Interference Phenomenon in Graphene-Enhanced Raman Scattering

Xi Ling and Jin Zhang*

Center for Nanochemistry, Beijing National Laboratory for Molecular Sciences, Key Laboratory for the Physics and Chemistry of Nanodevices, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

ABSTRACT: Graphene-enhanced Raman scattering (GERS) has been discovered, and the chemical enhancement mechanism based on charge transfer was thought as the main reason for the enhancement. We reported herein the effect of an interference phenomenon, a well-known reason for influencing the Raman scattering intensity, on the GERS using SiO2/Si substrates with different SiO2 thicknesses. First, it was found that the variation of Raman intensity of graphene on different thicknesses of SiO2/Si substrates followed the interference law. When the GERS system was moved on these substrates, where copper phthalocyanine (CuPc) and protoporphyrin IX (PPP) were constructed on graphene, the variation of the Raman intensity of the molecules on graphene and on SiO2/Si substrate also followed the interference law. However, for the GERS system, the Raman intensity of the molecules is obviously enhanced compared to the molecules on SiO2/Si substrates. The results show that when we compare the Raman scattering intensity of the molecule in the GERS system and non-GERS system on a SiO2/Si substrate with the same SiO2 thickness, an interference phenomenon will not influence the comparison of the intensity. Meanwhile, charge transfer between graphene and the molecule is proven existent regardless of the thick SiO2/Si substrate on which GERS occurs, by comparing the G-band shift of graphene before and after the deposition of the molecule, which further indicates the interaction between the molecule and graphene plays an important role in GERS. This work will be beneficial for the further understanding of the origin of GERS.

1. INTRODUCTION

Graphene, as a perfect two-dimensional hexagonal crystal of carbon atoms, has been thought of as a material which will never exist in nature, and there are only theoretical studies about it. Until 2004, A. Geim and K. Novoselov prepared monolayer graphene by mechanical exfoliation and got the Nobel Prize in physics in 2010 rapidly due to the discovery of the existence of the thinnest material in nature. During these years, graphene has caught many people’s eyes because of its excellent properties, such as ambipolar field effect, the quantum hall effect at room temperature, extremely high carrier mobility, and high sensitivity to some adsorption molecules.

In our previous paper, graphene as a substrate for suppressing fluorescence and enhancing Raman scattering has been reported. Briefly, when molecules were deposited on graphene and 300 nm thick SiO2/Si substrate, even though the number of the molecules is almost equal on graphene and the SiO2/Si substrate, the fluorescence and Raman signals of molecules on graphene were suppressed and enhanced, respectively. However, the origin of graphene-enhanced Raman scattering (GERS) is not so clear now even though the chemical mechanism based on charge transfer was thought as the main reason. In fact, there are several factors that will influence the intensity of the Raman signal, such as the number of the molecule, the distance between graphene and the molecule, the configuration of the molecule on graphene, the position of the Fermi level of graphene, the interference phenomenon from the substrate, and so on. The influence of the distance between graphene and the molecule has been discussed in our previous work, and the first layer effect was proved existent in the system.

The interference phenomenon usually occurs at an interface formed by a thin film with thickness in the subnanometer to micrometer range. In Fresnel equations, the degree of constructive or destructive interference between the two light waves is dependent upon their phase difference. In the graphene research, the interference phenomenon is widely used to make graphene visible and enhance its Raman signals. Usually, graphene is invisible on most of the substrates because of the low contrast between graphene and the substrate, while it becomes visible on a proper substrate, usually with proper dielectric layer thickness. For example, 300 nm thick SiO2/Si substrate is a now widely used substrate where monolayer graphene can be well distinguished. Moreover, because of the high transmission of incident laser through graphene and the small portion of graphene area used to generate scattered radiation during Raman measurement, the Raman signals of graphene are usually very weak on many substrates. However, on a substrate with proper dielectric layer thickness, interference enhancement will make the Raman signals of graphene visible. In the early period, there were many works in enhancing the Raman signals using the interference phenomenon, and an enhancement factor of about 30 is achievable. Wang and Yoon had studied the effect of...
the thickness of graphene sheets and the SiO2 layer thickness on a Si substrate to the Raman signals of graphene sheets. Both of their results show the multiple reflections of the incident laser at the upper and lower surfaces of the dielectric layer, and the multiple reflections of the Raman signal inside the graphene layer will induce the interference phenomenon at the interfaces and modify the intensity of the Raman signals of graphene sheets. As mentioned before, to “see” graphene and get strong enough Raman signals of graphene for determining its layer number, the GERS system usually uses the SiO2/Si substrate. It is a 300 nm thick SiO2/Si substrate in our previous work. Hence, the interference phenomenon exists inevitably in the GERS system and investigation into the effect of the interference phenomenon on GERS is necessary.

