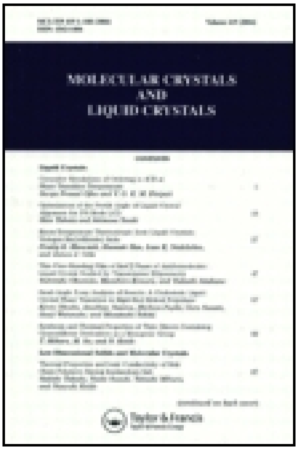

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Electro-active nano-graphite producedby electrochemical oxidation

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ELECTRO-ACTIVE NANO-GRAPHITE PRODUCED BY ELECTROCHEMICAL OXIDATION

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Nanoparticles of graphite are obtained by electrochemical oxidation in water with graphite anode. Carbon colloid is obtained as a result of electrolysis in deionized water. The surface of the colloidal carbon is chemically modified. This was confirmed by optical photo-absorption spectroscopy, ^{13}C-NMR and ESCA. These results indicate that the surface is chemically modified by -OH and -COOH groupes. X-ray diffraction spectroscopy was also performed and the results show that several diffraction peaks appear together with the peak which is attributed to graphite ($2\theta = 26.2°$). Regarding the particle size of the colloidal carbon investigation was performed with SEM, AFM and STEM (scanning transmission electron microscope) and it was found that the size of the colloidal carbon is 2–6 nm.

Keywords: nano-graphite; chemical modification; electrochemical doping

INTRODUCTION

Nanocarbons such as fullerenes [1,2] and nanotubes [3] are already well known. In addition to fullerenes and nanotubes, other nano size carbons are also reported. One is carbon particles produced by plasma CVD method under high pressure [4]. The other nano-graphite is obtained by heat treatment of nano-diamond [5]. We have reported that nano-graphite is produced by an electrochemical oxidation of graphite anode, that the surface of carbon particles are modified with -OH and -COOH groupes and

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that the nanocarbon is effective for elongation of life-time of lead acid batteries [6]. However, we could not obtain a picture of carbon particles with a good quality. In this paper we will report an AFM image of nano-graphite and that the size of nano-graphite was confirmed by STEM.

EXPERIMENTAL

Artificial graphite (TYK GL-500) was mixed with small amount of pitch, pressed to form electrode and then heated up to 2800°C. Using this graphite plate as an anode and a platinum plate as a cathode, de-ionized water was electrolyzed with applying DC voltage ($3 \sim 7\,V$) between them. Electric current was very weak at first stage. However after some retardation ($\sim$7 hr) appreciable current was observable and the water turned to yellow or brown near the anode for a short period and then the colloidal carbon started to appear. For the analysis of properties, ^{13}C-NMR, optical photo-absorption spectroscopy, Raman spectroscopy, ESCA and voltammetry were performed. For WAXD spectroscopy measurement was carried out by WAXD spectrometer (Rigaku-Denki RAD-RX) with a Cu-Kα X-ray source. To obtain images of nano-graphite, SEM, AFM and STEM (Scanning transmission microscope) were employed.

RESULTS AND DISCUSSION

Carbon colloid was obtained from the electrolysis of de-ionized water after some period of delay. Dispersity of carbon was very good without adding any dispersive reagent. ESCA spectrum was taken for the dried colloidal carbon and two peaks were observed at ~ 533 eV and ~ 285 eV, and these can be ascribed to O_{1s} and C_{1s}, respectively. The spectrum was also taken for graphite which is not subjected to electrochemical oxidation (the raw material used for the electrode). In this case only trace peak was seen for O_{1s}. These results indicate that the carbon was oxidized as a result of electrolysis. Fortunately, C_{1s} band can be separated into subpeaks and this is shown in Figure 1. These subpeaks reflect chemical shifts. The assignment and the area of each peak are given in Table 1. The amount of oxygen on the surface was estimated to be 32.5 atomic %.

