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# High Temperature Phase Transitions of Graphene Oxide Paper from Graphite Oxide Solution

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Graphene oxide paper (GOP) can be prepared through simplified filtration of a graphite oxide solution. It possesses similar properties to graphene. In this study, the graphite oxide solution was synthesized from commercial graphite by means of Hummer's method. It corresponds to the dried GOP that was prepared by deposition on a cellulose filter. It is found that the mesophase of the dried graphene oxide papers obtained from the graphite was thermotropic hexagonal columnar liquid crystal. Its higher temperature transitions were found at 80 °C, 150 °C and 170 °C−180 °C. Therefore, it could be used for thermal storage and conductive materials in the future.

**KEY WORDS: Graphite oxide; Graphite; Graphene; Phase transition**

## 1. Introduction

Graphene is a kind of monolayer graphite with higher electron and hole mobility than silicon, high heat conductivity and special optical properties. Therefore, it shows potential for new materials, such as a semiconductor. Graphene can be used in a transparent conductive oxide thin film process[1] or serve as solar cells[2−5] or a super capacitor. Many manufacturing methods of graphene have been proposed, such as chemical vapor deposition[6], chemical reduction of graphene oxide[7] and the exfoliation method[8,9]. In some studies of graphene, researchers have used a combination method with ozone exposure and annealing temperatures at 530 K to produce graphene from highly oriented pyrolytic graphite[10].

Graphite oxide and graphene oxide (GO) are both precursors of the production of graphene materials. Their structures are similar to graphene, but the surface of graphene oxide is bonded with hydroxyl radicals[11]. Therefore, it can be applied as dye-sensitized solar cells[12], a super capacitor[13] or doped with polymer and metal materials to make nanocomposites. It can also be used in the degradation of dyes and heavy metals[14−18]. The GO is obtained from oxidation processes of graphite materials. Generally, the oxidation processes of graphite are conducted by using strong oxidants or acid liquid. In some studies, researchers have used graphite powder in dry air (the water content <2 ppm) as an oxidant and conducted heating to produce GO[19].

Since liquid crystal (LC) has flow, crystallization and special photoelectric properties, it can be used in displays, navigation systems and view finders. The molecular structure of LC contains nematic, smectic, cholesteric, discotic, thermotropic LC and reentrant LC[20,21]. Common LC materials are alkenyl, phenyl-cyclo hexane or a symmetrical structure of polymers. In several studies, graphene and graphene oxide (GO) have been reported to possess a discotic nematic LC phase in suspended solutions[22−25]. However, almost no literature has ever been reported on the property of thermal phase transitions of GO in a solid phase, for example graphite oxide paper made from graphite. In this study, we investigated home-made graphene oxide paper (GOP) on its mesophase transition temperature and tried to identify the LC phase in the mesophase state of the GOP. Therefore, we would like to report on the property of phase transitions of the material.

## 2. Experimental

### 2.1. Synthesis of graphite oxide solution and graphene oxide paper

A graphene oxide solution (GOS) was used as synthesized using oxidation of commercial graphite using a wet-type oxidation process, called Hummer's method. $H_2SO_4$ and $H_3PO_4$ in a ratio of 9:1 and then, 2.25 g of $KMnO_4$ were added

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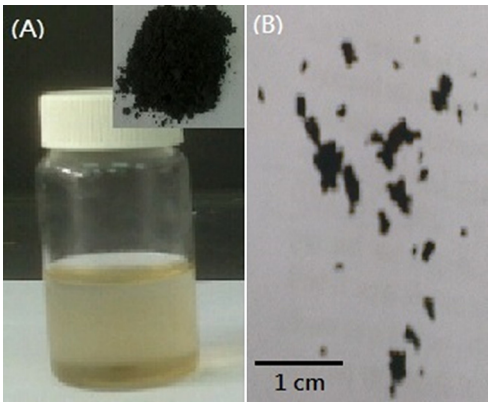


**Fig. 1** Photos of (A) commercial graphite powder and as synthesized GOS and (B) GOP.

into the above mixed acid solution. Next, 0.375 g of graphite powder was added to the oxidant and heat-treatment was performed at 50 °C for 24 h. After cooling, 3 mL of $H_2O_2$ and 200 mL of $H_2O$ were added into the cooled solution. Then, the above mentioned solution underwent centrifugation at 3000 r/min, and the sediment was collected. Next, the sediment was added to 200 mL of 30% HCl followed by centrifugation again. The steps were repeated until the sediment was dissolved and uniformly dispersed in the solvent (as shown in Fig. 1(A)). The GOP was prepared simply by filtration of the GOS using a No. 1 paper filter (as shown in Fig. 1(B)), and the thickness was about 0.1−0.5 nm.

