

Carbonaceous Materials Prepared from Carbon Tetrachloride and Dimethyl Sulfoxide

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ABSTRACT: A novel liquid/solid two-phase reaction has been discovered that enables destruction of carbon tetrachloride (CCl_4) to a black carbon-based material. The solid phase is potassium hydroxide, and the liquid phase is a dimethyl sulfoxide (DMSO) solution of carbon tetrachloride and contains a certain amount of tetrabutylammonium bromide (TBAB) as the phase-transfer catalyst. The reaction can be carried out at room temperature and under normal pressure. Pyrolysis of the carbon-based materials at 700°C and under a nitrogen atmosphere resulted in the formation of amorphous carbonaceous nanoparticles with diameters in the range of 30–60 nm. The carbonaceous materials have a specific surface area of $430\text{ m}^2/\text{g}$ and an average pore size of 16 Å. Raman spectral and elemental analysis results show the carbonaceous material consists of sp^3 and sp^2 carbons and also contains a small amount of hydrogen ($\text{H/C} = 0.08$). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 785–791, 2002

Key words: carbonaceous material; carbon tetrachloride; dimethyl sulfoxide; pyrolysis

INTRODUCTION

It is known that low molecular weight chloro-/bromo-hydrocarbons can be carbonized by solid potassium hydroxide under a phase-transfer condition.^{1–3} However, saturated halogenated carbons such as carbon tetrachloride are much more stable than are corresponding hydrocarbons and cannot be carbonized by the same technique. In this article, we report a novel reaction of carbon tetrachloride and dimethyl sulfoxide (DMSO) in the presence of solid potassium hydroxide. The

product is a powdery carbon-based material. Pyrolysis of the carbon-based materials led to the formation of a new carbonaceous material.

EXPERIMENTAL

Materials

Carbon tetrachloride (Tianjin Yuehua Chemical Factory, Tianjin, China) and DMSO (Beijing Yili Fine Chemical Co., Beijing, China) were chemically pure and used after distillation. Tetrabutylammonium bromide (TBAB; Beijing Daxin Fine Chemicals Institute, Beijing, China) and potassium hydroxide (>85%, Tianjing Yuehua Chemical Factory) were analytical-grade pure and used without further purification. KOH was ground into particles with diameters less than 2 mm before use.

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Table I Elemental Analysis Results of the Carbon-based Materials

Sample No.	Molar Ratio ^a	PH ^b	C %	H %	S %	O %	Cl %	Composition Formula
1	2:3	2–3	38.43	2.69	15.00	15.53	28.36	C _{6.83} H _{5.70} S _{1.00} O _{2.07} Cl _{1.70}
2	2:3	7–8	33.47	2.675	12.74	13.40	37.72	C _{7.00} H _{6.72} S _{1.00} O _{2.10} Cl _{2.66}
3	2:3	~ 7 ^c	44.45	3.71	15.62	18.49	18.16	C _{7.64} H _{7.65} S _{1.00} O _{2.32} Cl _{1.06}
4	1:1	7–8	41.49	3.92	15.62	16.78	22.20	C _{7.08} H _{8.03} S _{1.00} O _{2.14} Cl _{1.28}
5	1/2	7–8	41.83	3.65	16.22	15.08	23.22	C _{6.88} H _{7.20} S _{1.00} O _{1.86} Cl _{1.29}

^a The initial molar ratio of DMSO and CCl₄.

^b pH of the solution before product separation.

^c The product was separated directly without neutralization with aqueous HCl and then washed to a PH close to 7.

Carbonization

A typical reaction is 0.08 mol DMSO mixed with 0.12 mol CCl₄ and 0.006 mol TBAB. The solution was dropped slowly into 0.96-mol solid KOH particles and finished in about 2 h. The system was stirred mechanically and the reaction temperature was controlled at 20–30°C by a water bath. The reaction was carried out under a nitrogen environment and a condensing tube was used to prevent the escape of carbon tetrachloride. After the solution was added, the reaction was continued for another 4 h. DMSO reacted with carbon tetrachloride quickly, and a black product formed immediately and covered on the surface of the base. Finally, the reaction mixture was put into a large amount of ice-cooled water to dissolve the excess base and the salt formed during the reaction process. The dark brown rough product was separated by centrifugation and then washed with water repeatedly. In an alkaline solution, the product dispersed well and a long time was needed for complete deposition. Therefore, we also neutralized the solution with 2 mol/L HCl to pH 6–8 or to 2–3 for accelerating the deposition rate. Well-washed clean products were dried under a vacuum at 60°C for 24 h before characterization.

