus
Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139 USA

Ruowen Fu
PCFM Laboratory, Zhongshan University, Guangzhou, 510275 China

Joe Satcher and Ted Boumann
Lawrence Livermore National Laboratory, P.O. Box 808, Livermore 94551 USA

Cu-loaded carbon aerogel was prepared by soaking sol-gel production, obtained from K-salt of 2,4-dihydroxybenzoic acid, into $Cu(NO_3)_2$ *solution. XPS measurement demonstrated that Cu concentration is higher in the outside region of bulk samples, indicating that Cu may be incorporated through an immersing process rather than ion-exchanging. TEM observation showed that, like an aerogel sample with K ions, Cu-loaded organic aerogels had porous texture in which gel particles about 20–30 nmϕ were interconnected with each other. Metal-loading process used in this study was considered as a promising method to disperse metals without changing original structure of carbon aerogels.*

Keywords: carbon aerogel; sol-gel polymerization; TEM; XPS; Cu

INTRODUCTION

Carbon aerogels, synthesized for the first time by Pekala [1], are novel mesoporous carbon materials with a low mass density, a large amount of mesopores, a high surface area, a high electrical conductivity, and other interesting properties.

Porous structure of carbon aerogel can be modified by several methods. Before preparation of aerogel, mixing ratio and concentration of starting materials, and a type and amount of catalyst are considered as important factors in sol-gel process. Furthermore, introduction of metal into their structure has other possibility to control pore structure as well as surface property of the aerogel samples. So far, loading of some types of transition metals, TiO_2, Ce and Zr etc. have been reported mainly for catalytic applications [2–4]. Meanwhile, Cu has been pointed out as one of the candidates for electrochemical applications. It was indicated that porous carbon material prepared by carbonization of commercial ion-exchanged resin with Cu^{2+} ion showed very high performance for an electronic double-layer capacitor [5]. Carbon aerogel itself, actually, attracts much attention in this field because of its ideal pore structure.

We attempted to obtain Cu-loaded carbon aerogel by an ion-exchange method to achieve high dispersion of the metal. In this paper, structural dependences of samples upon preparation condition are summarized.

EXPERIMENTAL

Cu-doped organic aerogels were prepared by sol-gel polymerization of a K-salt of 2,4-dihydroxybenzoic acid and formaldehyde followed by soaking in $Cu(NO_3)_2$ in aqueous solution. Then, organic aerogels obtained through a supercritical drying process. The samples thus obtained are denoted as TFB-Cu. The blank aerogel sample prepared without immersed in $Cu(NO_3)_2$ is denoted as TFB-K. Finally, both the blank and copper-loaded aerogels were carbonized at 1323 K in a nitrogen atmosphere. The corresponding carbon aerogels were obtained and denoted by TFB-K-c and TFB-Cu-c, respectively. Densities and specific surface areas of these samples are summarized in Table 1.

TABLE 1 Preparation, Density and Surface Area of Samples

Sample	Metal	Carbonization/K	Density/mg cm^{-3}	Specific surface area/ m^2 g^{-1}
TFB-K	K	–	230	630
TFB-K-c	K	1323	325	465
TFB-Cu	Cu	–	220	615
TFB-Cu-c	Cu	1323	340	490

XPS was measured with AXIS HIS 165 and ULTRA Spectrometer made by Kratos Analytical Ltd. England, using A1 Kα radiation with a pass energy of 10 eV, a 0.1 eV step, and a dwell time of 50 ms. TEM observation was carried out with JEOL 2000FX at an accelerating voltage of 200 kV. For characterizations of micro- and mesoporous structure, Fourier transformation of electron diffraction patterns and fractal analysis of particle images were applied.

