Near-Infrared Photoluminescence Spectral Imaging of Chemically Oxidized Graphene Flakes

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(Rceived 29 December 2011; Accepted 29 August 2012; Published 15 September 2012)

In order to determine the local structure of carbon sp² clusters in chemically modified graphene oxide (GO) flakes, their luminescence was analyzed, using near-infrared photoluminescence (NIR PL) spectral imaging. GO flakes emit a broad PL spectrum of wavelengths of 500 to 1400 nm, indicating that they contain sp² clusters, whose size is theoretically estimated to be in the 1.3 to 2.3 nm region. The size distribution of such sp² clusters is fairly uniform at different positions and for different numbers of layers of GO, at the spatial resolution of NIR PL image (5 μm). The analysis by transmission electron microscopy directly confirmed the existence of such sp² clusters and the estimated size of the sp² clusters was widely ranged from 0.5 to 4 nm. The effect of the GO reduction to the local structure of carbon sp² clusters was also studied and it was found that the NIR PL intensity decreased as the reduction progressed and that there was no large spectral shift. [DOI: 10.1380/ejssnt.2012.513]

Keywords: Photoluminescence; Raman scattering spectroscopy; Surface structure, morphology, roughness, and topography

I. INTRODUCTION

Graphene consists of a two-dimensional single atomic layer of sp² bonded carbon atoms and exhibits notable electronic and mechanical properties [1]. However, the applications of graphene based on its optical properties have been limited because defect-free graphene exhibits a zero band gap. Graphene oxide (GO) is a partially oxidized graphene sheet and has demonstrated interesting electronic and mechanical properties [1]. However, the reduction of GO by exposing the GO flakes on the plate to hydrazine vapor. A few clusters induced by GO reduction. 2

To understand the emission mechanism, PL behavior has been studied with thin films and liquid GO samples [7], and in terms of pH dependence [5], and reduction levels [6-8]. The reduction of GO makes it possible to change its optical and electronic properties. A common reduction method involves exposure to hydrazine vapor, which enables us to obtain an electrically conductive material [3]. As regards the change in the optical properties, a study of PL spectra obtained with UV and visible light showed that reducing GO weakens the PL intensity, but no spectral shift was observed [6]. The results do not indicate a significant change in the size of the clusters, and would suggest rather the formation of additional clusters.

In this study, we used NIR PL, transmission electron microscopy (TEM), and Raman spectroscopy to determine the size of the sp² clusters contained in an individual GO flake. We also studied the change in the structure of the sp² clusters induced by GO reduction.

II. EXPERIMENTAL

A. Reagents and Materials

The natural graphite was a gift from Ito Kokuen Co., Inc. Hydrazine solution (35 wt% in water) and ammonia solution (28 wt% in water) were purchased from Aldrich and Kanto Chemical Co., Inc., respectively. Superior quality pure water was used in all the processes involved in aqueous solution preparation and washing.

B. Sample preparation

We synthesized an aqueous dispersion of GO from natural graphite using a modified Hummers method [3, 9]. The GO dispersion was spin coated on the hydrophilic surface of a 10×10 (mm) quartz plate, prepared by treatments in piranha (H₂O₂:H₂SO₄=1:4) and NH₄F. We prepared reduced GO by exposing the GO flakes on the plate to hydrazine vapor. A few μL of a mixture solution (hydrazine solution: ammonia solution = 1:7) was contained

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*This paper was presented at the 6th International Symposium on Surface Science –Towards Nano, Bio and Green Innovation–, Tower Hall Funabori, Tokyo, Japan, December 11-15, 2011.
in the same vial with the plate, which was kept at 65°C for 10 min (rGO-1) or at 95°C for 60 min (rGO-2).

C. Characterization

Atomic force microscope (AFM) images were recorded in the AC (tapping) mode under ambient conditions using a D3100 Atomic Force Microscope (Digital Instruments). The samples for the AFM image were prepared by spin-coating the GO dispersion on the hydrophilic surface of a quartz plate or a SiO$_2$ (285 nm)/Si plate, treated by the method described above.

The size of the sp$^2$ clusters was investigated by employing TEM with a JEOL ARM-200F at an acceleration voltage of 200 kV. The TEM images were prepared by pipetting a few μL of GO dispersion onto holey carbon mesh grids, which were then rinsed with distilled water. We used the reduction process described above to prepare rGO-2 on a mesh grid.

D. NIR PL and Raman measurement

Prior to the PL measurements, we obtained Raman images to determine the number of layers and the positions of the GO flakes on the plate. We measured the Raman and NIR PL spectra employing a Raman microprobe system (inVia Reflex/StreamLine microRaman spectrometer, Renishaw), and using a CCD and an InGaAs array detector for the Raman and PL measurements, respectively. The excitation light sources were the 532- and 785-nm lines of a laser-diode continuous-wave laser for the Raman and PL measurements, respectively. We performed all the measurements at room temperature.