Here, to investigate the influence of the interference phenomenon on the GERS system, series of SiO2/Si substrates with different SiO2 layer thicknesses 

The different background color is due to different SiO2 layer thicknesses. Figure 1 shows the typical structure of the system with the monolayer Langmuir—Blodgett (LB) film of CuPc on graphene on a SiO2/Si substrate. The laser power on the sample was controlled to about 0.5 mW to avoid heating the sample. For the soaking technique as a deposition method, the coverage of molecules is the same on graphene and the SiO2/Si substrate, where both of them are monolayer coverage. For the soaking technique as a deposition method, if the concentration of the soaking solution is the same, we suppose the adsorption of the molecule on graphene is negligible. Hence, in this work, the comparison of the Raman intensity of graphene on different SiO2/Si substrates is out of the influence of the difference of the number of the molecule.

Raman Measurement. Raman spectra were collected on a Horiba HR800 Raman system with a 514.5 nm line from an Ar+ laser (Spectra-Physics model 163-C4205) and a 632.8 nm line from a He—Ne laser. A 100× objective was used to focus the laser beam. The laser power on the sample was controlled to about 0.5 mW to avoid the heating effect and the decomposing of the molecules. The spectra in comparison were obtained under the same conditions. The intensities of the peaks were obtained by fitting them with the Lorentzian function.

3. RESULTS AND DISCUSSION

A. Interference Phenomenon in Pristine Graphene. Figure 2 showed the optical images of few-layer graphene sheets on the ten kinds of substrates with different SiO2 layer thicknesses. The different background color is due to different SiO2 layer thicknesses.
thicknesses, and the graphene sheets are marked by the red dashed circle. Most of them are about 2-layer graphene which are determined by Raman spectra, except the first sample on the original Si substrate without a SiO₂ layer, which is about 5-layer because of the low contrast of the thinner graphene sheets. The corresponding Raman spectra in Figure 3 (a) show the typical 2-layer graphene line shape of G₀-bands at about 2650 cm⁻¹ for most of the samples. It is also obvious that even though the graphene sheets are all 2-layer the contrasts of them are much different. Some can easily be distinguished, while some are nearly invisible, which is a result of the difference of the interference effect.

To evaluate the interference effect from the SiO₂/Si substrates, Raman spectra of pristine graphene on the ten kinds of SiO₂/Si substrates were collected. From the series of spectra in Figure 3 (a), we can see that the Raman intensity of the G-band of graphene sheets varies a lot with the change of the SiO₂ layer thickness d. The curve in Figure 3 (b) with the Raman intensity of the G-band as a function of SiO₂ layer thickness d (bottom x-axis) and the a value (top x-axis). The dashed lines in (b) and (d) are a guide for the eye.

Figure 3. (a) and (c) are the Raman spectra of pristine graphene (<5 L) on the SiO₂/Si substrates with different SiO₂ layer thicknesses excited by a 632.8 nm laser and a 514.5 nm laser, respectively. (b) and (d) are the corresponding change of the intensity of G-band as a function of the SiO₂ layer thickness d (bottom x-axis) and the a value (top x-axis). The dashed lines in (b) and (d) are a guide for the eye.