RESULTS AND DISCUSSION

Survey scanning spectra for the TFB-K and TFB-Cu samples showed that K was completely disappeared after the treatment in $Cu(NO_3)_2$ solution, while Cu was incorporated in the aerogel samples. However, content of Cu in TFB-Cu is smaller than expected, indicating that modification of ion-exchange condition is necessary to increase Cu content in the aerogels sample. It is also found by the feature of Cu_{2p} peak that Cu in TFB-Cu takes two status, i.e., Cu^{2+} and Cu^{+}, probably due to a partial reduction of Cu^{2+}. Distribution of K and Cu in the cross section of the samples was further studied in a cross section of the aerogels. As shown in Table 2, concentration of Cu in outside region is much higher than in the center region. This gradient of Cu content must be due to the dispersion of copper when the aerogel cylinder was immersed in a Cu^{2+} solution for the ion exchange process.

Observations with TEM shows (Fig. 1) that the organic aerogels (TFB-K and TFB-Cu) have highly dense packing texture with a network of carbonaceous particles (15–20 nm). Mesopores with almost the same, or often larger, size relative to those particles were found among the particles. There were not any Cu or related compounds particles large enough to be seen by TEM. Carbonized sample (TFB-K-c and TFB-Cu-c) also had a dense packing texture. Particulate structure in these carbonized samples shows low crystallinity, and the network of carbon particles seems more collapsed than the non-carbonized sample. The carbon particles show clear

TABLE 2 Distribution of Atomic Percentage of Elements in Aerogel Samples

Sample	Position	C(1s)	O(1s)	K(2s)	Cu(2p)
TFB-K	center	70.7	26.2	3.1	–
	middle	70.5	26.3	3.1	–
	outside	70.8	26.2	3.0	–
TFB–Cu	center	72.3	27.1	–	0.3
	middle	72.0	26.9	–	0.4
	outside	71.4	28.0	–	0.6

