

# Strain effect on the hydrogen storage capacity of graphite oxide

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## ABSTRACT

In this study we investigated the effect of strain on the interlayer separation of graphite oxide (GO). This high-energy milling process is used to provide defects in graphite structure via mechanical impact of balls during the milling process. After the milling process this parameter is found to increase about 10%, showing a possibility to improve uptake hydrogen capacity. We will discuss the results in terms of defect density and crystal structure along with the thermal stability of GO structure

**Keywords:** graphite oxide, hydrogen storage, milling process

## 1 INTRODUCTION

Among clean fuel alternatives hydrogen is one of the most attractive fuels due to its abundance, easy synthesis, and non-polluting nature when used in fuel cells. Carbon, a common and abundant element in the earth, is well known for its great ability to absorb gases because of its ability to be prepared in a fine powdered form with a highly porous structure.

Therefore carbon-based materials have been studied as hydrogen storage media. From CNT (Carbon Nano Tube) to AC (Activated carbon), several types of carbon materials are researched.[1-3] Carbon materials with higher microporosity have extremely enhanced adsorbing properties toward gaseous molecules. Graphite Oxide (GO) is one of the candidates that can be turned into a gas storage material.[4] GO is first developed by Brodie in 1859.[5] He made GO by reacting graphite with  $\text{KClO}_3$  and  $\text{HNO}_3$ . After then, L. Staudenmaier[6] and Hummers[7] developed their own way to synthesize GO. GO contains a range of reactive oxygen functional groups such as epoxide, carboxyl group and so on.[8]

In principle hydrogen can be stored between the layers of basal planes of this material.[4] With a well known spillover mechanism (even though still being debated)[9, 10], they show the feasibility of using GO for hydrogen storage. But in normal GO case interlayer separation is just limited to  $6\sim 7\text{\AA}$ , which is too close to store hydrogen along with decorating molecules between the layers. Thus, to enlarge the interlayer distance is the main task in the hydrogen storage application of thi material.

There are some papers regarding this work. Among those, Taner Yildirim et al. used the reaction between boronic acid and hydroxyl groups to intercalate boronic ester between the layers [11] and synthesized GO with the interlayer

distance of almost  $11\text{\AA}$ , which is ideal for hydrogen storage. But since it's difficult to control the quantity of boronic ester, the intercalation of boronic ester often became excessive. Thus, the goal for the open structure remains unsolved.

To achieve the goal, we introduced a technique with high-energy ball milling. In such a mechanical milling process, we anticipate the reduction of carbon particle size along with an increase of defect density and micro (lattice) strain. It is known that the main factors that affect the carbon microstructure include rotation speed, size of balls, weight ratio of balls to powder, medium of milling, and milling time.

## 2 EXPERIMENT

Raw graphite (99.9% purity, Aldrich) is subjected to planetary high energy ball milling machine (Pulverisette 7, Fritsch, Germany). To minimize the contamination from the milling chamber and impeller during milling, the chamber and impeller were coated with WC. Tungsten carbide balls were mixed with graphite at a ball-to-powder ratio (BPR) of 30:1 by weight. WC-coated bowls was used, and all milling were carried out at a speed of 250 rpm. The milling time is 0, 1, 2, and 5h. After then, GO samples were synthesized following the Brodie's method. Graphite (1g), fuming nitric acid (20mL), and sodium chloride oxide (8,5g) were mixed at room temperature. The mixture was stirred for 24h and washing, filtrations, cleaning were done in a regular sequence. We named the GO samples with milling time of 0, 1, 2, and 5h as GO(0), GO(1), GO(2), and GO(5), respectively.

All specimens were analyzed by X-ray diffraction (M18XHF-SRA, MacScience, Japan). Also ESCA (SIGMA PROBE) was used to measure XPS (X-ray photoemission spectroscopy). Raman spectrometer (T64000-HORIABA Jobin Yvon) was also used.

