Chemical moification of graphene oxide

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Graphene oxide (also called graphite oxide or graphitic acid, abbreviated as GO) which was first synthesized in the 19th century is one of the covalent type of graphite intercalation compounds. Recently it has attracted much attention as a precursor of graphene, because it is easily exfoliated into individual sheets in an aqueous solution. The structure of GO has not been fully solved yet, however, it possesses acidic hydroxyl, epoxy and carbonyl groups. Among these functional groups, the acidic hydroxyl groups are usually used for further chemical modification of GO and various novel intercalation compounds of GO have been synthesized. When alkyl groups are attached to the layers of GO, the resulting materials are hydrophobic and are well exfoliated in organic solvents. In this paper, synthesis, properties and reactions of chemically modified GO are summarized.

Preparation and properties of of hydrophobized GO

The addition of the aqueous solution of cationic surfactants such as alkyltrimethylammonium ions to the GO dispersion readily provides the precipitation of surfactant-intercalated GO. The orientation of alkyl groups between the layers of GO varies depending on the content of surfactant. As the increase of the content it changes form monolayer, bilayer, interdigitated monlayer and paraffin type bilayer. An example of hexadecyltrimethylammonium ion–intercalated GO is shown, ogether with the bilayer type orientation of alkyl chains between the layers of GO. Alkylamines with long alkyl chain lengths are also intercalated into GO simply by mixing them mechanically in the presence of a small amount of hexane. Starting from the alkylamine intercalated GO, silylated GO can be synthesized by the reaction GO with silylating reagents in organic solvents. Most of the resulting intercalation compounds are hydrophobic and are easily dispersed in organic solvents such as chloroform. When the dispersion of hydrophobized GO containing organic molecules are cast on the substrates, they are included in the thin film sample of hydrophobized GO. A large amount of organic molecules are adsorbed between the layers of hydrophobized GO. When GO was silylated with 3-aminopropylethoxysilanes, the resulting samples efficiently adsorbed formaldehyde from the gas phase.

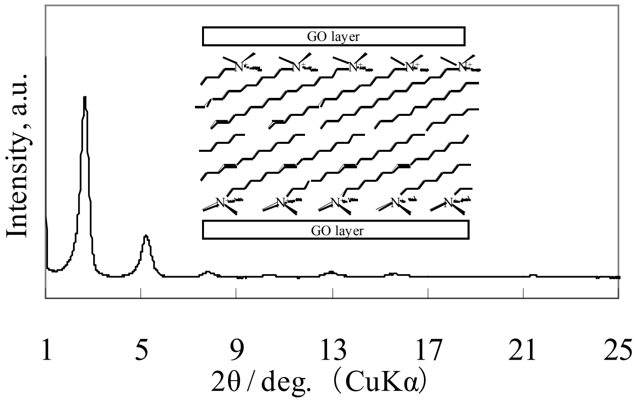

Fig.1 X-ray diffraction pattern of hexadecyltrimethylammonium ion–intercalated GO. The inset shows the c- axis structure model with paraffin type bilayer orientation of alky gourps.

Preparation of transparent and conducting electrode from silylated GO

When the cast films of silylated GO are heated under vacuum at higher than 500°C, they are converted to carbon films containing a small amount of silica. The resulting films were transparent and the thickness of them was controlled by the concentration of the dispersion. The sheet resistance of the films decreased as the increase of film thickness as shown in Fig.2. The resistance of grain boundary seems dominant when the thickness of the film was small.

Thermal decomposition of highly silylated GO and formation of pillared carbons

When silylated GO samples containing appropriate amounts of silicon are heated under vacuum between 450 and 600°C, pillared carbons in which adjacent carbon layers are connected by silsesquioxanes as shown in Fig. 3 are obtained. The interlayer spacing varied from 1.1 – 1.8 nm, depending on the starting materials. Fig.4 shows the adsorption isotherms of pillared carbons with different interlayer spacings of 1.28 and 1.56 nm. While the pillared carbon with a smaller interlayer spacing showed type H4 isotherm, that with larger interlayer spacing showed type I isotherm. It was revealed that the content of micropores increased while that of mesopores decreased, as the interlayer spacing increased. The BET surface area almost linearly increased with the increase of interlayer spacing and reached 750 m_2/g. The α_s plots indicated that the width of the micropores was around 0.45 nm.

References

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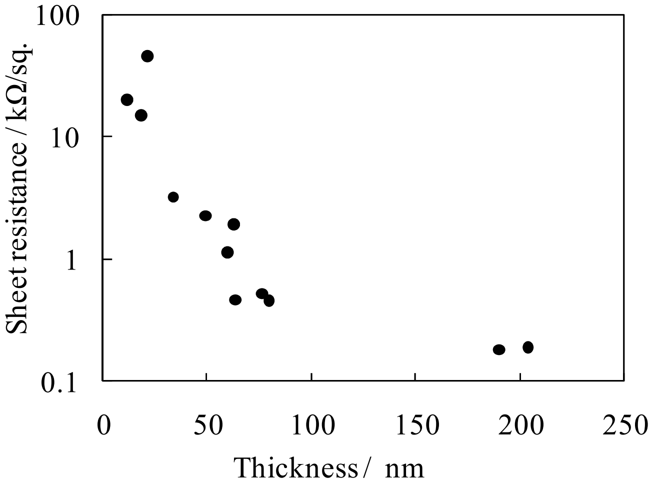

Fig.2 Variation of the sheet resistance of carbon films preapred from silylated GO as a function of film thickness.

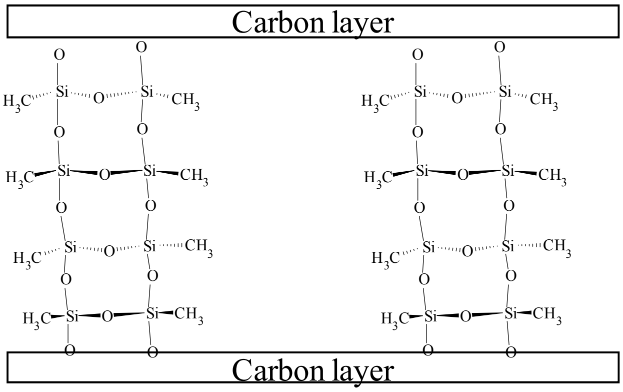

Fig.3 A structure model of pillared carbon.

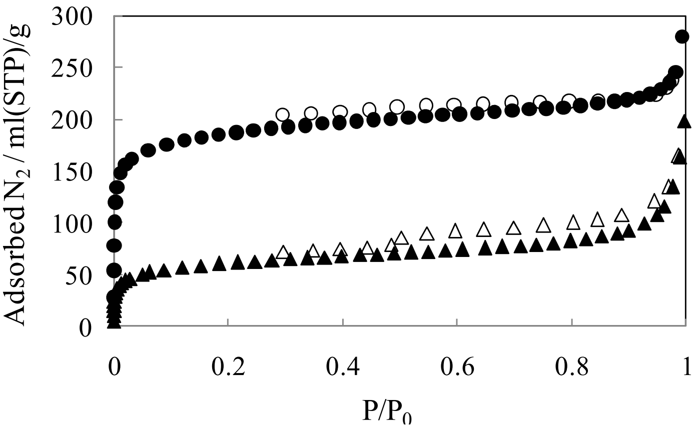

Fig.4 Adsorption isotherms of pilalred carbons prepared from GO silylated by ○, ●: octyltrichlorosilane and then 3-aminopropyltriethoxysilane, and, △ , ▲: 3-aminopropyldiethoxymethylsilane. Filled and open marks indicate he data during adsorption and desorption.