The yield (f) of carbonization was determined by weighting the product and using eq. (1):

$$f = [W_p r_p / (W_d r_d + W_c r_c)] \times 100\% \quad (1)$$

where W_p , W_d , and W_c are the weights of carbonization product, DMSO, and carbon tetrachloride, respectively. r_p , r_d , and r_c are their corresponding carbon contents. The reaction conversion, f , depends strongly on the reaction and purification conditions and a maximum of 37% was obtained. The initial molar ratio of DMSO/CCl₄ was con-

trolled at 3 : 2 and the product was separated from the acidic medium.

Pyrolysis of the carbon-based products prepared through the procedures described above was carried out in a tube furnace for general experiments. Generally, the raw material was placed in a ceramic boat and introduced into the tube furnace. Air in the furnace was replaced by N₂ for at least 20 min. The sample was heated at a rate of 10°C/min to a given temperature under a nitrogen atmosphere, which was maintained for 2 h. The obtained carbonaceous material was cooled to room temperature under a nitrogen atmosphere.

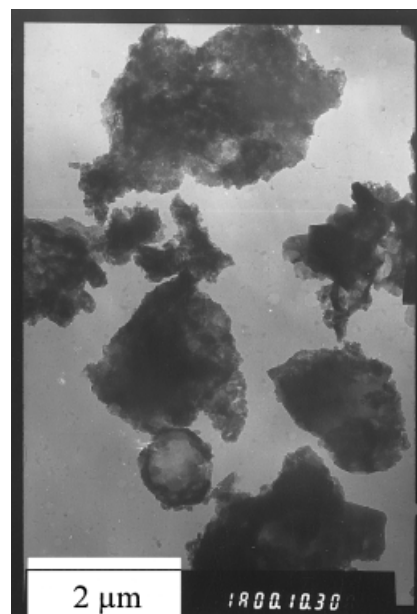


Figure 1 Transmission electron micrograph of sample 1.

