Effect of light exposure on the $\mu$SR asymmetry of graphene oxide film

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Abstract. Graphene has received a lot of attention due to its promising properties for electronic devices application such as energy storage device. Due to the amount needed for application, graphene oxide is widely used as a precursor to obtain graphene-like material. The GO film is thermally reduced or photoreduced to obtain graphene-like that known as reduced graphene oxide (rGO). We intend to measure microscopic intrinsic charge carrier motion of GO film by means of muon spin rotation relaxation ($\mu$SR). We prepared thick film of GO by stacking a lot of GO sheets using 4 mg/ml GO-water dispersion. The rGO material was obtained by thermally reduced GO film at 200°C for 2 hours under argon flowing. We measured zero field (ZF) $\mu$SR measurements of GO and rGO from 10 K and 300 K. During the $\mu$SR measurement we exposed the light into the samples. We discuss the effect of light exposure on the $\mu$SR asymmetry and compare to $\mu$SR asymmetry of rGO sample.

1. Introduction

Graphene oxide (GO) is two dimensional materials that was prepared from graphite using oxidation process and followed by exfoliation. Schematic illustration of the structural model of a GO sheet is shown in figure 1. The GO sheets are decorated with oxygen-containing functional groups such as carboxyl, hydroxyl and epoxy groups [1]. Due to oxygen containing group, the conjugation on GO chains are interrupted and therefore GO is nearly an insulator. The reduction process for removing the oxygen-containing groups from GO that will heal the defects of the conjugated $\pi$-electron of GO need to be applied in order to obtain graphene like material.

Thermal reduction is amongst the technique that commonly applied to remove the contained oxygen. A schematic view of the conversion of GO to reduced graphene oxide (RGO) that shown in figure 1, illustrates a recovery of sp$^2$-binding sites of RGO. The restoration of sp$^2$-carbon sites and the recovery of the conjugated $\pi$-electron system is indicated by the strongly increasing UV-Vis absorption spectra of RGO as previously reported [2]. Our previous result also shows that change of GO to rGO accompany by the change of structures [3].

We used muon spin rotation relaxation ($\mu$SR) spectroscopy to study the microscopic intrinsic charge carrier motion of GO with varied oxygen content. The study of microscopic intrinsic charge carrier motion by $\mu$SR spectroscopy has been performed for several organic and hybrid materials [4-
7]. The first muon spectroscopy investigation of graphene was reported in 2011, showing evident muon spin precession that originated from muon–hydrogen nuclear dipolar interactions [8, 9]. In graphene oxide (GO), light illumination has important role on the healing of conjugated bonds by removing oxygen functional group from the molecule, such that the conjugation length increases and GO becomes more conductive [1]. We are interested to probe how the charge transport properties changes related to the change of structure due to light exposure. We performed zero field (ZF) μSR measurements of GO and RGO sample under light illumination. μSR measurement of Si and Ge under light illumination has been reported previously [10].

Figure 1. Schematic illustration of the reduction of graphene oxide (GO) to reduced graphene oxide (RGO) [1].

2. Experiments
The free standing GO papers were prepared in petri dish from 4 mg/ml GO dispersed in water, and following by evaporation of water in atmospheric and room until it is almost dried, as previously described [3]. It was further dried at 50°C the vacuum oven overnight and then detaches from the petri dish. In order to obtain graphene-like film that known as rGO, the free-standing GO film then thermally reduced by heating the samples for two hours at 250°C inside the Pyrex tube that flow with Argon gas. We applied Scanning Electron Microscope (SEM) for morphology inspection.

We also exposed thin film of GO with UV light using a home-made UV light source with intensity of 0.12 mW cm$^{-2}$ for varied time exposure and measured its absorbance in the range of 200 nm to 800 nm using UV-Visible spectrometer (PG T70). Sample for the measurement (photoreduction) was very thin and it was deposited in fused silica substrate using spin coating technique.

We have performed zero field (ZF) μSR at varied temperature for both GO and RGO samples under light irradiation at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK. The samples were stacked and wrapped in a silver foil and mounted on a silver plate in the cryostat. Measurements were done at temperature varied from 10 K to 300 K using a pulsed positive surface muon beam. In this measurement, the light were exposed to the sample during the μSR measurements.

