Investigation of Interaction between Graphene and Steel Using Raman Spectroscopy

Y. Fushiwaki*, A. M. Abdelkader*and R. J. Young*

*School of Materials, The University of Manchester
Oxford Road, Manchester, M13 9PL, UK
yusuke.fushiwaki@postgrad.manchester.ac.uk

ABSTRACT

The purpose of this study is to understand the interaction between graphene and steel using Raman spectroscopy. Graphene was firstly coated on polished steel, and then, the interaction between the graphene and the steel was investigated by obtaining Raman band shifts in a four-point bending test. It has been found that there is a shift of the 2D band to lower wavenumber. These results might enable us to know the interfacial shear strength between the graphene and the steel. The results obtained showed that it is possible to determine the influence of the unit strain on the 2D band shift for the graphene coated on the steel. In the case of large graphene flake with a diameter of around 15 µm, more than -20 cm^{-1} band shift per 1% strain was detected. However, only -1 to 0 cm^{-1} was found on a small graphene flake with a diameter of ~5 µm.

Keywords: graphene, steel, composites, Raman spectroscopy

1 INTRODUCTION

Since single-layer graphene was successfully exfoliated at the University of Manchester in 2004 [1], it has attracted increasing attention in material science [2, 3], including the application in graphene-reinforced nanocomposites. Graphene represents a class of new materials with unique properties that are just beginning to find applications in emerging and existing industries. Graphene is a single-layer sheet of sp^2 carbon atoms and has attracted tremendous attention and research interest, owing to its exceptional electronic, optical, magnetic, thermal and mechanical properties [2, 3]. It is the strongest material ever measured with a Young's modulus reported of 1 TPa and the ultimate strength reaching 130 GPa [4]. The thermal conductivity of graphene can reach 5000 $W \cdot m^{-1} \cdot K^{-1}$ [5]. It also has a remarkable electrical conductivity up to 6000 $s \cdot cm^{-1}$ [6]. Its high surface area theoretically can be up to 2630 $m^2 \cdot g^{-1}$ and it has complete gas impermeability [7].

Nanomaterials are generally different from the large particles. They have large specific areas which make the area of interface between the reinforcement and matrix much larger than that in conventional composites [8-10]. Thus, due to the excellent properties and high surface area, graphene is an ideal reinforcement with great potential to be used in nanocomposites.

Compounding graphene might also lead to creating some newly functional properties for metal. However, very little information is available on the interaction between the graphene and the metal. Threfore, in this project, after coating graphene on steel, investigation of interaction between the graphene and the steel was carried out by obtaining Raman band shifts thorough a four-point bending test in Raman spectroscopy.

2 EXPERIMENTAL

2.1 Preparation of Steel Substrate

The steel samples used in the present study as substrates were full hard cold-rolled mild steels with a thickness of 1.0mm. The chemical composition of this steel is shown in Table 1.

Table 1: Chemical composition of the steel used.

(mass%)

C	Si	Mn	P	Al
0.01	0.03	0.01	0.02	0.02

The samples were pre-cleaned by electric degreasing, which was performed in an alkaline solution of 3.4 mass% NaOH at 500 $A \cdot m^{-2}$ for 10 s. The steel samples were then pickled in an acidic solution of 5 mass% HCl at 60 °C for 5 s. After pickling, the specimen surface was removed by a thickness of 0.05 mm through polishing not only by dry emery paper to #2000 but also by electric polishing to obtain fresh surface of the steel. Electric polishing was conducted in the solution consisting of acetic acid glacial of 95 vol%, perchloric acid of 3.5 vol% and water of 2.5 vol%. A temperature of the solution was kept cool by ice. The steel was served as a working electrode, and Type 304 stainless steel was used as a counter electrode for the electric polishing. Both electrodes were immersed in the solution and connected to a DC power supply, which is Programmable Power Supply, GWINSTEK, Taiwan. The working and counter electrodes were then applied as an anode and a cathode, respectively. A potential of 60 V was applied for 2 mins. The working distance between the cathode and anode was adjusted at 15 mm. After the electrodeposition, all specimens were immediately dried at 60 °C in a vacuum furnace for 24 hrs to avoid any corrosion and oxidation.

2.2 Preparation of Graphene

Preparation of relatively thin and large graphene flake was conducted using an electrochemical exfoliation method developed by Abdelkader et al. [11]. Natural graphite (Graphexel, 2369) was used as a raw material. The graphene flake obtained was exfoliated in water under mild sonication for 60 mins in order to achieve an aqueous dispersions of graphene. And the centrifugation was then carried out at a high centrifugation rate of 11000 rpm for 1hr, separating small flakes in the supernatant from large flakes in the sediment. Redispersion of the sediment, followed by the second centrifugation, separation and redispersion cycles were also conducted to separate the small flakes by decreasing the centrifugation rate, eventually to 8000 rpm. After the centrifugation, the sediment was dried at 60 °C in a vacuum furnace for 24 hrs.

