

# Synthesis and characterization of anisotropically expanded graphite oxide compounds derived from spherical graphite



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## ABSTRACT

Anisotropically expanded graphite oxide (GO) compounds with controlled interlayer distances were synthesized through the intercalation of various quaternary ammonium cations in GO derived from mesocarbon microbeads (MCMB). It was found that the interlayer distance of the as-prepared anisotropically expanded GO varies with the intercalated cations. In tetrabutylammonium (TBA), tetraoctylammonium (TOA) and dioctadecyldimethyl ammonium (DDA) cation intercalated GO compounds (TBA-GO, TOA-GO, TOA-GO) the corresponding interlayer distances were found to be 1.1 nm, 1.9 nm and 2.9 nm, respectively. Moreover, significant morphology changes were observed for TOA-GO and DDA-GO. Our study suggests that it is possible to tailor both the interlayer distance and morphology of GO by choosing proper intercalated cations. It was also found that the expanded GO compounds show lower water content and improved thermal stability than those of pristine GO. The obtained GO compounds were investigated as electrode material for electrochemical capacitors and all of them delivered typical capacitive behavior.

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## 1. Introduction

Graphite oxide (GO) has been studied intensively since it is considered as the best starting material for mass production of graphene nanosheet as well as graphene based materials [1–3]. The reduced graphene oxide with large surface area and high electric conductivity has great potential as electrode materials for energy storage devices [4–6]. However, the history of graphite oxide can date back to many decades and the chemistry of graphite oxide has caught the eyes of many researchers even before the discovery of single layer graphene. The early researches mainly focused on the chemical composition and structure of GO [7–10]. Moreover, it has been proved that the containing of various oxygen functional groups in GO makes it hydrophilic and thereby lead to rich intercalation chemistry [8,11]. Besides epoxy, hydroxyl and carboxylic groups, recent researches proved that sulfonic groups are present in GO [12–14].

GO intercalation compounds have been prepared and characterized by many researchers because of their potential application in many areas [15–17]. Matsuo et al. are among the pioneers in the development of GO intercalation compounds. They have successfully synthesized various organic molecules and polymers intercalated GO compounds by various methods [18–20]. Also,

the properties of cationic surfactant [21] and alkylamine intercalated GO [22,23] have also been investigated by them. In their recent work, microporous pillared carbon has been successfully prepared from the silylated graphite oxide and it is considered to be a potential candidate for hydrogen storage [24,25].

So far, most of the researchers focused on the GO intercalation compounds with natural graphite as starting material. The use of natural graphite as precursor for the preparation of GO does have the advantages such as it is suitable for the preparation of thin film materials and GO intercalation compounds with large surface area [26–28]. Unfortunately, the dispersion and restacking of graphene layers in GO causes the irreversible aggregation of graphene layers, which makes it is difficult to control the texture of GO. Mesocarbon microbeads (MCMB) with lamellar structure has been recognized as an excellent precursor for the synthesis of high density and high strength carbonaceous material. Zheng et al. have investigated non-porous activated MCMB as the negative electrode for asymmetric electrochemical capacitors with improve energy and power density [29]. Furthermore, deprotonation of carboxylic and phenolic groups in GO can provide negative charge sites on the planes of GO [9,11]. Characterization and electrochemical properties of neutralized GO prepared from MCMB have been reported in our previous study [30]. In this study, we will focus on the preparation of anisotropically expanded GO derived from spherical graphite. Since we used quaternary ammonium hydroxide as the starting materials, deprotonation of GO can be accelerated by acid–base reaction. Thus,

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quaternary ammonium cations can intercalated into GO and form ion pairs with the negative charged sites in GO. Various expanded GO compounds with controlled interlayer distances were synthesized by the intercalation of selected ammonium cations. The properties of expanded GO compounds and the application as electrode materials in electrochemical double layer capacitors will also be discussed.

## 2. Experimental

### 2.1. Materials and methods

Graphite, mesocarbon microbeads (MCMBs, average particle size: 15  $\mu\text{m}$ ), was purchased from Hosen Co., Japan. Potassium permanganate, sodium nitrate, concentrated sulfuric acid and hydrogen peroxide were from Wako Corporation. Quaternary ammonium salts and tetraalkyl ammonium hydroxide solutions were purchased from Wako Corporation. The intercalants were displayed in Table 1.

### 2.2. Preparation of GO

GO was synthesized from MCMB according to the traditional Hummers method [31]. Typically, MCMB (10 g) and  $\text{NaNO}_3$  (5 g) together with  $\text{H}_2\text{SO}_4$  (220 ml) were mixed in a flask placed into the water ice bath. To avoid vigorous reaction,  $\text{KMnO}_4$  (20 g) was gradually added into the mixture at 0–10  $^\circ\text{C}$ . After the addition of  $\text{KMnO}_4$ , the mixture was kept at 35  $^\circ\text{C}$  for 1 h. Subsequently, the mixture was transferred to 460 ml  $\text{H}_2\text{O}$  and hold strictly at 98  $^\circ\text{C}$  for 30 min. The reaction was terminated by adding 1400 ml  $\text{H}_2\text{O}$  and 10 ml  $\text{H}_2\text{O}_2$ . Then the diluted solution was kept for 24 h followed by filtering and drying at 80  $^\circ\text{C}$  for 12 h.

