

Tuning Chemical Enhancement of SERS by Controlling the Chemical Reduction of Graphene Oxide Nanosheets

Xinxin Yu,[†] Hongbing Cai,[†] Wenhua Zhang,[†] Xinjing Li,[‡] Nan Pan,[†] Yi Luo,^{*,†,§} Xiaoping Wang,^{*,†,‡} and J. G. Hou[†]

[†]Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China,

[‡]Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China, and [§]Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Among many exciting applications of graphene discovered in recent years,^{1–3} the use of graphene to study surface-enhanced Raman spectroscopy (SERS) of molecules is particularly interesting^{4,5} because it allows the separation of the often entangled two well-known mechanisms in SERS, namely, the chemical enhancement and the electromagnetic enhancements. The electromagnetic enhancement generated by the surface plasmon of the metal substrates has been extensively investigated for various systems in recent decades.^{6–10} However, the origin and the role of the chemical enhancement are constantly under debate because of its entanglement with the electromagnetic enhancement. It is, therefore, important to find a substrate that does not possess the electromagnetic enhancement, retaining the chemical enhancement alone and independently tunable. The use of graphene is particularly interesting in this case. Indeed, a recent experiment has shown that the mechanically exfoliated graphene (MG) can result in the fluorescence quenching and Raman enhancement of molecules with a maximal factor of 17.⁴ Such a modest enhancement is believed to be caused by the electron transfer between the graphene and the molecule adsorbed on the surface,^{4,5} although the charge-transfer process itself has not been well understood. Nevertheless, graphene can provide a good platform for studying the chemical enhancement in SERS because its structure can be easily modified and controlled through either physical or chemical processes. In this context, graphene oxide (GO) could be the first choice because of its rich chemical structures. As a result of the oxidation treatment

ABSTRACT Chemical enhancement is an important mechanism in surface-enhanced Raman spectroscopy. It is found that mildly reduced graphene oxide (MR-GO) nanosheets can significantly increase the chemical enhancement of the main peaks by up to 1 order of magnitude for adsorbed Rhodamine B (RhB) molecules, in comparison with the mechanically exfoliated graphene. The observed enhancement factors can be as large as $\sim 10^3$ and show clear dependence on the reduction time of graphene oxide, indicating that the chemical enhancement can be steadily controlled by specific chemical groups. With the help of X-ray photoelectron spectra, these chemical species are identified and the origin of the observed large chemical enhancement can thus be revealed. It is shown that the highly electronegative oxygen species, which can introduce a strong local electric field on the adsorbed molecules, are responsible for the large enhancement. In contrast, the local defects generated by the chemical reduction show no positive correlation with the enhancement. Most importantly, the dramatically enhanced Raman spectra of RhB molecules on MR-GO nanosheets reproduce all important spectral fingerprints of the molecule with a negligible frequency shift. Such a unique noninvasive feature, along with the other intrinsic advantages, such as low cost, light weight, easy availability, and flexibility, makes the MR-GO nanosheets very attractive to a variety of practical applications.

KEYWORDS: mildly reduced graphene oxide · surface-enhanced Raman spectroscopy (SERS) · chemical enhancement · oxygen-containing groups · π -conjugation molecular fingerprint · noninvasive

in its preparation process, GO possesses sufficient active oxygen sites, which can notably enhance the graphene–metal/molecule binding.^{11,12} With GO, one can at least study the impacts of local chemical groups and global π -conjugation network on the SERS of molecules. Moreover, GO is valuable in many other areas, such as highly sensitive biosensing,¹³ biocompatible drug delivery,¹⁴ and high-capacity hydrogen storage.^{15,16} With the underlying enhancement mechanisms well understood and controlled, SERS might eventually become a powerful tool to study the interface of these GO-related systems.

* Address correspondence to yiluo@ustc.edu.cn (Y.L.), xpwang@ustc.edu.cn (X.W.).

Received for review September 6, 2010 and accepted December 20, 2010.

Published online January 06, 2011
10.1021/nn102291j

© 2011 American Chemical Society

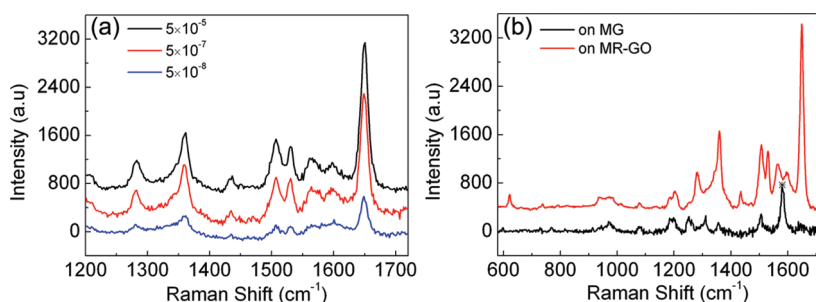


Figure 1. (a) Raman spectra of RhB on the 3 min-reduced GO. A series of soaking concentrations were used: 5×10^{-5} M (black line), 5×10^{-7} M (red line), and 5×10^{-8} M (blue line). The integration times were all 10 s. (b) Raman spectrum on 3 min-reduced GO (red line) compared with that on MG (black line). Both samples were soaked in 5×10^{-5} M RhB aqueous solution before the measurement. The G peak of graphene is marked by a star. The integration times were both 20 s. The spectra have been offset vertically for visualization.

