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ScienceDirect

Carbon 45 (2007) 1005–1012

CARBON

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Preparation and characterization of alkylamine-intercalated graphite oxides

Yoshiaki Matsuo *, Tadaaki Miyabe, Tomokazu Fukutsuka, Yosohiro Sugie

Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

Received 2 June 2006; accepted 19 December 2006
Available online 27 December 2006

Abstract

Various *n*-alkylamine-intercalated graphite oxides were synthesized in the presence of a small amount of hexane and their compositions, chemical bonding and orientation of alkyl chains in them were characterized. The interlayer space of graphite oxide was saturated when about 11 mmol/g of *n*-hexadecylamine was included in it. Three types of alkylamines in GO were identified in the resulting intercalation compounds, hydrogen-bonded neutral amines, hydrogen-bonded protonated amines and ionically bound protonated amines, based on the infrared and XPS studies. The equilibrium between these species was established. Immersion of GO saturated by *n*-hexadecylamine in ethanol resulted in the de-intercalation of amines and the amount of residual amines was 3.0 mmol/g, which was rather similar to that of readily exchangeable protons in GO of 3.5 mmol/g. When alkyl chain length became shorter, the resulting intercalation compounds contained less alkylamine due to insufficient hydrophobic interaction between alkyl chains. The X-ray diffraction and polarized-infrared spectroscopic data indicated that alkyl chains of alkylamines took interdigitated monolayer and bilayer orientations for smaller and larger interlayer spacings, respectively.

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1. Introduction

Recently, the space with nano or sub-nanometer size in solid materials such as that in zeolite and layered materials has been used as reaction media for photochemical reaction, matrices for photofunctional molecules, adsorbent of non-ionic organic chemicals (NOCs) and so on [1–6]. In case of layered materials, various interesting results have been reported. These include the inclusion of ionically bonded organic dyes at high concentrations with controlled aggregation state [2,7], reversible photo-isomerization of diarerethene [8], spiropirane [9], azobenzene derivatives [10], selective photochemical dimerization of ionically bonded organic molecules [11–13] and so on. When the amphiphilic molecules are introduced into the layered materials, the two-dimensional interlayer is filled with the hydrophobic part of these molecules, which provides a hydrophobic medium. Accordingly, various neutral molecules were included in the resulting organic interlayers by hydrophobic interaction. Based on these properties, the suppression of the aggregation of organic dyes [14], selective adsorption of non-ionic organic molecules [15–17], photochemical isomerization of azobenzene [18,19], etc. have been reported. The properties of the space such as polarity, size and free volume are important factors to determine if such space is useful or not. These determine how many or what kind of guest molecules can be introduced in the space and the mobility of the introduced molecules. In this context, recently we have found that graphite oxides hydrophobized by alkyltrimethylammonium ions or alkylamines can selectively include various aromatic molecules [20,21] control aggregation state and orientation of organic dyes [22], and photochemical reaction proceeds efficiently in them [23–25]. For the fundamental properties of these host materials, detailed studies of alkyltrimethylammonium ion-intercalated graphite oxides showed that

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* Corresponding author. Tel./fax: +81 79 267 4898.
E-mail address: ymatsuo@eng.u-hyogo.ac.jp (Y. Matsuo).

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doi:10.1016/j.carbon.2006.12.023

alkyltrimethylammonium cations are ionically bonded to C–O$^-$ groups of graphite oxide formed by dissociation of acidic C–OH groups [26,27]. Therefore, the amounts of intercalated ammonium ions depend on the ion exchange capacity of graphite oxide and the size of the ammonium cations. On the other hand, concerning the fundamental properties of alkylamine-intercalated graphite oxides such as chemical bonding between alkylamine and graphite oxide, composition of them, etc., sufficient data have not yet been provided [21,28], though some are reported by Bourlinos et al. for graphite oxide intercalated by alkylamines with shorter alkyl chain lengths [29]. It appeared that higher amounts of alkylamines are introduced into graphite oxide than those observed for alkyltrimethylammonium ions [21], which suggests different interaction between alkylamine and graphite oxide other than ionic bonding. In this study, therefore, we have investigated the properties of alkylamine-intercalated graphite oxides in detail.

2. Experimental

Graphite oxide was obtained from natural graphite powder (57–74 μm) based on Brodie's method [30]. It was oxidized by potassium chlorate in fuming nitric acid for 3 h at 60 °C and the resulting solution was put in excess water. The precipitate was filtered off and then dried at 60 °C overnight. This procedure was repeated for 5 times and the composition of $C_8O_{4.2}H_{1.4} \cdot 0.94\,H_2O$ was obtained based on the elemental analysis of carbon and hydrogen. The water content was determined from the weight decrease below 200 °C observed by thermogravimetric (TG) analysis. The amount of exchangeable acidic groups in the obtained GO was determined by the back titration of sodium hydroxide solution (0.05 M, 50 ml) of GO (99.5 mg) by 0.05 M hydrochloric acid solution. All the chemicals including potassium chlorate, fuming nitric acid, sodium hydroxide solution, hydrochloric acid solution, *n*-alkylamines chloroform and cyclohexane were purchased from Nacalai tesque Co. Ltd. and were used as received.

