# Preparation of Pillared Carbons by Pyrolysis of Silylated Graphite Oxide

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Pillared carbons containing silica between their carbon layers were first prepared by the pyrolysis of graphite oxide silylated by 3-aminopropyldiethoxymethylsilane between 450 and 550 °C under vacuum. They possessed both microporosities and mesoporosities existing between their carbon layers.

Carbon materials with a large surface area or controlled pore sizes are very useful for adsorbents, support of catalysts, electrode material of electric double layer capacitors, etc. Activated carbons are well known for this type of carbons; however, it is rather difficult to control the pore sizes and structure. Therefore, recently, the synthesis of various carbons with controlled pore structure and high surface area such as templated carbons has been reported.[1–3] Pillaring is also one of the technique to open the pore structure of various layered materials such as clays, etc.[4–6] In this context, several attempts to obtain pillared carbons starting from the intercalation compounds of graphite oxide (GO) have been provided recently.[7,8] Precursors of the pillar were first introduced between the layers of GO by soft chemical techniques such as ion exchange and then the intercalation compounds were pyrolyzed. Porous carbons were obtained; however, the order of carbon layers was almost lost in the resulting materials probably because the decomposition of the intercalation compounds occurred prior to the transformation of GO to carbons. On the other hand, we have recently reported silylation of GO using various silylating reagents.[9–11] In the resulting silylated GOs, the intercalated species are bonded to the layer of GO tightly by covalent bonding. Thermal decomposition of these materials would give pillared carbons because of the higher thermal stability of silylated graphite oxide, avoiding the aggregation of the precursor of pillar prior to the decomposition of GO layer to carbon. This type of pillared carbons is expected to possess pores between the carbon layers as was reported for metal oxides and would be very useful for the above-mentioned applications. In this study, therefore, silylated GO was thermally decomposed and the resulting material was investigated.

GO was prepared by oxidizing graphite powder (Aldrich, 1–2 µm) with $KClO_3$ in fuming nitric acid at 60 °C by the Brodie's method, and GO with the composition of $C_8O_{4.5}H_{3.0}$ was obtained. GO (100 mg) was silylated by 3-aminopropylmethyldiethoxysilane ($NH_2C_3H_6SiCH_3(OC_2H_5)_2$, hereafter abbreviated as AP2ES; 0.87 mL) in toluene (20 mL) under reflux for 6 days.[11] After centrifugation, the precipitate was washed with acetone several times. The obtained samples (abbreviated as GO-AP2ES) were dried at 60 °C under reduced pressure for 12 h. The Si content was calculated from the weight of residual $SiO_2$ after thermogravimetric measurement and 13.3% was obtained. Pyrolysis of silylated GO was performed by heating it at various temperatures under vacuum for 5 h. The temperature increasing rate was 1 °C/min. The products (abbreviated as PGO-AP2ES) were treated by 47% aqueous HF solution overnight, in order to remove Si-containing species. These samples were analyzed by X-ray diffraction (Rigaku, Rint-2100, Cu K$\alpha$), FT-IR (Nicolet Avatar 360 KBr method), TEM (Hitachi H-9000, accelerating voltage of 300 kV), and nitrogen adsorption (Bel Japan Inc., BELSORP-miniII, 77 K) measurements.

Figure 1 shows the X-ray diffraction patterns of GO-AP2ES and those heated at various temperatures. At 400 °C, the (001), (002), and (003) diffraction peaks at $2\theta = 6.8$, 13.5, and 21.0° observed for the pristine GO-AP2ES[11] seemed to shift to higher angles and became very road; however, at 450 °C, new and relatively sharper diffraction peaks at 14.3 and 22.1° appeared. These peaks can be indexed as (002) and (003) lines, respectively, and the interlayer spacing was calculated to be 1.23 nm. As the temperature increased, these peaks slightly shifted to lower angles, became broader, and disappeared at 600 °C, providing a new peak

