

Characterization of Few-Layer Graphene on Stretchable Substrate Using Thermally-Treated Exfoliation

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Graphene, sp^2 -bonded carbon atoms highly packed in a two-dimensional (2D) honeycomb lattice, has emerged a promising material because of its unique properties such as high mobility, high saturation velocity, and transparency for future electronic components.¹⁻⁴ The excellent properties of graphene make it possible to fabricate various attractive devices, such as inorganic and organic field-effect transistors,⁵⁻⁸ gas sensors,⁹ and energy harvesting cells.¹⁰ In particular, single graphene layer has an ultrathin thickness as 0.5-1.5 nm which enables it to be applicable on a stretchable substrate. Also, the graphene monolayers have the potential to be suitable for flexible device applications. For this reason, it is a significantly important step to investigate the presence of graphene layer on a flexible substrate that would be used, prior to those graphene-based device fabrications. Raman mapping, atomic force microscopy (AFM) and optical microscopy have been generally considered as a powerful method for identification and counting of graphene layers.^{11,12} These analyses have been carried out for figuring out the number of graphene layers on a solid substrate such as a silicon and glass. However, significant experiments have not been established for identifying a single graphene layer's presence on a flexible substrate so far.

In this paper, we report Raman spectra analysis that confirms whether the graphite flakes on flexible substrates consist of few-layer graphene (FLG) sheet. The FLG obtained by a thermally-treated exfoliation technique to get intrinsic properties of the graphene on a stretchable substrate. This approach provides the accurate counting of graphene flakes and is beneficial for high performance graphene-based devices.

Figure 1 shows the chemical structures of graphene and polymethylmethacrylate (PMMA), as well as schematic representation of FLG on a stretchable substrate. A polyethylene naphthalate (PEN) film was utilized as a flexible substrate. Spin casting (4000 rpm for 30s) was performed to form a 250-nm-thick dielectric layer of PMMA (950,000 molecular weight, Microchem Co.) as glue which enhances a strong adhesion with graphene molecules. The substrate was put in a baking oven at 120 °C for 15 min. Then the scotch tape on the PMMA/PEN substrate was taken off by micromechanical exfoliation - repeated peeling flakes of graphite, as soon as the substrate was taken out of the oven.^{8,13,14} The exfoliation technique with a scotch tape is used to fabricate graphene which is then transferred, using a

thin layer of glue-like PMMA, onto a stretchable substrate. It obtained a large, high-quality layer of graphene printed on the flexible substrate by using our proposed thermally-treated exfoliation technique. Aluminum (Al) film with a thickness of 100 nm was thermally deposited over the transparent PEN substrate using a metal mask in order to gather accurate signals of Raman spectra. We measured the Raman spectra to identify the presence of FLG. The Raman data were obtained using 514-nm argon-ion laser excitation at room temperature.

Figure 2 shows the comparison of the 514 nm Raman spectra between the FLG and PMMA layer. The most prominent features in the Raman spectra as were also seen in other studies,^{8,15,16} i.e., G band at $\sim 1580\text{ cm}^{-1}$ and a band 2D band at $\sim 2700\text{ cm}^{-1}$: the 2D peak of the FLG formed by a single Lorentzian peak. The two peaks are enough data to prove the presence of the FLG. The PMMA did not show a peak in the Raman spectra. Prior to obtaining the Raman spectra above, we tried to get the Raman data of the graphene on PMMA layer, but without Al film, meaning the sample was entirely transparent. The Raman spectra we captured were out of the range that can be analyzed. The main cause is that the argon laser goes through the sample without any scattering. Thus, the layer to block the laser is needed to get the Raman spectra of the graphene. In addition to the Raman spectra analysis, the atomic force microscopic (AFM) measurement was performed in order to confirm the thickness of the FLG on the PMMA layer, since the number of the graphene layer can be estimated by the thickness.