Intercalation of *n*-alkylamines ($C_nH_{2n+1}NH_2$; abbreviated as C*n*, $n = 4, 8, 12, 16$) was performed by grinding the mixture of GO (100 mg) and C*n* in a pestle in the presence of a small amount of hexane (ca. 1 ml) at room temperature until hexane was evaporated. The resulting samples were kept at 60 °C overnight. The nominal C*n*/GO molar ratio was changed between 0.7 and 2.4. When the nominal C*n*/GO was smaller than 0.7, unreacted GO remained in the sample. The compositions of the obtained C16-intercalated GOs (hereafter $(Cn)_x$GO; *x*: C*n*/GO ratio) were determined from the data of elemental analysis of carbon, nitrogen and hydrogen by combustion method performed at Center of Organic Elemental Microanalysis of Kyoto University. The content of oxygen was calculated by subtracting those of carbon, nitrogen and hydrogen from 100%.

The resulting samples were analyzed by X-ray diffraction (Rigaku Rint-2100), FT-IR spectroscopy (Nicolet Avatar-360, KBr method), X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-3400) and TG measurements (Shimadzu TGA-50). TG measurement was performed under air with the temperature increase rate of 5 °C/min between room temperature and 800 °C. XPS data were recorded after drying the sample under vacuum at room temperature overnight. The binding energies observed were corrected based on those of $Au_{4f}^{7/2}$ electrons.

The powder $(C16)_{0.93}$GO sample was submersed in a mixture of cyclohexane and chloroform (1:1 by volume, 2 mg/ml) and a homogeneous solution was obtained. This solution was cast on a silicon substrate and thin film (thickness about 1 μm) samples were obtained. The SEM image showed that the layers of the $(C16)_{0.93}$GO sample were deposited parallel to the substrate. The angle of the C16 chains against the GO layer was determined by polarized IR spectroscopy [31] and X-ray diffraction for the obtained film samples. The tilt angle relative to the normal on the GO layer planes, γ, of the transition moment of the –CH$_2$– stretching vibration of alkylamine against the GO layer was calculated from the dichroic ratio, $Ry'x'$, using the following formula for *trans* alkyl chains:

$$Ry'x' = \frac{A_y}{A_x} = \frac{2 - \frac{2}{n^2}\sin^2\alpha_1 - \left(\frac{3}{n^2}\sin^2\alpha_1 - 1\right)\sin^2\gamma}{2 - \sin^2\gamma} \qquad (1)$$

where n indicates the refractive index, α_1 is the incident angle of the polarized light, and 90° was used for the angle of the optical transition moment of the –CH$_2$– stretching vibration against the GO layer [31].

3. Results and discussion

3.1. Characterization of GO

The interlayer spacing of the obtained GO was 0.67 nm, which is typical for that prepared by Brodie's method and the color was light brown. The pH titration curve of GO dissolved in 0.05 M NaOH aqueous solution toward H$^+$ ion is given in Fig. 1. When 21.6 mmol of H$^+$ was added to the well dispersed colloidal solution of GO, the pH value of the solution reached 7 and inflection point appeared. Therefore, the exchangeable acidic groups in GO was evaluated as 3.5 mmol/g (0.63 mol/GO). This value was comparable to or slightly smaller than those reported by Cassagneau et al. [32] (3.24–6.04 mmol/g), Liu et al. [27] (4.4 mmol/g) and Scholz and Boehm (about 6 mmol/g) [33]. Recent report by Szabó et al. [34] pointed out that the cation exchange capacity or acidity of GO determined from titration varies in a wide range, depending on the pH and ionic strength. The exchangeable acidic groups in GO determined in this method, however, was similar to that of the maximum amount of the exchanged hexadecylpyridium cation (4.0 mmol/g) [26].

3.2. Preparation and composition of $(C16)_x$GO

Table 1 summarizes the compositions of $(C16)_x$GO samples calculated from the data of elemental analysis of carbon, hydrogen and nitrogen. Here, the *x* values were determined as the molar ratios of nitrogen to eight carbons

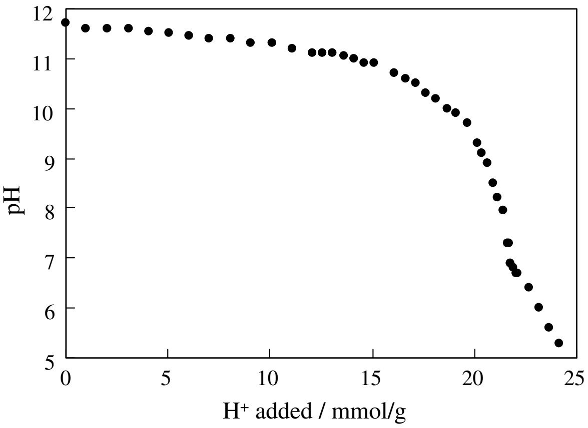

Fig. 1. The pH back titration curve of GO dissolved in 0.1 M NaOH aqueous solution toward H$^+$ ion.