III. RESULTS AND DISCUSSION

Figure 1(a) shows an AFM image of the synthesized GO flakes deposited on a hydrophilic SiO$_2$/Si surface. Most of the GO flakes were single-layer and had various shapes and sizes. The height of a single sheet was 1.3±0.1 nm (Fig. 1(b)), similar to that reported in the literature [10]. This is significantly thicker than that of ideal graphene owing to the presence of oxygen-containing functional groups and adsorbed water above and below the carbon basal plane. Next, we characterized the GO flakes on the quartz plate by using an AFM image to determine their thickness, which means the number of layers in a flake (Fig. 2(a)). The height of a single sheet was from 1.3 to 1.5 nm (Fig. 2(b)), which is similar to those observed in Fig. 1. The height at position A is the substrate level. The numbers of GO layers at positions B to D changed from single, to double, and triple layers. Then, we obtained a Raman image of the same GO flake (Fig. 2(c)). The Raman spectra extracted from the image at positions A to D show the typical spectral features of GO, namely it contains G and D bands at about 1590 and 1355 cm$^{-1}$, respectively [11]. The Raman intensities of both the G and D bands are roughly proportional to the number of layers. This means that we can determine the number of layers in any flake for further analysis simply from the Raman image.

Figure 3(a) shows an NIR PL image of GO flakes at an emission wavelength of 1300 nm for several different numbers of GO layers, which were determined from a Raman image of the same GO flakes (Fig. 3(c)). The patterns agree well with the corresponding Raman image of the same GO flakes, indicating that the PL was derived from individual GO flakes. The PL spectra extracted from the image at positions A to C show a broad GO emission of 800 to 1400 nm (Fig. 3(b)). According to theoretical cal-
FIG. 3: (a) NIR PL image of GO flakes at an emission wavelength of 1300 nm overlaid on a Raman image. Maximum intensity = white and minimum intensity = black; (b) PL spectra extracted from the image at positions A to C. Positions of the Raman bands around 874 (D band) and 894 nm (G band) are indicated by arrows; (c) corresponding Raman image of the same GO flakes in the D band (1530 cm\(^{-1}\)). Bar = 20 \(\mu\)m; (d) Raman spectra extracted from the image at positions A to C without a baseline offset. The numbers of layers determined by the Raman intensity were A (triple), B (single), and C (none).

FIG. 4: (a) NIR PL image of rGO-1 flakes at an emission wavelength of 1300 nm overlaid on a Raman image. Maximum intensity = white and minimum intensity = black; (b) PL spectra extracted from the image at positions A to C. Positions of the Raman bands around 874 (D band) and 894 nm (G band) were indicated with the arrows; (c) corresponding Raman image of the same rGO-1 flakes in the D band (1530 cm\(^{-1}\)). Bar = 20 \(\mu\)m; (d) Raman spectra extracted from the image at positions A to C without a baseline offset. The numbers of layers determined by the Raman intensity were A (triple), B (single), and C (none).

culations [8], the spectral range corresponds to the emission of \(sp^2\) clusters whose \(d\) is from 1.3 to 2.3 nm. The Raman bands of the GO corresponding to the D and G bands were also observed around 874 and 894 nm in the PL spectra, which supports the view that the observed PL originated from GO flakes. The dip at around 1110 to 1130 nm is caused by the detector, not by the sample. Figure 3(d) shows the Raman spectra measured at positions A to C. The numbers of layers determined by the Raman intensity were A (triple), B (single), and C (none). Although the PL intensity increased with the number of GO layers, unlike the Raman intensity it was not proportional to the number of layers. This can be explained by the self quenching of the PL by the layered GO area, since GO has been reported to behave as a fluorescence quenching material [5, 12]. Moreover, there was little spectral shift resulting from the position or the number of layers, indicating that the size distribution of the \(sp^2\) clusters, which is sufficiently large for them to have small gaps that correspond to the NIR emission, is fairly uniform at different positions and for different numbers of layers, at least at this spatial resolution. A similar result has already been reported for GO luminescence in the UV-visible region [6].

Next, we studied the effect of reducing GO. We controlled the degree of reduction by controlling the reduction temperature and processing time. Figures 4(a) and 5(a) show NIR PL images of rGO-1 and rGO-2 flakes, respectively, at an emission wavelength of 1300 nm, with several different numbers of layers, which were determined from the Raman images of the same rGO-1 and rGO-2 flakes (Figs. 4(c) and 5(c)). Again, the PL patterns agree well with the corresponding Raman images of the same rGO-1/rGO-2 flakes. There was no clear spectral shift caused by the reduction (Figs. 4(b) and 5(b)). Thus, it is difficult to determine whether a reduction induced a change in the size of the \(sp^2\) clusters solely by using NIR PL.