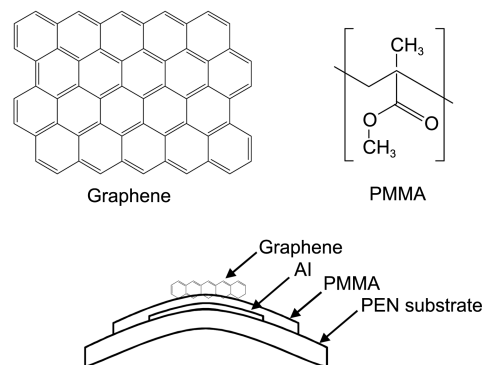


Figure 1. The chemical structures of graphene and PMMA are shown in the up panel. Schematic of FLG on a flexible PEN substrate in the down panel.

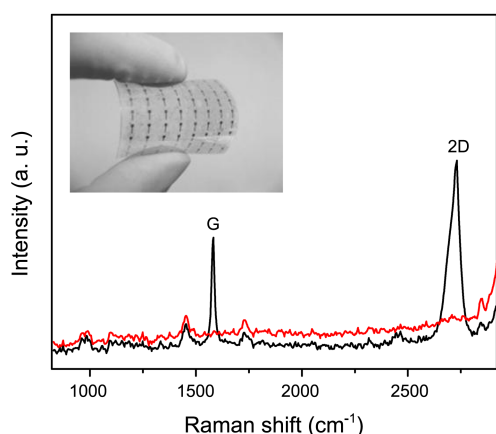


Figure 2. Raman spectra of PMMA (red line) and FLG (black line) by using the 514-nm argon-ion laser excitation at room temperature. Inset: Photograph of graphene films on the PEN substrate.

However, we could not confirm the thickness based on the AFM images because the surface of the PMMA layer is considerably rough compared to the thickness of the FLG. Organic materials like PMMA are known to be soft and rugged, so it is hard to characterize between the signal and the noise when surface of organic materials is examined. It is noted that our study clearly shows that the Raman mapping is powerful and proper method for identifying the presence of the FLG on organic material as well as a stretchable substrate.

The photograph of the bended sample utilized in the study is shown in the Figure 2 (inset) and the flexibility of the sample is quite excellent. The device has the following architecture: PEN substrate/Al (100 nm)/PMMA (250 nm)/FLG. In order to see if there is any difference of Raman scattering transition due to physical transformation, we compared the Raman spectra of before and after bending the sample. With an increase in strain, the Raman peak shows a universal red-shift over the entire strained graphene. However, according to the comparison of two Raman spectra that there was little difference, our data shows that the FLG is undamaged conserved regardless of outside influences like bending. This might be due to the reversible and quick recovery property of the excellent elasticity of graphene. Yu *et al.* also observed that graphene is able to recover immediately once the strain is released.¹⁷ When it comes to the whole surface of the sample, the sample is seen to be a little dirty as shown in the Figure 2 (inset). It results from bulk graphite that is concurrently and randomly produced when the FLG is prepared by using the exfoliation technique. To address this problem, a lot of researchers are currently making effort to devise a novel technique that is able to obtain the FLG without bulk graphite and place the graphene on the position we want. It is expected to be able to completely eliminate the issue mentioned above soon.

We have demonstrated the presence of FLG on a flexible substrate because identifying and counting the FLG is significantly important step before applying the FLG into novel electronic devices, especially flexible devices in this

paper. AFM proved not to be a good method for verifying the number of graphene layer due to rough surface of the sample. As another method for checking the number of layers, Raman spectra analysis is considered and proven to be a powerful method for experiments based on flexible substrates. Our research clearly shows that the presence of the FLG on a flexible substrate fabricated by a thermally-treated exfoliation technique can be verified by the Raman spectra analysis as proved in other studies that were conducted on a solid substrate. Furthermore, we have illustrated that the FLG is able to be utilized for organic-based flexible devices. Accordingly, this approach could lead to the development of next-generation graphene applications with a flexibility.

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