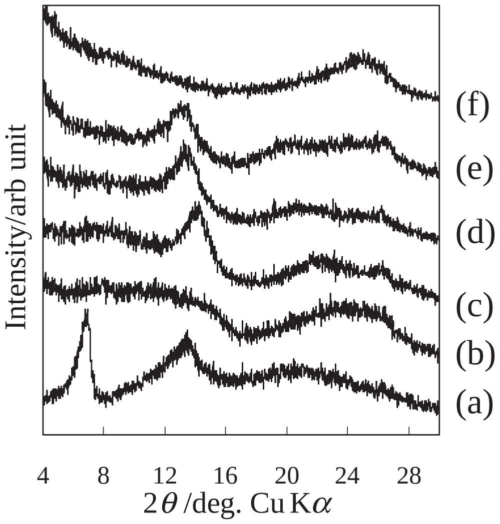

**Figure 1.** X-ray diffraction patterns of (a): GO-AP2ES and those pyrolyzed at (b): 400, (c): 450, (d): 500, (e): 550, and (f): 600 °C.

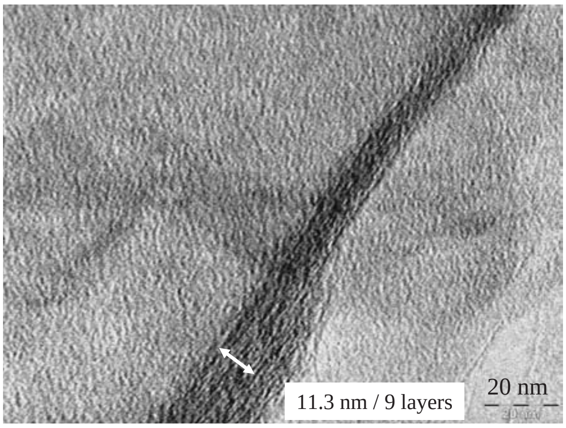

**Figure 2.** TEM image of PGO-AP2ES obtained at 500 °C.

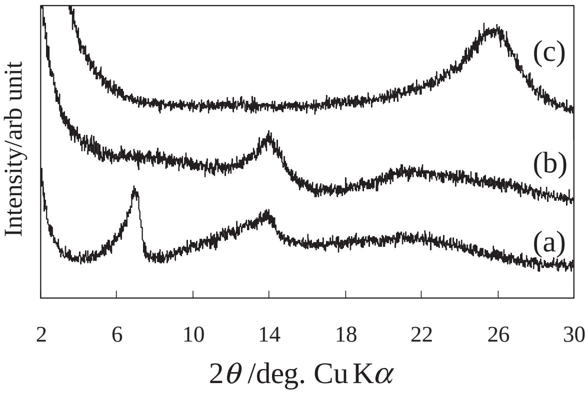

**Figure 3.** X-ray diffraction patterns of (a): GO-AP2ES, (b): PGO-AP2ES obtained at 500 °C and (c): PGO-AP2ES (500 °C) immersed in HF solution overnight.

at 25.2° probably due to the residual carbon. In addition to this, in the IR spectrum of the PGO-AP2ES obtained at 500 °C, the absorption peaks around $2920\,\mathrm{cm}^{-1}$ derived of alkyl groups of silylating reagent completely disappeared. The absorption peak around $1100\,\mathrm{cm}^{-1}$ was observed, indicating that Si–O bonding still survives even after pyrolysis.

Figure 2 shows the TEM image of the PGO-AP2ES obtained at 500 °C. The samples were mainly consisting of plate-type particles which are typical for carbon species, and particles with other shapes were hardly observed. The lattice images of the layered structure were clearly observed, and the distance between the adjacent layers was calculated to be 1.26 nm, which was almost the same as that obtained from X-ray diffraction data (1.29 nm). These strongly indicate that the organic components in GO-AP2ES were completely removed from the silylated GO and that the carbon pillared by silica was obtained between 450 and 550 °C. The sizes of the silica between the carbon layers were about 0.9 nm.