3. Results
The prepared GO paper were brown-black with a thickness about 30 microns to 50 microns. After thermal reduction for 2 hours at 250°C, the GO paper become darker with a metallic-like. For μSR measurements, about tenth of samples were then stacked in order to get an appropriate mass. Figure 2 shows surface image of GO and RGO samples that measured using SEM. Figure 2(a) shows that GO paper seems quite dense. The surface of rGO film (figure 2(b)) is look similar compare to the GO paper (figure 2(b)), but the rGO paper has more surface roughness in comparison to surface of the GO paper.

While GO sample using for photoreduction experiment was quite thin and transparent. As prepared, it has a brown-look, but after exposed with a UV light with intensity of 0.12 mW cm$^{-2}$, the sample becomes darker compare to condition before photoreduction process. Quantitatively the change was observed by using UV-Vis spectra that measured at varied time exposure as shown in figure 2. We found that there is an obvious increment of absorption in the range of 230 nm to 800 nm, but the lambda max is remained in 230 nm. The shoulder at 300 nm seems disappeared after exposing
GO sample for 7 hours’ irradiation. The intensity of light used in photoreduction is quite low, but it is still show a change of absorption spectra after light irradiation. It will take long time to observe significant change of absorption spectra of GO. This absorption data has confirmed the effect of light irradiation on GO sample.

Figure 2. Comparison SEM images of (a) surface of GO paper and (b) rGO paper.

Figure 3. UV-Vis spectra of GO film before and after light irradiation using UV light with intensity of 0.12 mW cm\(^{-2}\) at varied time exposure.

The raw data of μSR measurement were shown as an asymmetry parameter as function of time. The asymmetry parameter \(A(t)\) at a time \(t\) is defined in equation (1).

\[
A(t) = \frac{[F(t) - \alpha B(t)]}{[F(t) + \alpha B(t)]}
\]  

(1)

with \(F(t)\) is total muon events counted by the Forward counters, \(B(t)\) is total muon events counted by the backward counters, \(\alpha\) is the calibration factor reflecting the relative counting efficiencies between the forward and backward counter. The asymmetry of GO and RGO samples at zero field measuring from 10 K to 300 K were shown in figure 4(a) and figure 4(b), respectively. At high temperature of 300 K, the asymmetry of GO and RGO shows a Gaussian-like depolarization. An exponential-like
Depolarization of spectra is observed at low temperatures below 100 K. The degree of depolarization is significant different between asymmetry spectra of GO and RGO. The degree of depolarization in GO samples is larger than that of rGO samples. This phenomenon is probably due to the different intrinsic properties of GO and rGO. When muon implanted to the samples, a muonium, created from a positive muon and an electron, is formed and reacted with other charges in GO or rGO. Since the mobility of GO lower than that of rGO, muonium can feel the intrinsic charge larger in GO than in rGO resulting the large degree of depolarization in GO.

Figure 4. Asymmetry of (a) GO sample and (b) rGO sample at zero field at varied temperature from 10 K to 300 K.

Figure 5. Asymmetry of (a) GO sample and (b) rGO sample at temperature of 10 K and 300 K in condition of light illumination off (red line) and on (blue line).

Figure 5 shows asymmetry data of GO and rGO before and after light illumination at zero field either at 10 K and 300 K. We can see a small shifted of asymmetry of GO sample after light illumination both at 10 K and 300 K (figure 5(a)). This result shows that both at 10 K and 300 K, μSR asymmetry of GO are affected by light illumination.

The shifted due to light illumination is only small. It is may related to intensity of used white light that not high enough. As compare to change of absorption spectra in figure 3 which the effect only
small due to low intensity of light. In order to magnify the effect of light exposure it is necessary to use higher light intensity.

In figure 5(b) we also can see a very small shifted of asymmetry of rGO sample at 10 K after light illumination, but it is not the case at 300 K. This shows that the light illumination seems not change μSR asymmetry of rGO sample at 300 K. There is no distinguishable shifted of Asymmetry rGO at 300 K due to light exposure. More detail result needs more analysis by fitting the asymmetry data.

4. Conclusion
We have obtained asymmetry data of GO and rGO sample using μSR method at zero field measured at varied temperature from 10 K to 300 K. Both GO and rGO samples show that at low temperature the asymmetry consists of fast component and slow component, but at room temperature the asymmetry seems only consist of fast component. At 10 K the GO sample has shorter fast component in compare to rGO sample. Light illumination has a distinguish effect on GO asymmetry, but not on rGO sample.

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