Figure 2. Optical images of 2-layer graphene on the SiO₂/Si substrate with different SiO₂ layer thicknesses (except the No. 0 sample which is a few-layer graphene <5 L). The numbers on the left top corner show the thickness of the SiO₂ layer. The red dashed circle is a guide for the eye of the few-layer graphene.
the incident laser wavelength dependence of the interference phenomenon, but the interference pattern also follows the interference law with the peak point at about \( a = 1.25 \) and valley point at about \( a = 1.00 \). Hence, whether under 632.8 or 514.5 nm laser excitation, both of the interference patterns of the G-band of graphene follow the interference law well. The result indicates that the SiO\(_2\) layer thickness will really influence the Raman intensity of graphene on it and follow the interference law well.

B. Interference Phenomenon in the CuPc-LB/Graphene/SiO\(_2\)/Si and CuPc-LB/SiO\(_2\)/Si Systems. Since the interference pattern of the Raman intensity of graphene on the ten kinds of SiO\(_2\)/Si substrates follows the interference law, we consider the interference pattern of the Raman intensity of the molecule in the GERS and non-GERS system. Two systems were used for comparison, one with a monolayer LB film of CuPc on the SiO\(_2\)/Si substrates with graphene and the other with a monolayer LB film of CuPc on the SiO\(_2\)/Si substrates without graphene.

The schematic structure of the system was shown in Figure 1. Since the LB technique is a useful way to construct uniform and ordered monolayer molecular films, the number of molecules on graphene sheets and the SiO\(_2\)/Si substrates is the same. Figure 4 shows the AFM images of graphene with monolayer LB film of CuPc on top of them on the ten kinds of substrates, and the cross section analysis show that the films with a fluctuation of about \( \pm 1 \) nm are smooth, uniform, and have almost no difference between molecules on graphene and on the SiO\(_2\)/Si substrate. Figure 5 (a) and (c) show the Raman spectra of CuPc in both systems with a series of SiO\(_2\) layer thicknesses. The structures of the system are shown in the inset of Figure 5 (b) and (d). It can be seen that the Raman intensities of the peaks at 1340, 1450, and 1530 cm\(^{-1}\) change obviously with the SiO\(_2\) thickness. Taking the Raman signal at 1530 cm\(^{-1}\) from CuPc as a reference, which was assigned to the symmetric motion of all four isoindole groups, the interference patterns were obtained in both systems shown in
Figure 6. Raman spectra of PPP, deposited on top of graphene by solution soaking (a) and deposited on the bottom of graphene by LB technique (c), on the series of SiO₂/Si substrates excited by a 514.5 nm laser. (b) and (d) are the corresponding change of the Raman intensity of the peak at 1330 cm⁻¹ from PPP as a function of the SiO₂ layer thickness d (bottom x-axis) and the a value (top x-axis). The peak marked by †† is the G-band of the graphene. The dashed lines in (b) and (d) are a guide for the eye. The insets in (b) and (d) are the corresponding schematic structures of the systems.

Figure 5 (b) and (d), respectively. It shows that the patterns are so consistent in both systems with the peak point and the valley point at the same position, where the peak point at a = 1.25 and the valley point at a = 1.00 are also consistent with that in Figure 3 (b) for the G-band of pristine graphene. It indicates that the existence or not of graphene will not influence the interference pattern obviously. In other words, for the GERS systems on a series of SiO₂/Si substrates, the change of the Raman intensity is almost due to the interference difference induced by the different SiO₂ layer thicknesses, and the contribution from GERS can be thought of as the same for the series of substrates. Hence, in our previous work,₇ for the same 300 nm thick SiO₂/Si substrate, we compared the Raman signals of the molecule on graphene and the SiO₂/Si substrate and observed the enhancement phenomenon, which is independent of the interference effect from the substrate but completely due to the interaction between graphene and the molecule.