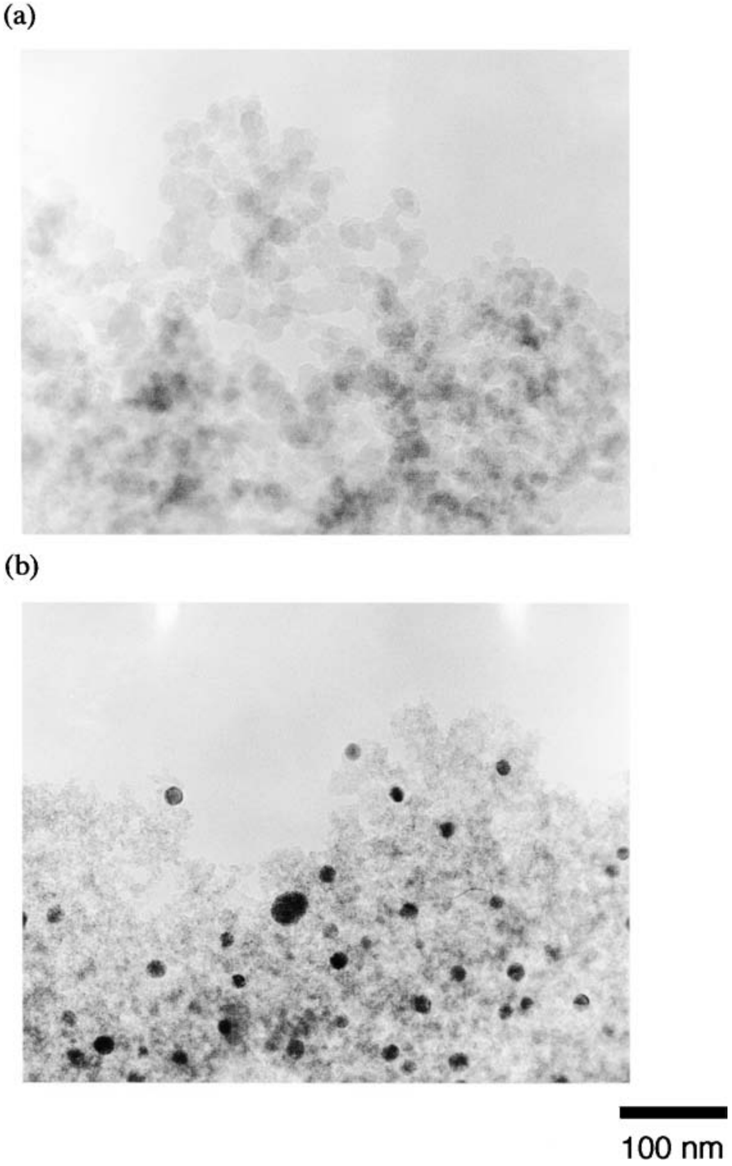

FIGURE 1 Typical TEM observation images for (a)TFB-Cu and (b)TFB-Cu-c.

TABLE 3 Fractal Dimension of Powders Taken from Each Sample

Sample	D	Density/mg g^{-1}
TFB-Cu	1.20	210
TFB-Cu-c	1.20	320
TFB-K	1.20	240
TFB-K-c	1.18	330
LM130(carbonized)	1.35	130
LM90(carbonized)	1.40	90
LM25(carbonized)	1.52	25

shrinkage to 10–15 nm, but mesopores are still present among these particles. We also found a lot of round Cu metal particles (10–30 nm) with a cubic lattice. But their concentration in the cylinder-shaped sample is lower in the central region, coinciding with a gradual penetration of Cu^{2+} ions into the sample.

We further investigated if there are any effects of the carbonization and Cu-loading upon the structure of aerogel samples. Studies were carried out by two methods: One is the Fourier transformation of electron diffraction patterns around carbon 002 peak, and the other was an evaluation of the fractal dimension of TEM images showing aggregation of carbon particles in texture. From the analysis by electron diffraction patterns, it is clear that an oscillation continues in a longer range for TFB-Cu-c, indicating that stacking structure of aromatic layers are developed by carbonization. However, very few differences were found between TFB-K and TFB-Cu.

About the fractal dimension (D), Table 3 summarizes the results for the samples estimated by a perimeter (X) and an area (S) with the equation $S^{1/2} = X^{1/D}$ [6]. Some data for carbon aerogel samples prepared with lower densities are also shown for comparison. Considering the same D values observed for TFB-K and TFB-Cu, aggregation of the particles did not change by the treatment with $Cu(NO_3)_2$ solution. Decrease of D seems to be related to the shrinkage of carbon particles during heat-treatment, but to a very small extent. These results lead to the conclusion that texture of the organic aerogel was almost unchanged during the metal-loading method used in this study.

CONCLUSION

Copper-loaded carbon aerogel was prepared by soaking a gel sample into $Cu(NO_3)_2$ solution of water. We should study more in detail upon the condition of ion-exchange process, considering that amount of Cu is far less than expected from K content originally kept in the gel sample. Nevertheless, this method has a great possibility to incorporate metals into aerogel sample, because of its capability to make the process without changing aerogel texture.

REFERENCES

[1] Pekala, R. W., Alviso, C. T., Kong, F. M., & Hulsey, S. S. (1992). *J. Non-Cryst. Solids.*, *145*, 90.

[2] Maldonado-Hodar, F. J., Moreno-Castilla, C., Rivera-Utrilla, J., Hanzawa, Y., & Yamada, Y. (2000). *Langmuir*, *16*, 4367.

[3] Maldonado-Hodar, F. J., Moreno-Castilla, C., & Rivera-Utrilla, J. (2000). *J. Applied Catalysts.*, *A203*, 151.

[4] Bekyarova, E. & Kaneko, K. (1999). *Langmuir*, *15*, 7119.

[5] Sakata, Y., Muto, A., Azhar Uddin, Md., Yamada, N., Marumo, C., Ibaraki, S., & Kojima, K. (2000). *Electrochem. Solid-State Lett.*, *3*, 1.

[6] Endo, M., Oshida, K., Takeuchi, K., Sasuda, Y., Matsubayashi, K., & Dresselhaus, M. S. (1994). *IEICE trans., C-II*, *J77-C-II*, 139.