## 3 RESULTS AND DISCUSSION

Figure 1 shows the Raman spectroscopy results of raw graphite and GO(5). High ordered graphite has only two Raman-active bands. First one is caused by the in-phase vibration of the graphite called G band. It appears at  $1575\text{cm}^{-1}$ . Second one is appeared at  $1355\text{cm}^{-1}$  and its intensity is very weak compared to former one.[12] It is called D band caused by disorder band at the graphite edges. When GO is synthesized, this D band's intensity increases due to the symmetry breaking. After 5h high energy ball milling, GO structure is still remained.. appear on separate

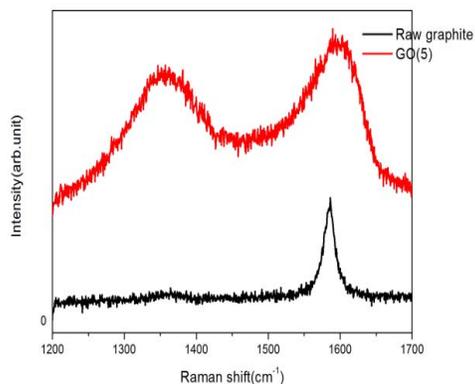


Fig 1 Raman spectroscopy result of Raw graphite and GO(5)

Figure 2 shows the XRD patterns of the GO samples. The main peak corresponding to the (002) diffraction shifts to the lower angles with increasing milling time. Until 5h, there are diffraction peaks and graphite structure is still existed. The (002) peak for each GO samples yields an interlayer distance.

These interlayer distances are summarized in Table 1. As the milling time increases, the interlayer distance gradually increases to 5.78, 5.92, 6.12 and 6.20. Even though the (002) peak intensity was decreased, it shifted to low angle significantly.

To further assess the functional groups present in GO(0) and GO(5), XPS data were acquired. Figure 3 shows the XPS results. The spectra for the samples were deconvoluted into three peaks. GO's characteristic peaks (C-O-C at

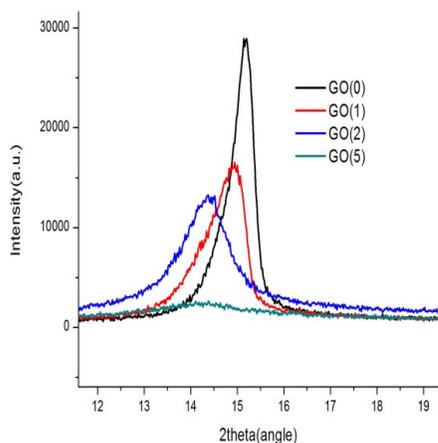


Fig 2 XRD pattern of GO samples obtained after high-energy ball milling for 1,2 and 5h

Sample	Interlayer distance(Å)
GO(0)	5.78
GO(1)	5.92
GO(2)	6.12
GO(5)	6.20

Table 1. Interlayer distance of each GO

287eV, COOH at 289eV) appeared in both samples and  $SP^2$ , normal graphite peak appeared around 285eV. Also the peak intensity shows that among the several functional groups, epoxide is the most abundant group. Atomic ratio of C/O for two samples were 2.91, 2.49 for GO(0) and GO(5), respectively.

Since it is impossible to remove water from these samples, not all oxygen is considered attached to graphite back bone. But still we can compare GO(0) to GO(5). The milled graphite shows high tendency to get oxygen group to its own carbon backbone compared to unmilled graphite. Also after oxidation, this graphite had more carboxylic group than raw graphite. In fact GO's real structure is not disclosed yet, however, in general, carboxylic group is known to form at the edge of the graphite. After milling process, the crystalline size became smaller and the edge of the graphite are formed. Thus, this result is consistent with the reduction in graphite particle size caused by milling, which is desirable for applications.

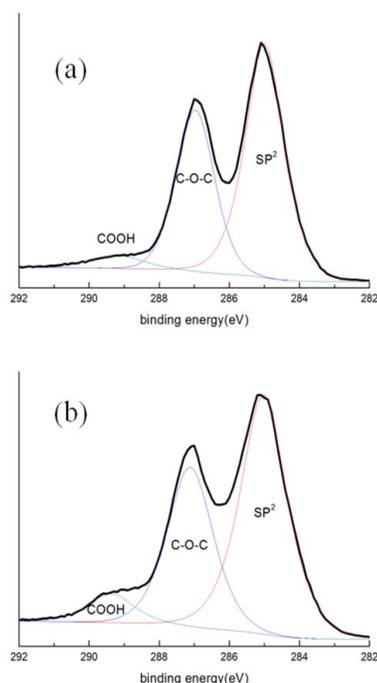


Fig 3 XPS results of GO(0) and GO(5). Each result is deconvoluted into three peaks

## 4 CONCLUSION

GOs with high energy ball milled graphite have been synthesized by Brodie's method and characterized by Raman, XRD, XPS. Until 5h ball milling, GO's structure was retained, resulting in 10% increase in the interlayer distance. Further, more carboxylic group was obtained when ball milled graphite was used. Even though it is still far from the optimum interlayer distance to store hydrogen, we show some possibility to enlarge distance without filler. The optimization of milling processing and structure characterization of milled GO are yet to be done.

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