C. Interference Phenomenon in the PPP/Graphene/SiO₂/Si and Graphene/PPP-LB/SiO₂/Si Systems. For further investigation, PPP, which is a widely used molecule in our previous work,₇,₈ was also used. Meanwhile, two different constructions between graphene and the molecule were considered, one with flat PPP deposited by solution soaking on graphene and the other with upright PPP deposited by the assistance of LB technique on the bottom of graphene. Figure 6 (a) and (c) show the series of spectra of PPP in the two systems on the substrates with different SiO₂ layer thicknesses, and Figure 6 (b) and (d) are the corresponding curves of the Raman shift of the peak at 1330 cm⁻¹ from PPP as a function of the SiO₂ layer thickness d (bottom x-axis) and the a value (top x-axis). It is as expected that the interference patterns for both of the systems are the same and follow the interference law which is similar with that in Figure 5. Besides, as discussed in our previous work,₇,₈ the Raman signals of PPP are nearly invisible on the blank SiO₂/Si substrate without graphene for both of the systems. However, regardless of whether the molecule is flat or upright on graphene, well-distinguished signals from PPP were observed. If the interference phenomenon is the main reason for the enhancement, the enhancement factors should be the same on graphene and the SiO₂/Si substrate, and well-distinguished signals should also be observed on the SiO₂/Si substrate without graphene because the existence or not of graphene will not influence the interference phenomenon as discussed in part B. However, it is obviously not. Hence, the interference phenomenon can be excluded from the contribution to GERS. Here, in Figure 6, the change of the Raman intensity of PPP on the series of SiO₂/Si substrates is due to the different interference effect induced by the different SiO₂ layer thicknesses but insignificant contribution from graphene and the difference of the structures.

D. Charge Transfer in Graphene-Enhanced Raman Scattering. As discussed before, the interference effect is not the main contribution to GERS. The interference phenomenon is similar if the objects we are studying are on a SiO₂/Si substrate with the same SiO₂ thickness. Since chemical enhancement based on charge transfer is thought of as an important factor of GERS, the G-band shifts of graphene after soaking by PPP solution were investigated here for the series of SiO₂/Si substrates. Figure 7 clearly shows the downshift of the G-band of graphene after soaking for all kinds of SiO₂/Si substrates under either the 514.5 nm or the 632.8 nm laser excitation. Under 514.5 nm laser excitation, the shift is about −3 cm⁻¹, and it is about −2 cm⁻¹ under 632.8 nm laser excitation even though the Raman signals of PPP on graphene under the 632.8 nm laser excitation are very weak or invisible (see Figure 3 in ref 7). The Raman shift is an important character proving the existence of charge transfer.₂₃ For molecular doping to graphene, the G-band of graphene will upshift if the molecule is an electron acceptor, and it will downshift if the molecule is an electron donor. Here, the downshift of the G-band of graphene means that PPP is an electron donor to graphene. The result indicates that charge
transfer between graphene and the molecule occurred regardless of which thickness of SiO$_2$/Si substrate and how large the degree of the interference effect is.

4. CONCLUSION

By designing the SiO$_2$ layer thickness, ten kinds of SiO$_2$/Si substrates are used to investigate the influence of the interference phenomenon on GERS. Since the interference patterns are the same for the GERS system and non-GERS system and all of them follow the interference law well, the interference effect is thought as just working for the different thicknesses of SiO$_2$/Si substrates. If on a SiO$_2$/Si substrate with the same SiO$_2$ layer thickness, the interference phenomenon will not influence the Raman intensity in the GERS system and non-GERS system. Furthermore, charge transfer between graphene and the molecule was proven existent no matter which thickness of SiO$_2$/Si substrate is used. The results give powerful evidence showing the interference effect from the substrate is not the main reason for GERS, but the interaction between the molecule and graphene. This work will be beneficial for the further study of the origin of GERS.

AUTHOR INFORMATION

Corresponding Author
*Tel. & Fax: 86-10-6275-7157. E-mail: jinzhang@pku.edu.cn.

ACKNOWLEDGMENT

This work was supported by NSFC (20725307, 10774006 and 50821061), MOST (2011CB932601), and “the Fundamental Research Funds for the Central Universities”.

REFERENCES

(3) Zhang, Y. B.; Tan, Y. W.; Stormer, H. L.; Kim, P. Nature 2005, 438, 201–204.