2.3 Drop casting of Graphene Solution

A Solution of graphene in N-methylpyrrolidone (NMP) of a concentration of 1.0 $mg \cdot ml^{-1}$ was made by mild sonication for 60 mins. About 1 ml of the solution was then dropped onto the steel substrate using a pipette. After dropping the solution, all specimens were immediately dried at 60 °C under vacuum furnace for 24 hrs to avoid any corrosion or oxidation.

2.4 Raman Spectroscopy

The Raman spectra of the graphene coated on the steel were obtained using a Renishaw 1000 Raman microprobe system with a Helium/Neon laser of wavenumber at 633 nm. The measurements were performed on several random areas for each sample. The power used was 1% to avoid down shift of the heating effect. The objective lens used was x50 and the laser spot size focused on the sample was 2 μm. The resolution of Raman scanning was 1 cm^{-1}.

2.5 Four-point Bending Test

As shown in Fig. 1, a strain gauge was attached onto the surface of the steel substrate in the middle of the beam besides the coating of graphene. The configuration of the steel substrate under tensile loading is also shown as a cross-sectional diagram in Fig. 1.

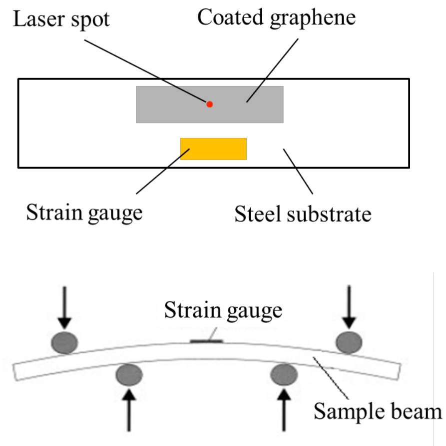

Fig. 1: A schematic diagram of the sample for the four-point bending test and Raman measurement area and of the cross-sectional sample under the four-point loading [12].

The strain of the surface was measured using a resistance strain gauge. The Raman measurements were carried out on the graphene coating near the middle of the strain gauge.

3 RESULTS AND DISCUSSION

3.1 Characterization of Graphene

At first, neat graphene put on Si substrate by drop casting was investigated through Raman measurements. Fig. 2 shows Raman spectra of the graphene and the steel.

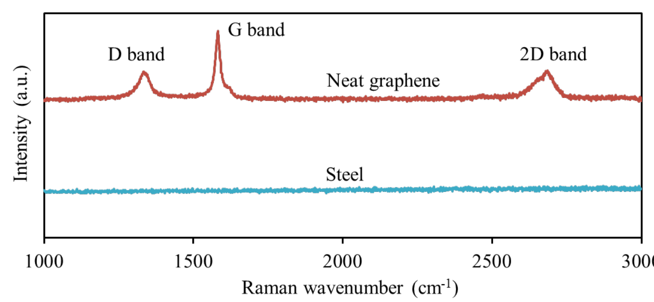

Fig. 2: Raman spectra of neat graphene and the steel.

The D, G and 2D Raman band which are unique to graphene were observed on the graphene flakes. However, the position of 2D band was at around 2675 cm^{-1}. Therefore, it was supposed that these graphene flakes were multilayer whose number of layer was at least more than five layers [11].

Secondly, the graphene was coated on the steel surface by drop casting. After coating the graphene, optical micrograph observations and Raman measurements were conducted and these results are shown in Fig. 3.

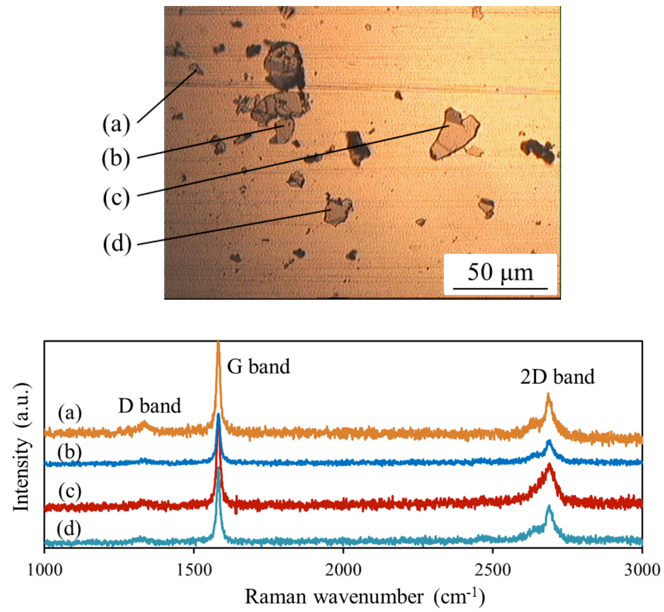

Fig. 3: Optical micrograph and Raman spectra of the graphene coated on the steel by drop casting.