The production of colloidal carbon is initiated by the reaction between electron and oxygen and these turn to be OH^- at the final stage. OH^- could move to the graphite anode by the electric force, looses the charge and then is consumed for oxidation of graphite. Thus, -C(O)O- and -C-O- in Figure 1 and Table 1 are probably -C(O)OH and -COH. In fact the pH value of the obtained carbon colloid was about 2.5. The dispersibility of the colloid comes from the existence of -OH and -COOH groupes on the surface

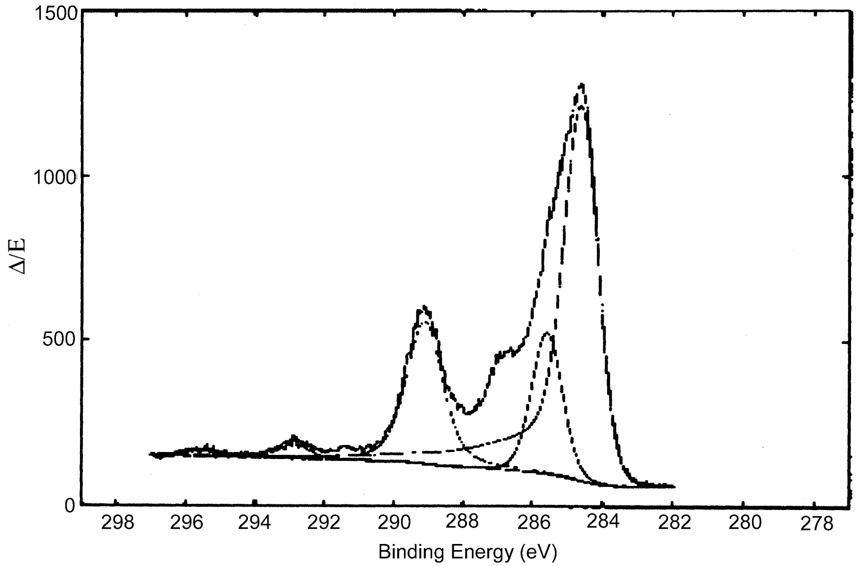

FIGURE 1 C_{1s} band of the dried colloidal carbon. The sub-bands are given by computational work.

of carbon particles. It should be mentioned that an information from ESCA spectroscopy is limited at surface area in substance not in the bulk. Therefore the results in Figure 1 indicate that surface of colloidal graphite is chemically modified.

We have tried to measure FTIR spectrum for the colloidal carbon but did not succeed because of strong absorption by graphite of itself. However the carbon colloidal aqueous solution exhibits photo-absorption peak at about 230 nm. This absorption could be due to carboxyl groups. Optical absorption spectra were taken during the process of electrochemical oxidation. Shift of absorption peak to longer wavelength was observed in the

TABLE 1 Peak Energy, Area and Assignment of Peaks

Peak (eV)	Area (%)	Assignment
290.9	19.91	π-π^* satellite
288.8	5.94	-C(O)O- carboxyl
286.8	10.33	-C-O-
285.6	14.44	$-CH_3$
284.6	52.85	graphite

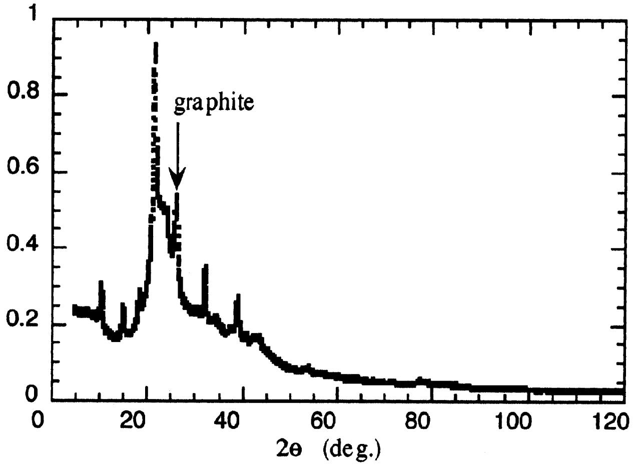

FIGURE 2 WAXD spectrum of the dried colloidal carbon.

beginning of electrolysis. This could reflect an oxidation process. The result from ^{13}C-NMR spectroscopy also showed that graphite was oxidized.

WAXD spectrum is shown in Figure 2. Several peaks are observed together with that at 26.2° which can be ascribed to graphite (0 0 2). These unidentified peaks could be due to the modified chemical structure on the surface of the nano-graphite. The nano-graphite still holds good conductivity.