### 2.3. Preparation of anisotropically expanded GO compounds

Fig. 1 displays the schematic procedure for the synthesis of expanded GO compounds with controlled interlayer distance. The as-prepared GO (1 g) was dispersed in  $\text{H}_2\text{O}$  (100 ml) and stirred for 30 min until the pH of the suspension became constant. The concentration of the tetrabutylammonium hydroxide (TBAOH) solution was 0.24 M. The tetraoctylammonium hydroxide (TOAOH) as well as dioctadecyl dimethyl ammonium hydroxide (DDAOH) solution was prepared by ion exchange reaction from tetraoctylammonium bromide and dioctadecyl dimethyl ammonium chloride, respectively. The other kinds of quaternary ammonium hydroxide used in this study were prepared with the same procedure as that of TOAOH and DDAOH. The concentration of the as-prepared TOAOH and DDAOH solution were determined by HCl titration. Then the as-prepared TOAOH as well as DDAOH solution was titrated into GO suspension with quite slow speed to ensure a completely intercalation. The pH value was monitored during the

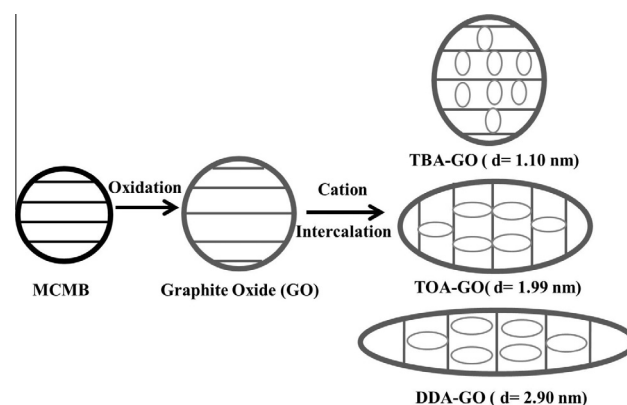


Fig. 1. Schematic procedure for the synthesis of expanded GO compounds with controlled interlayer distances.

whole reaction. The addition of hydroxide was terminated until the pH value of the suspension reached to 11. Then the suspension was stirred for 12 h, filtrated and dried at 80  $^\circ\text{C}$  for 24 h. The obtained GO intercalation compounds were hereafter noted as TBA-GO, TOA-GO and DDA-GO, respectively.

### 2.4. Characterization

X-ray diffraction (XRD) profiles of the as-prepared GO and GO intercalation compounds were recorded for two theta value from 2 $^\circ$  to 80 $^\circ$  (Cu  $K\alpha$  radiation, XRD-7000, SHIMADZU). The morphology of GO and GO intercalation compounds were studied by Scanning Electron Microscope (SEM, JEOL, JSM-5200). Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded on a JASCO 400 FTIR spectrometer (KBr pellets method). Thermo-Gravimetric/Differential Thermal Analysis (TG-DTA) measurement was performed at a heating rate of 5  $^\circ\text{C min}^{-1}$  from room temperature to 500 in air (Thermoflex TG-DTA 8110, Rigaku). Raman spectra were recorded on a homemade Raman spectrometer from 750 to 2000  $\text{cm}^{-1}$  using a 441.6 nm laser line. Nitrogen adsorption-desorption isotherm were carried out after the samples were outgassed and dehydrated at 180  $^\circ\text{C}$  for 24 h (Micromeritics Gemini 2360, SHIMADZU). The specific surface area of each sample was calculated from the Brunauer-Emment-Teller (BET) method.

### 2.5. Electrochemical characterization of anisotropically expanded GO compounds

The electrochemical properties of the anisotropically expanded GO compounds were investigated by cyclic voltammetry (CV). As for cyclic voltammetry measurement, conventional three electrode cell was fabricated using lithium metal as reference electrode and counter electrode. For the fabrication of working electrodes, 10 mg active material together with 4 mg conducting binder (Teflon:Acetylene black = 1:2) was mixed and pressed on the stainless steel mesh. Then, the electrodes were dehydrated by a vacuum dry at 160  $^\circ\text{C}$  for 12 h. The electrolyte used was a mixture of 1 M lithium phosphorus hexafluoride ( $\text{LiPF}_6$ ) and 1 M triethyl-methylammonium phosphorus hexafluoride ( $\text{TEMAPF}_6$ ) in propylene carbonate (PC) with volume ration of 1:4. The potential range was chosen from 1.2 V to 4.8 V and 1.5 V to 4.8 V. The capacitance estimated from CV ( $C_{cv}$ ) was calculated according to following equation:

$$C_{cv} = \left( \int idV \right) / v\Delta Vm \quad (1)$$

Table 1

List of selected quaternary ammonium salts.

Quaternary ammonium salts	Chemical formula
Tetramethyl ammonium hydroxide	$(\text{CH}_3)_4\text{NOH}$
Tetraethyl ammonium hydroxide	$(\text{C}_2\text{H}_5)_4\text{NOH}$
Tetrabutyl ammonium hydroxide	$(\text{C}_4\text{H}_9)_4\text{NOH}$
Tetrapentyl ammonium bromide	$(\text{C}_5\text{H}_{11})_4\text{NBr}$
Tetraphenyl phosphonium bromide	$(\text{C}_6\text{H}_5)_4\text{PBr}$
Tetraoctyl ammonium bromide	$(\text{C}_8\text{H}_{17})_4\text{NBr}$
Hexadecyl trimethyl ammonium bromide	$\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$
Octadecyl trimethyl ammonium chloride	$\text{C}_{18}\text{H}_{37}(\text{CH}_3)_3\text{NCl}$
Dihexadecyl dimethyl ammonium bromide	$(\text{C}_{16}\text{H}_{33})_2(\text{CH}_3)_2\text{NBr}$
Dioctadecyl dimethyl ammonium chloride	$(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{NCl}$

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