At all the points from (a) to (d) on the steel surface shown in the micrograph, Raman D, G and 2D bands which are unique to graphene were observed. The coated graphene on the steel surface was also observed by SEM as shown in Fig. 4. It was indicated that some graphene flakes have a diameter of more than 10 µm.

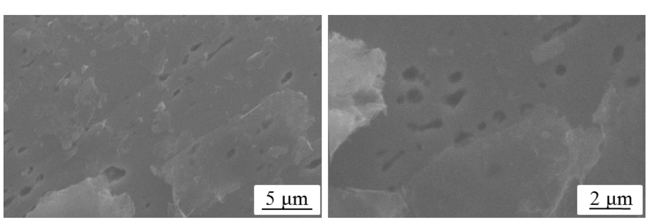

Fig. 4: SEM morphology of the steel surface on which the graphene was coated by drop casting.

3.2 Four-point Bending Test

Fig. 5 shows optical microscope morphology of the graphene coated on the steel by drop casting. And the four-point bending tests of these two flakes of (a) and (b) shown in Fig. 5 were then conducted.

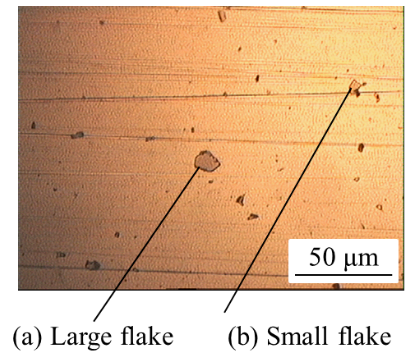

Fig. 5: Optical micrograph of the steel surface on which the graphene was coated by drop casting.

Fig. 6 and Fig. 7 show results of the four-point bending tests for a large graphene flake (a) and a small graphene flake (b), respectively. And Fig. 8 shows the influence of Raman band shift upon the applied strain for the steel sample. As shown in Fig. 6 to 8, the Raman band shift rate of the large flake (a) was different from that of the small one (b) despite both flakes being on the same steel sample. The shift rate of large flake was -22 cm^{-1} per 1% strain but that of small one -1 to 0 cm^{-1}. It was also thought that the band shift rate is determined by not only the condition of the sample but also the size of graphene flake. These results might enable us to know interfacial shear strength between the graphene and the steel using Shear Lag theory [13].

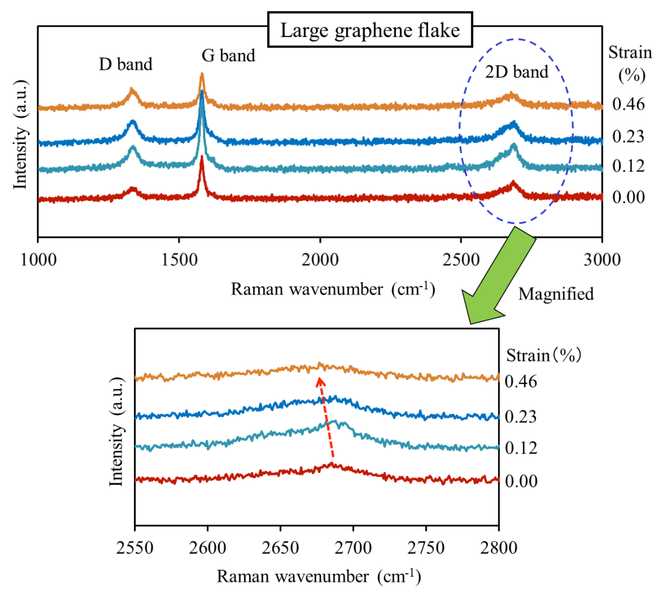

Fig. 6: Raman spectra at each strain for the large graphene flake, shown in Fig. 5 (a), coated on the steel.