Figure 3 shows the X-ray diffraction patterns of PGO-AP2ES obtained at 500 °C and that after immersed in HF solution, together with the sample before pyrolysis. The diffraction peaks due to pillared carbon at $2\theta = 14.0$ and 21.0° disappeared after HF treatment and a peak at $2\theta = 26.1°$ ($d = 0.34$ nm) was observed. The silicon-containing species easily dissolved in HF solution; therefore, this peak is ascribed to the residual carbon. In addition, SEM observation showed that PGO-AP2ES samples consist of the aggregated plate-type particles, and the SEM images of PGO-AP2ES samples before and after HF immersion were very similar to each other. These also suggest that the PGO-AP2ES samples possess a layered structure and include silicon-containing species between the carbon layers. The silicon contents determined from the TG data were 19.0% and the Si/C ratio was calculated to be 6.2, by the elemental analysis of carbon and the above silicon contents. These types of carbon were obtained only when GO-AP2ES with a silicon content higher than 12.0% was pyrolyzed, otherwise a diffraction peak at $2\theta = 25°$ due to carbon appeared, together with the peaks around $2\theta = 14$ and 21° of pillared carbon. It seems that an appropriate amount of silicon was needed in order to maintain regularly stacked layered structure.

Figure 4 shows the nitrogen adsorption isotherm of PGO-AP2ES, together with that for PGO-AP2ES after HF treatment. The PGO-AP2ES after HF treatment presents type II, and the amount of adsorbed $N_2$ was very low. The Brunauer–Emmett–Teller (BET) surface areas was only $21\,\mathrm{m}^2/\mathrm{g}$. On the other hand, the isotherm of PGO-AP2ES presents the shape of type IV. The evident adsorption hysteresis suggests the existence of mesoporosity. A steep increase at $P/P_0 < 0.1$ was observed, indicating the existence of micropores. The total specific surface area determined by the BET method was $226\,\mathrm{m}^2/\mathrm{g}$. These strongly suggest that the outer surface of carbon is not responsible for the mesoprosity and microporosity and that they exist most likely between the carbon layers of PGO-AP2ES samples. The $\alpha_s$-plot of the adsorption isotherm of PGO-AP2ES built up based on detailed standard adsorption data on a nonporous carbonaceous material[12] showed that the average micropore width was 0.85 nm, which was very similar to the space between two adjacent carbon layers obtained from the datum of X-ray diffraction. Considering that the pristine GO-AP2ES showed type II isotherm and gave a low BET surface area, the pores are formed as the result of the removal of organic components originating from the silylating reagent. The desorption branch does not close with adsorption branch, indicating that there are very narrow micropores in which the diffusion of nitrogen molecules needs activation energy.

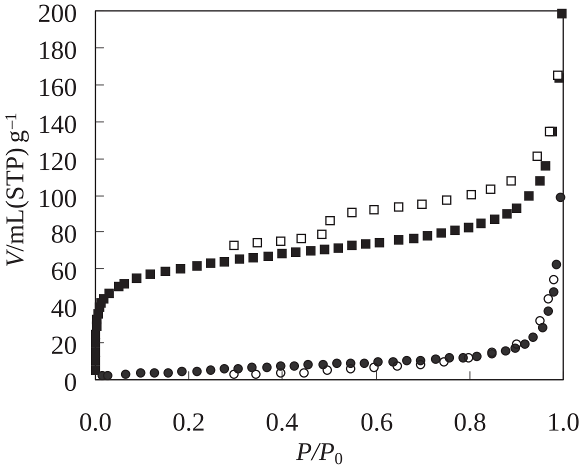

**Figure 4.** Nitrogen adsorption isotherms of square: PGO-AP2ES (500 °C) and circle: PGO-AP2ES after HF immersion. The filled and open marks indicate the adsorption and desorption branches, respectively.

In conclusion, starting from the silylated GOs, carbons pillared by silica were successfully obtained for the first time. They possessed both microporosities and mesoporosities existing most likely between carbon layers.

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