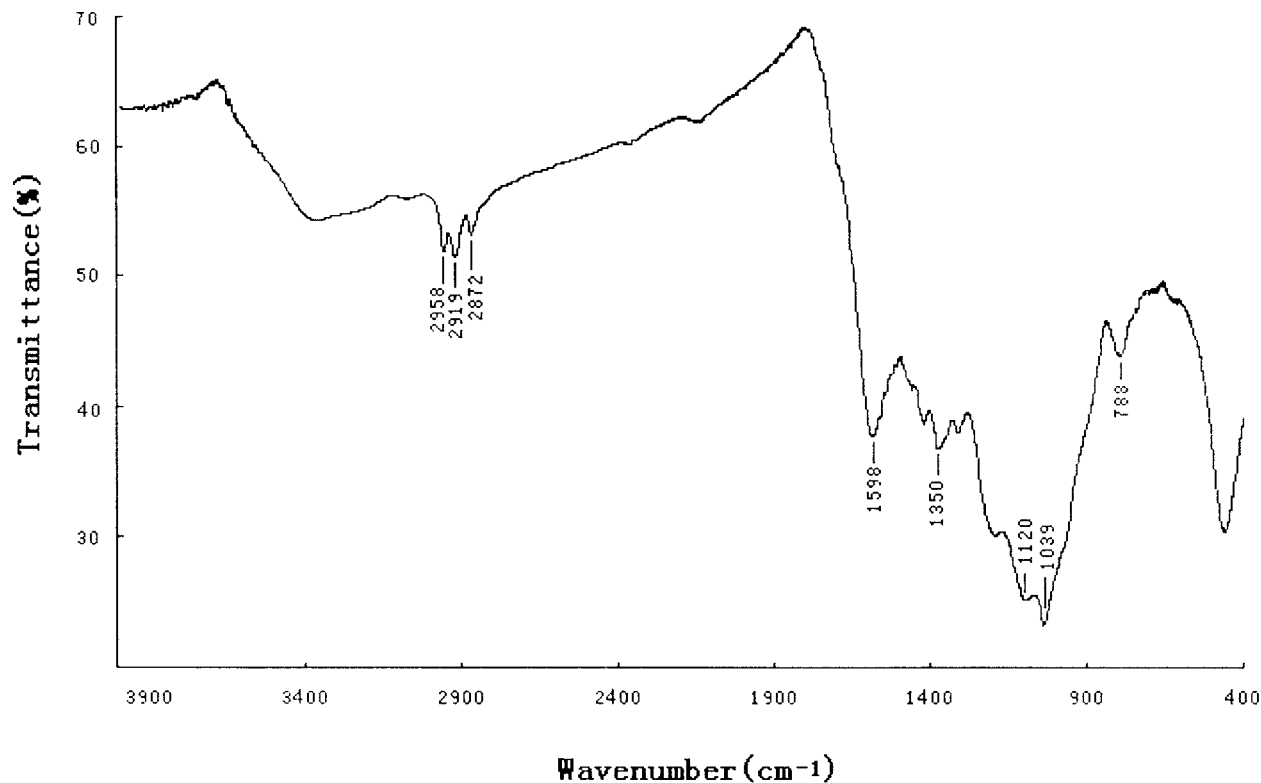


Figure 2 FTIR spectrum of sample 2.

Structure Characterization

Infrared and Raman spectra were recorded on a Nicolet Avata 360 FTIR spectrometer and an RM1000 Raman spectrometer of the Renishaw Co., respectively. The Raman spectra was performed with a 632.8-nm laser light, excited at 0.5 mW, and accumulated for 60 s. Elemental analysis was carried out using an Elementar Vario EL elemental analyzer (Germany). A transmission electron micrograph was taken using an EM-200CX electron microscope. X-ray diffraction analyses were carried out on an XD-3A X-ray diffraction analyzer with a Cu target. The Brunauer–Emmett–Teller (BET) surface area and pore-size distribution of the carbonaceous materials were measured using a Quantachrome Nova 1200. The samples were heated under a vacuum at 200°C for 0.5 h prior to the measurements.

RESULTS AND DISCUSSION

Carbon-based Material Made from Carbon Tetrachloride and DMSO

Five samples of the carbonization product prepared under different reactions and purification

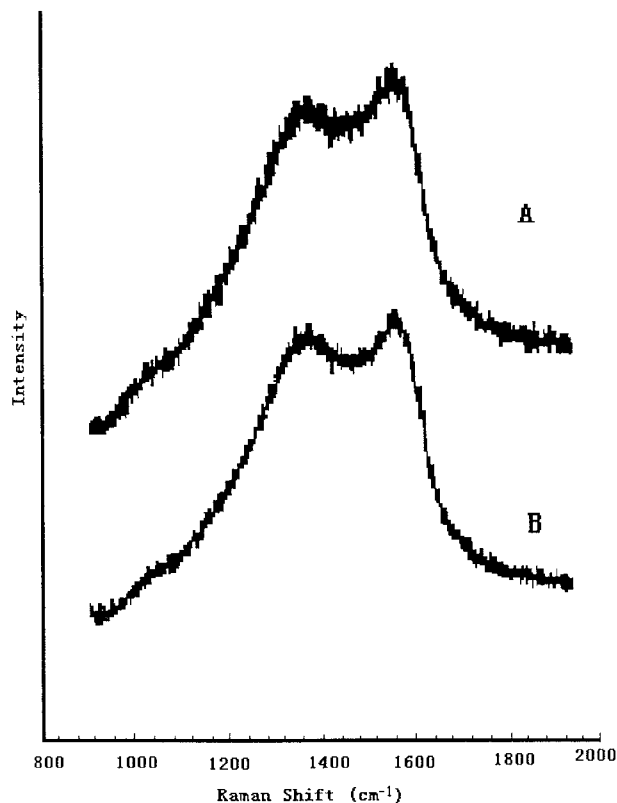


Figure 3 Raman spectra of samples (A) 1 and (B) 2.