In general, the chemical enhancement in SERS is thought to be originated from the formation of chemical bonds, the resonance, and light-induced charge transfer between the molecule and the substrate.^{17–19} All these effects could, in principle, affect the geometrical or electronic structure of the adsorbed molecules, leading to observable spectral shifts and intensity changes. In this paper, we have systematically studied the performance of mildly reduced graphene oxide (MR-GO) as an active substrate for SERS. Using Rhodamine B (RhB) molecules as a probe, it is found that, under well-controlled reduction conditions, the enhancement factors (EFs) of the main peaks can be increased by almost 1 order of magnitude in comparison with that of MG. It shows that the Raman signals can still be clearly detected even at a very low concentration of RhB, which is down to $\sim 10^{-8}$ M or less. Another striking observation is that the SERS of RhB molecules on MR-GO completely resemble the spectral features of those in solution with inappreciable frequency shifts, in contrast to those that might be expected from chemical enhancement. In combination with X-ray photoelectron spectra (XPS), the chemical groups on MR-GO that affect the molecular Raman signals dominantly are determined, and the possible enhancing mechanisms are suggested.

RESULTS AND DISCUSSION

As known, GO produced by oxidation treatment of graphite, followed by exfoliation, contains domains of sp^2 carbon atoms as well as randomly distributed sp^3 hybridized carbons²⁰ bearing the oxygenated surface functional groups. The lateral size of GO can be up to several hundreds of micrometers,²¹ which makes it exceptionally suitable for the practical use as a substrate. Although it has a modest contrast on most substrates, it can be recognized easily on the SiO_2/Si substrate with a 300 nm SiO_2 top layer after reduction (as shown in Figure S1 in the Supporting Information). We used AFM to characterize the thickness and surface topology of the MR-GO, by which a thickness of ~ 1.0 nm is determined from the step height. Compared to pure

graphene, the disturbed hexagonal structure in GO makes the D and G peaks in its Raman spectrum undergo significant changes: Both the G and the D peaks are broadened, and the intensity ratio of D to G peak becomes larger. After reduction, the D/G ratio is further increased (Figure S1, Supporting Information). One possible reason is that the π -conjugation network of the graphene framework could not be fully restored by the chemical reduction; instead, the oxidation/reduction process decreases the size of individual sp^2 domains but increases their overall presence in the material.²²

Figure 1a shows a series of Raman spectra of RhB on the surface of 3 min-reduced MR-GO, which can be identified definitely by the main peaks of the vibration modes at 1281, 1359, 1508, 1564, and 1649 cm^{-1} . The samples were prepared by separately soaking the substrates with a series of RhB aqueous solutions, from 5×10^{-5} to 5×10^{-8} M, and the signals were found to monotonically diminish with the decreased concentration. One particularly interesting case is that the Raman signals can even be clearly observed on MR-GO soaked with RhB solution at a concentration as low as 5×10^{-8} M. Although the concentration of the soaking solution and the amount of the adsorbed molecules are not always linearly related, for the substrate with a large size, it is reasonable to believe that the coverage (or adsorption probability) of the molecules could be low at such a low concentration. It should be stressed that RhB is a dye molecule with an intensive fluorescence background and is generally difficult to detect through conventional Raman at such diluted concentrations. However, herein, the vibration fingerprints of RhB can be clearly observed on MR-GO despite the low soaking concentration. Moreover, on the surface of 3 min-reduced MR-GO, we found that the fluorescence background is sufficiently depressed and the Raman/fluorescence signal-to-noise ratio is significantly increased. The appearance of Raman signals under such a low concentration suggests that there may be an enhancement effect. For comparison, we also prepared RhB-soaked few-layer MG (the morphological information can be found in Figure S6, Supporting Information) and