### *2.2. Property analysis of samples*

In order to analyze the properties of the products, scanning electron microscopy (SEM) as well as energy dispersive spectrometry (EDX) was used to analyze the structure and exterior of different samples (S-3000N, HITACHI, Japan). Fourier transform infrared spectrometry (FTIR) was used to analyze the functional groups of the samples (Vector22, Bruker, Germany). The parameters of this instrument were a scanning time of 128 times, with a wave number of 4000 to 400 $cm^{-1}$. X-ray diffraction (XRD) was used to analyze the lattice structure (D8 Advance, Bruker, Germany). The scan angles were from 10° to 80° (2θ). Differential scanning calorimetry (DSC) was used to analyze the thermology transitions of the samples (DSC-822, Mettle Toledo, Switzerland). The scan temperatures were

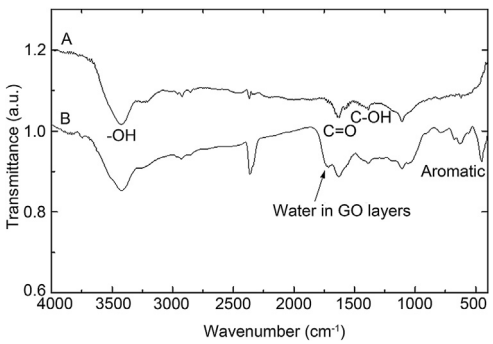


**Fig. 2** FTIR spectra of (A) commercial graphite and (B) as synthesized GOP.

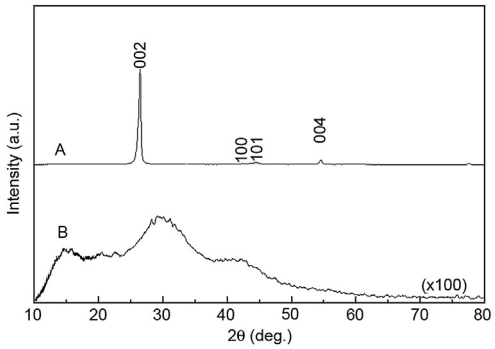


**Fig. 3** XRD patterns of (A) commercial graphite and (B) as synthesized GOP.

30 °C−260 °C; the heating rate was 20 °C/min; the holding temperature was 30 °C for 60 min and the carrier gas ($N_2$) flow rate was 50 mL/min.

## 3. Results and Discussion

Fig. 2 shows the FTIR spectra of commercial graphite and GOP. When the peak was between 3850 and 3745 $cm^{-1}$, it corresponded to the amide groups. The peak at 3500 $cm^{-1}$ corresponded to a −OH stretching vibration motion. The peak at 2950 $cm^{-1}$ corresponded to $-CH_2-$. When the peak was at 2250 $cm^{-1}$, it corresponded to the peak for absorbed $CO_2$ molecules. The range between 1700 and 1630 $cm^{-1}$ corresponded to a C═O stretching vibration motion, and the range between 1200 and 1000 $cm^{-1}$ corresponded to C−O and C−OH stretching vibration motions. The peaks at 1397 $cm^{-1}$ corresponded to a $-CH_3$ stretching vibration motion, while the peaks of 1450, 878, 650 and 590 $cm^{-1}$ corresponded to the aromatic groups.

As a result, there was an obvious decrease in the intensities of the amide groups, aromatic groups and $-CH_2-$ and $-CH_3$

**Table 1** Common mesophase for several rigid molecules

| Molecules | Mesophase formed |
|---|---|
| Calamitic liquid crystal | Nematic, smectic A, cholesteric phase |
| Discotic liquid crystal | Nematic discotic, columnar phase |
| Sanidic liquid crystal | Nematic, smectic A |
| Polycatener liquid crystal | Nematic, smectic A |

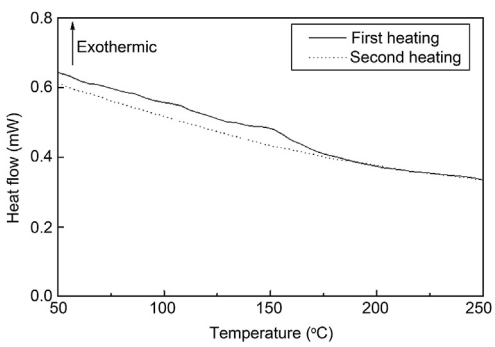


**Fig. 4** DSC curve of commercial graphite powder.