Table II Elemental Analysis Results of the Carbon Made by Pyrolysis of Sample 1

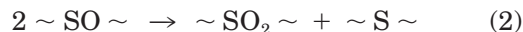
Pyrolysis Temperature (°C)	% C	% H	% S	% O	% Cl	Composition Formula
300	64.17	3.84	16.27	10.22	5.59	C _{10.52} H _{7.55} S _{1.00} O _{1.26} Cl _{0.31}
500	76.25	2.97	10.71	6.33	3.75	C _{18.99} H _{8.87} S _{1.00} O _{1.18} Cl _{0.32}
700	90.14	0.66	3.66	4.10	1.37	C _{71.43} H _{5.77} S _{1.00} O _{2.24} Cl _{0.33}

conditions are listed in Table I. The samples are amorphous and their X-ray diffraction patterns show only a broad peak at about $2\theta = 21^\circ$. They are insoluble in general organic solvents such as methanol, acetone, and benzene. A typical transmission electron micrograph of the product is shown in Figure 1. It is clear from this picture that the product is powdery with particle sizes in the nanoscale and aggregated to larger bodies.

Elemental analysis showed the product to have a general composition formula of C_{6.83–7.64}H_{5.70–8.03}O_{2.32–1.86}S_{1.00}Cl_{1.06–2.66} (Table I). This result indicates that DMSO is one of the reactants. The composition of the product changes slightly with the initial molar ratio of DMSO/CCl₄ and the pH value of the solution before product separation. According to Table I, the Cl/C and H/C atomic ratios of the product samples are in the ranges of 0.14–0.38 : 1 and 0.75–1.17 : 1, respectively. The former is much

lower than that of CCl₄ (4 : 1) and the latter is much lower than that of DMSO (3 : 1). These results confirmed that CCl₄ had reacted with DMSO and carbonized (or polymerized) into a new carbon-based material.

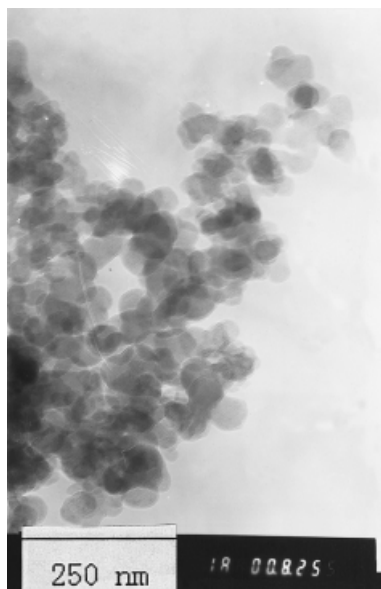
The FTIR spectra of different samples of the carbon-based materials are similar to each other and Figure 2 is an example. In this spectrum, two bands at frequencies lower than 800 cm⁻¹ appear, indicating the presence of a small amount of chlorine.^{4,5} This agrees well with the elemental analysis. The band at 1598 cm⁻¹ is attributed to C=C bonds.⁶ There are —CH₂ and =C—H vibration bands in the region of 2990–2850 cm⁻¹. The band at 1039 cm⁻¹ is attributed to the sulfoxide group (—S=O).⁷ The two sharp bands at 1350 and 1120 cm⁻¹ implied the presence of the sulfone group (—SO₂—).⁷ Elemental analysis indicated that the sulfur/oxygen atomic ratios of the products are close to 1 : 2, which also partly confirmed the presence of —SO₂—. The sulfone units possibly formed by the side reaction of sulfoxide are shown in eq. (2):



The special smell of sulfur ether was found in the rough products and disappeared in the clean samples. This finding also partly supported the assumption described above.

Figure 3 illustrates the Raman spectra of two samples of the carbon-based material. The two spectra in Figure 3 are almost the same, indicating that the two samples have similar carbon structures. The band centered at about 1600 cm⁻¹ is of the in-plane C—C stretching model of E_{2g} in graphite and the band centered at 1400 cm⁻¹ is a disorder-induced Raman band for small graphite crystallites.⁸

On the basis of the spectral examinations and elemental analyses described above, it is