We then conducted a TEM analysis to characterize the exact structures of the \(sp^2\) clusters in the rGO-2 flakes (Fig. 6). Large transparent sheets of rGO-2 sample were observed on the grid (Fig. 6 (a)). The selected area electron diffraction pattern (SAD) of rGO-2 showed both diffraction rings and spots (Fig. 6(b)). Compared with previously reported data for single-layer graphene [14, 15] and chemically reduced graphene under hydrogen plasma [16], the crystal structure was not completely restored by hydrazine reduction. A high-resolution TEM (HRTEM) image clearly shows that the rGO-2 sheet consists of two different structures; graphitic areas and the amorphous \(sp^3\) matrix, which was observed as fine and rough patterns, respectively (Fig. 6 (c)). The graphitic domains can be further separated into smaller \(sp^2\) clus-
ter. Figure 6(d) schematically shows the $sp^2$ clusters (indicated in pink) separated by linear defects (indicated by purple lines). We roughly estimated the size of the $sp^2$ clusters from the diameter of the inscribed circle in each $sp^2$ cluster. The clusters behave as luminescence centers and their diameter $d$ determines the luminescence energy. The distribution of $d$ showed that the size of the $sp^2$ clusters in the region varied from 0.5 to 4 nm (Fig. 7). The result is consistent with a previously reported TEM analysis of GO flakes synthesized with a similar method to ours, which reveals that a single GO flake contains $sp^2$ clusters with several different sizes ranging from 0.5 to 3 nm in the amorphous $sp^3$ matrix [16]. Thus, the distribution of the different size $sp^2$ clusters causes a broad NIR emission from GO in the 800 to 1400 nm range, whose size is theoretically estimated to be in the 1.3 to 2.3 nm region.

Raman spectroscopy is another useful technique with which to estimate the size of the $sp^2$ clusters in carbon materials such as graphene by using the Tung-En-Koenig (TK) relation $I_D/I_G = C(\lambda)/L_a$, where the crystallite size $L_a$ is obtained from x-ray data. Here, $I_D$ and $I_G$ represent the Raman intensities of the D and G bands, respectively, and $C(\lambda)$ is a constant, which depends on the excitation laser wavelength $\lambda$ [17]. However, for disordered carbon materials, which consist of smaller $sp^2$ clusters, namely where $L_a < 2$ nm region, the TK relation is no longer valid and $I_D/I_G \propto L_a^2$ dependence works well [18]. By using $I_D/I_G = 0.99$ (Fig. 2(d)) and 1.18 (Fig. 4(d)) for GO and rGO-2, respectively, we found that the size of the $sp^2$ clusters increased by about 9% as a result of the reduction. Although the exact definitions of $L_a$ and $d$ are different, the both are regarded as the size of the $sp^2$ clusters in our discussion. Together with the TEM analysis, the result indicates that the size distribution of the $sp^2$ clusters of GO is not largely different from that of rGO-2. It is therefore natural that no spectral shift was observed in the 800 to 1400 nm region when GO was reduced.

We also found that, as the reduction progressed, the PL intensity decreased (Figs. 4(b) and 5(b)). The decrease in the PL intensity is not likely caused by the change in the size distribution of the $sp^2$ clusters, according to our above Raman analysis. A possible reason is that the restoration of the line defects, which separate the graphitic domains into $sp^2$ clusters, is restored by hydrazine reduction. It may interrupt the recombination of localized electron-hole pairs within a $sp^2$ cluster and facilitate the relaxation of the excited states to the nonradiative recombination states [6]. However, the restoration mechanism of $sp^2$ clusters by reduction has not yet been directly confirmed. A further study will be needed to reveal the reason for

FIG. 5: (a) NIR PL image of rGO-2 flakes at an emission wavelength of 1300 nm overlaid on a Raman image. Maximum intensity = white and minimum intensity = black; (b) PL spectra extracted from the image at positions A to C. Positions of the Raman bands around 874 (D band) and 894 nm (G band) are indicated by arrows; (c) corresponding Raman image of the same rGO-2 flakes in the D band (1350 cm$^{-1}$). Bar = 20 μm; (d) Raman spectra extracted from the image at positions A to C without a baseline offset. The numbers of the same rGO-2 flakes in the D band (1350 cm$^{-1}$) are indicated by arrows; (c) corresponding Raman image

FIG. 7: Distribution of the size of the $sp^2$ clusters analyzed by using an HRTEM image of rGO-2.
the change in the PL intensity caused by the reduction of GO.

IV. CONCLUSIONS

In summary, GO flakes emit a broad NIR PL spectrum at wavelengths of 800 to 1400 nm, indicating that the GO flakes contain sp$^2$ clusters that are large enough to have a small energy gap that corresponds to the NIR emission. There is little spectral shift due to position or the number of layers, indicating that the size distribution of the sp$^2$ clusters is fairly uniform at least at the spatial resolution in our study. The TEM analysis of a reduced GO flake confirmed the existence of the sp$^2$ clusters. The size of the sp$^2$ clusters in rGO-2 flakes ranged from 0.5 to 4 nm, which can behave as luminescence centers in the NIR wavelength region. The cluster size was also evaluated by the Raman spectra, which showed that the size of the sp$^2$ clusters increased by about 9% as a result of the reduction. The little difference in the size distribution of the sp$^2$ clusters reasonably explains the little spectral shift in NIR PL caused by the reduction of GO.

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