Voltammetric spectrum of the 0.01% carbon solution is shown in Figure 3. Pb and PbO_2 electrode showed similar results. With proceeding voltammetric cycles the current in the potential region from −0.8 to +1.2 V in Figure 3 decreased, accumulation of carbon on the surface of the test

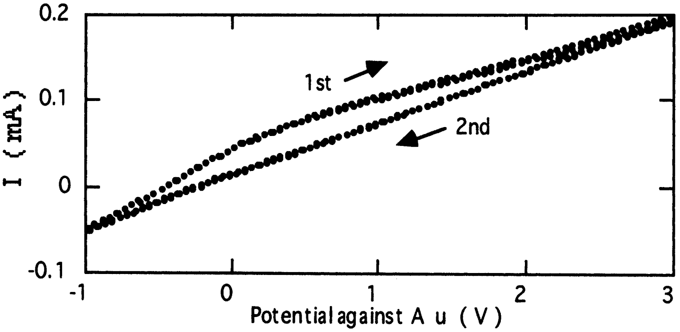

FIGURE 3 Voltammogram of the Pb electrode in the carbon colloid.

electrode was observed, and the content of carbon in the solution was decreased. Thus, the current in the potential region described above can be attributed to doping current of colloidal carbons. However, undoping current is not generally observable at the carbon concentration described above. The disappearance of undoping current could be due to accumulated charges on the test electrode. The doping could be that -COO$^-$ looses the negative charge at the electrode.

Carbon particles obtained by drying up the carbon colloidal solution was about 1 μm. However, carbon particles in the colloidal solution pass through a micropore membrane (0.2 μm). This means that carbon particles aggregate during the process of vaporizing water. Then colloidal solution was freeze-dried and carbon layer of 0.6 μm thickness was observed by SEM. However, no particle was observed.

The carbon colloidal solution was spread on a mica plane and AFM images were taken. One of those is shown in Figure 4. It is obvious that the diameter of the probe tip is far larger than that of carbon particles. Therefore any information on X-Y scale is not reliable at all. However the information on Z scale is reliable. The results from AFM images indicate that particle size of the carbon ranges from 2 to 6 nm. The mean value is about 4 to 5 nm. This value agreed well with that from Raman spectroscopy.

The colloidal solution was also spread on a Al foil with 0.8 μm thickness and observed with TEM. With increasing sensitivity of TEM no images were taken. When the thickness Al foil was decreased by a bombardment of Ar$^+$, particles of 4–5 nm size were observed but the image was not good for a presentation.

The carbon colloidal solution was then liquid-atomized by ultrasonic wave (2.4 Mhz). A scanning transmission electron microscope (STEM) was

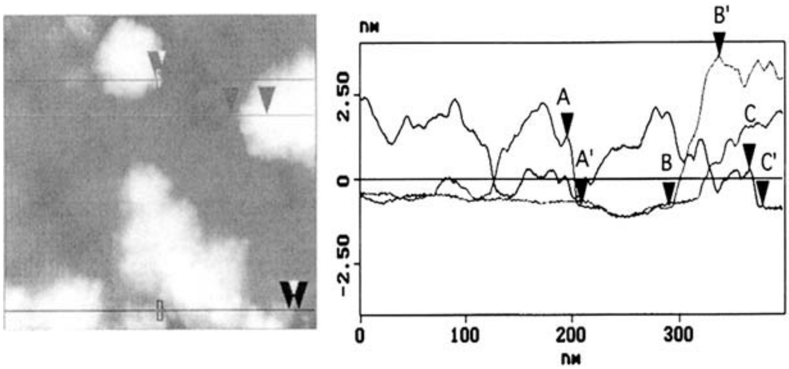

FIGURE 4 Atomic force microscope image (left) and the height of the dried carbon (right).

employed this time. When a microgrid for STEM measurement was sprayed directly, no image was observed. Then the microgrid was touched to a micropool caused by the atomization. In this case STEM images were observed and images of grains (about $2 \times 5\,\mathrm{nm}$) were obtained only in the dark field. The reason why no image was observed when the microgrid was directly sprayed is not known. There may be some spacial distribution for carbon concentration during liquid atomization.

REFERENCES

[1] Kroto, E. W., Hearth, J. R., O'Brien, S. C., Curl, R. F., & Smalley, R. E. (1985). ***Nature***, ***318***, 162.
[2] Ohsawa, E. (1970). ***Kagaku***, ***25***, 850.
[3] Iijima, S. (1991). ***Nature***, ***354***, 56.
[4] Yagi, H., Ide, T., & Toyota, H. Presented at the annual meeting of the Carbon Society of Japan, Ehime University, Dec., 1997.
[5] Enoki, T. & Prasad, B. L. V. (2001). ***Tanso***, 139.
[6] Kimura, T., Ishiguro, A., Andou, Y., & Fujita, K. J. (2000). ***Power Sources***, ***85***, 149.