**Figure 4** Transmission electron micrograph of the carbon made by pyrolysis of sample 1 at 700°C.

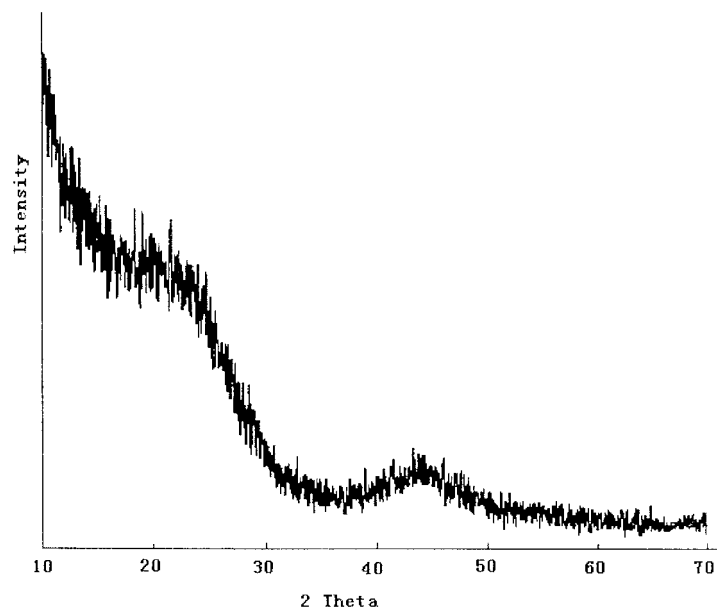


Figure 5 Wide-angle X-ray diffraction pattern of the carbon made by pyrolysis of sample 1 at 700°C.

reasonable to conclude that the carbon-based materials prepared from carbon tetrachloride and DMSO have various functional groups and contain both graphite and disordered carbon components.

Carbonaceous Materials Made by Pyrolysis of the Carbon-based Materials

Pyrolysis of the carbonization products described above changed the sample color from dark brown

to shiny black, indicating that the purity of the carbon sample was increased. The elemental analysis results shown in Table II also support this point. As can be seen from this table, the carbon content of the carbon sample was increased with increase of the pyrolysis temperature. The carbon sample prepared at 700°C contains about 90% (by weight) carbon and this value is about 2.4 times that of the original carbon-based material (~ 38%). A small amount of hydrogen, sulfur, and oxygen still remained in the

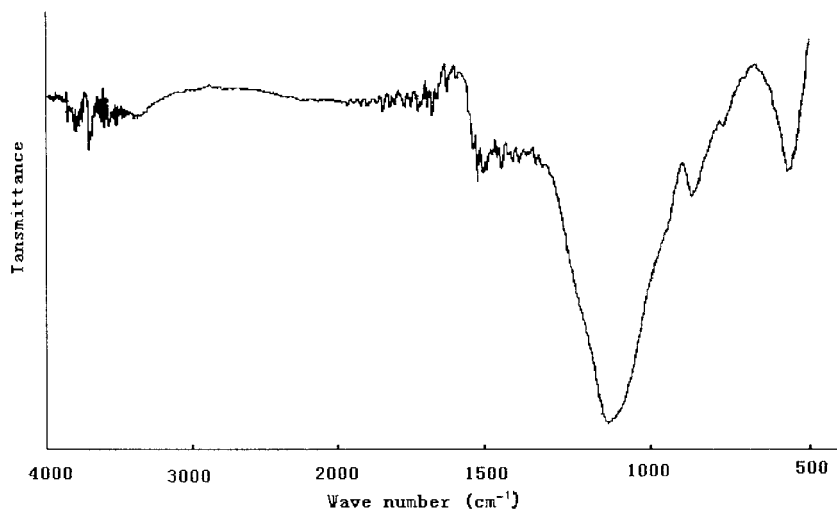


Figure 6 FTIR spectrum of the carbon made by pyrolysis of sample 1 at 700°C.

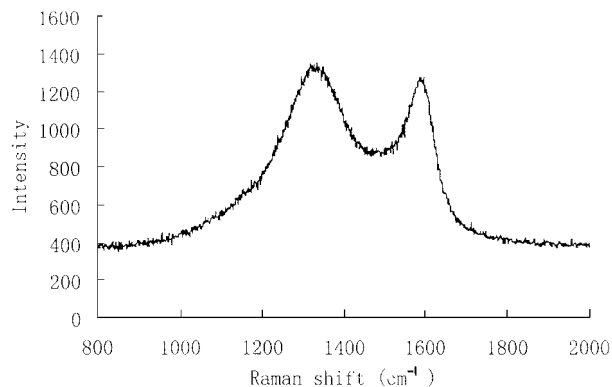


Figure 7 Raman spectra of the carbon made by pyrolysis of sample 1 at 700°C.

carbon and strongly influenced the carbon structure.