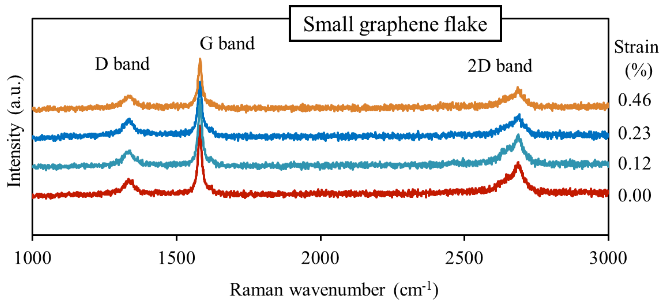

Fig. 7: Raman spectra at each strain for the small graphene flake, shown in Fig. 5 (b), coated on the steel.

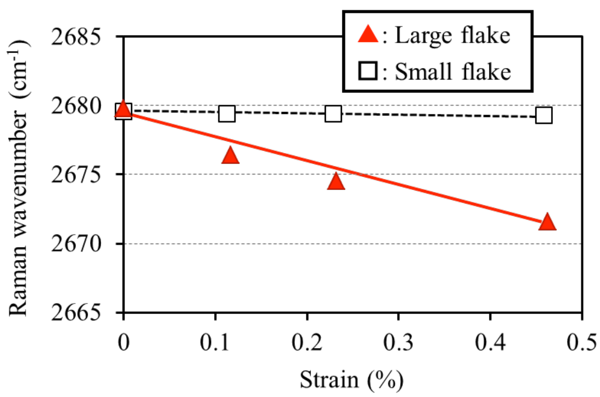

Fig. 8: Shift of the Raman 2D band with the strain for the graphene coated on the steel by drop casting.

4 SUMMARY

In order to understand an interaction between graphene and steel, the 2D Raman band shift of the graphene coated on the steel was investigated through a four-point bending test and Raman spectroscopy. As a result, it has been found that the influence of strain upon the 2D band shift was detected for graphene coated on the steel. When it comes to large graphene flake with a diameter of around 15 µm, more than -20 cm^{-1} band shift per 1% strain was obtained in the case of a strain up to 0.4% whereas only -1 to 0 cm^{-1} was on small graphene flake with a diameter of ~5 µm. The reason for this inconsistency in the Raman band shift may be attributed to the size of graphene flake as well as the condition of the sample surface such as a roughness.

In the future, some methods for graphene preparation will be considered to make the thickness of the graphene flake much thinner and to make the size of it much larger. Further characterization of graphene will also be conducted to clarify the size of each flake, the number of layers, the distribution of each flake on the substrate. The four-point bending test for graphene coated on the steel will also be tried in order to calculate the interfacial shear strength between the graphene and the steel using Shear Lag theory [13].

REFERENCES

[1] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., "Electric field effect in atomically thin carbon films," Science, 306, 666, 2004.

[2] Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S., "Graphene-based Composite Materials," Nature, 442, 282, 2006.

[3] Geim, A. K.; Novoselov, K. S., "The rise of graphene," Nature Materials, 6, 183, 2007.

[4] Lee, C. G.; Wei, X. D.; Kysar, J. W.; Hone, J., "Measurement of the elastic properties and intrinsic strength of monolayer graphene," Science, 321, 385, 2008.

[5] Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N., "Superior Thermal Conductivity of Single-Layer Graphene," Nano Letters, 8, 902, 2008.

[6] Du, X.; Skachko, I.; Barker, A.; Andrei, E. V., "Approaching ballistic transport in suspended graphene," Nature nanotechnology, 3, 491, 2008.

[7] Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; Van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L., "Impermeable atomic membranes from graphene sheets," Nano Letters, 8, 2458, 2008.

[8] Gibson, R. F., "Principles of composite material mechanics," 223, 2012.

[9] Young, R. J.; Lovell, P. A., "Introduction to polymers (Third edition)," CRC Press Tailor & Francis Group, London, 2011.

[10] Sengupta, R.; Bhattacharya, M.; Bandyopadhyay, S.; Bhowmick, A. K., "A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites," Progress in Polymer Science, 36, 638, 2011.

[11] Abdelkader, A. M.; Kinloch, I. A.; Dryfe, R. A. W., "Continuous Electrochemical Exfoliation of Micrometer-Sized Graphene Using Synergistic Ion Intercalations and Organic Solvents," ACS Appl. Mater. Interfaces, 6, 1632, 2014.

[12] Cooper, C. A.; Young, R. J., "Investigation into the deformation of carbon nanotubes and their composites through the use of Raman spectroscopy," Optical Devices and Diagnostics in Materials Science, 4098, 172, 2000.

[13] Gong, L.; Young, R. J.; Kinloch, I. A.; Riaz, I.; Jalil, R.; Novoselov, K. S., "Optimizing the Reinforcement of Polymer-Based Nanocomposites by Graphene," Acs Nano, 6, 2086, 2012.