The transmission electron micrograph of the carbon sample obtained at 700°C indicated that the carbon was nanoparticles with average particle diameters in the range of 30–80 nm (Fig. 4). The particles were well separated, not like in the

original carbon-based material where the particles are aggregated into large bodies. A wide-angle X-ray diffraction pattern of the carbon shows a nongraphitic character with broad diffraction bands (Fig. 5). This indicates that the carbon is amorphous and like that of the carbonaceous materials prepared from methylnaphthalene-derived isotropic pitches.⁹

The infrared spectrum of the carbon sample prepared at 700°C (Fig. 6) has only a few bands of graphite carbon about 1600 cm^{-1} and disordered carbon about 1070 cm^{-1} . The former is assigned to the stretching of the carbon–carbon double bond and the latter is attributed to a carbon–carbon single bond. The typical bands of functional groups such as —OH, —CH₂—, —CH= are very weak or have disappeared. This also indicates that the carbon has a high purity.

A Raman spectrum of the carbon was performed in the wavenumber range of 600–3000 cm^{-1} , as shown in Figure 7. The spectrum has well-separated G (graphite) and D (disorder) bands compared with those in the Raman spec-

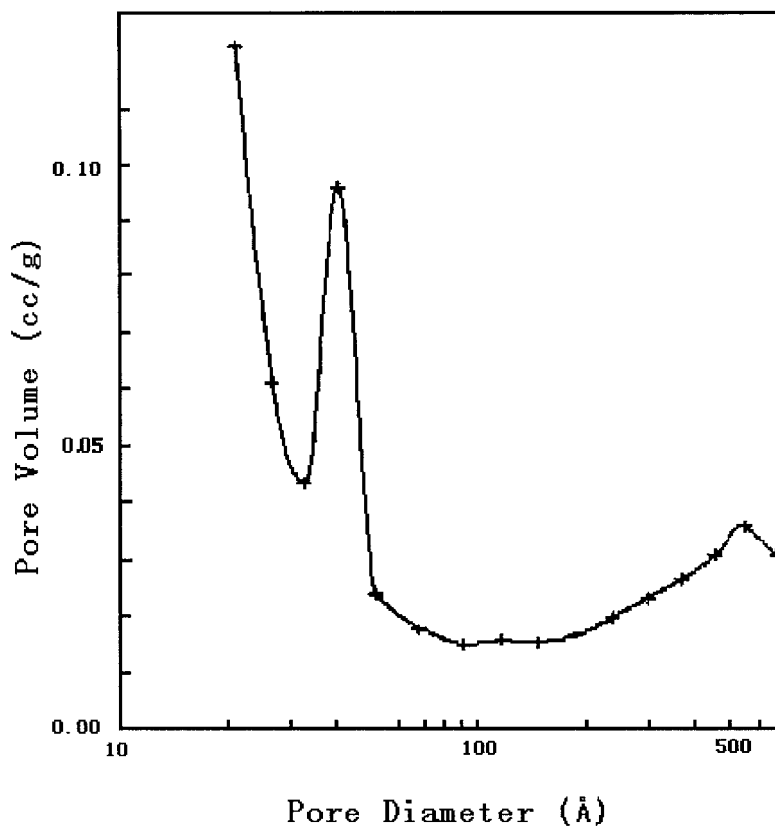


Figure 8 Pore-size distribution of the carbonaceous material made by pyrolysis of sample 1 at 700°C.

trum of the original carbon-based material (Fig. 3). Furthermore, the D band is stronger and broader than is the G band. The feature of this spectrum is similar to that of a hydrogenated diamondlike carbon¹⁰ or a porous carbon.¹¹

The specific surface area of the carbonaceous carbon prepared at 700°C was measured to be 430 m²/g. The large specific surface area indicates that the carbonaceous material was porous. The pore-size distribution was also measured. As shown in Figure 8, although mesopores having a broad distribution were observed (20–500 Å), most pores were found in the range of 20–50 Å.

CONCLUSIONS

Carbon tetrachloride can react with DMSO to form a carbon-base material under a phase-transfer condition. The material has a carbon structure of graphite containing disordered carbon. Furthermore, there are chlorine, sulfone, and sulfoxide groups in the carbonization products. Pyrolysis of the carbon-based materials at 700°C and under an inert atmosphere produces carbonaceous materials with high purity. The resulting carbons are amorphous nanoparticles with a high specific surface area and porosity. The mechanism of the reaction between carbon tetrachloride

and DMSO is not clear and needs to be investigated further. The application of carbonaceous materials to the lithium ion secondary battery also has been studied in this laboratory.

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