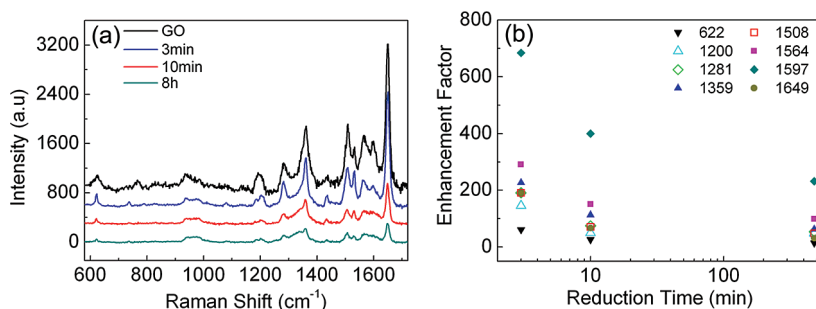


Figure 2. (a) Raman spectra of RhB on GO (black line) and various reduced GO substrates reduced for 3 min (blue line), 10 min (red line), and 8 h (green line). The concentration of the RhB solution used for the RhB adsorption is 5×10^{-5} M for all samples. The broad peak at 960 cm^{-1} is from the SiO_2/Si substrate. The integration time is 10 s for all cases. The spectra have been offset vertically for visualization. (b) Enhancement factors (EFs) for the main vibration modes of RhB on the series of reduced GO in (a).

obtained a Raman spectrum on it, which is shown in Figure 1b. The strongest Raman peak for the MG is the G peak of graphene, which is marked by a star. Compared with the spectrum on the MR-GO, it is found that the peaks at 1356, 1506, and 1649 cm^{-1} are much weaker. Also, there are some new peaks appearing, such as those at 768 and 1311 cm^{-1} . In fact, in the previous work on an MG substrate,^{4,5} it has been suggested that the use of graphene can improve the Raman/fluorescence ratio and enhance the Raman signals. However, due to the diverse Raman responses of the different vibration modes, the main characteristic peaks, such as those at 1356, 1506, and 1649 cm^{-1} , can only be marginally enhanced; furthermore, the Raman fingerprints of the molecule on MG have been greatly changed. In this context, it is interesting to find out that the MR-GO studied here is a much better SERS substrate, providing much enhanced Raman signals with the molecular spectral fingerprints much better preserved, and this is vital for identification of molecules. A more detailed comparison of the EFs for the MG and the chemically reduced GO at the 1649 cm^{-1} characteristic peak (as shown in Figure S8, Supporting Information) reveals that the EF is at least 1 order of magnitude larger for MR-GO than that for MG. The large difference between the spectrum on MG and that on MR-GO indicates that the surface electronic states of these two substrates are quite different. As the surface structure of MR-GO can be simply controlled by the reduction time, we have prepared a series of chemically reduced GO at different reduced stages and examined their Raman performances.

In Figure 2a, Raman spectra of RhB on the surfaces of as-prepared GO and 3 min-, 10 min- and 8 h-reduced GO are compared. All of these samples are carefully chosen to make their sizes, morphologies, and thicknesses comparable, as demonstrated in Figure S2 (Supporting Information). The sizes of the chemically reduced GO and MG are much larger than the laser spot size to ensure the equal excitation condition, and the thicknesses are confirmed by AFM to be *ca.* 1–1.2 nm, all corresponding to a single-layer graphene or GO sheet.^{23,24} The features of the Raman spectra are similar for all

samples under our investigations. It should be mentioned that, although the as-prepared GO has a much worse Raman/fluorescence ratio and a poor optical contrast, further and appropriate reduction can significantly improve the both. Therefore, our study is focused on the performance of the chemically reduced GO at different reduced stages. In general, the intensities of the Raman signals decrease with the increase of the reduction time. On the surface of the 8 h-reduced GO, the signal is so weak that the peaks at 1359 and 1597 cm^{-1} are almost covered up by the D and G peaks of the graphene substrate. To compare the enhancement more quantitatively, we have calculated the EFs (the detailed method is described in the Supporting Information) for the main Raman peaks of RhB on a series of chemically reduced GO substrates, which are given in Figure 2b. As shown, the EFs are different for different Raman peaks, which could be a result of inhomogeneous interaction between the substrate and the molecule. Besides, the vibrational coupling between the molecule and MR-GO is possibly another contributing factor that cannot be ruled out.^{4,25,26} Generally, the EF exhibits a monotonic decrease with respect to the reduction time, although it could remain almost unchanged against very slight reductions (Figure S8, Supporting Information). In the case of the 3 min-reduced GO, the largest EF value is about 684 for the vibration mode at 1597 cm^{-1} , whereas the smallest one is 61 for the vibration mode at 622 cm^{-1} . As for the 8 h-reduced sample, the EF is only 232 for the peak at 1597 cm^{-1} and 14 for the peak at 622 cm^{-1} . It is also noted that the peak around 1649 cm^{-1} shows the sharpest drop as the reduction time increases. Apart from the greatly improved enhancement, the most striking observation is that, under all conditions, each Raman peak remains at the same position, indicating that the changes in chemical compositions on chemically reduced GO have little effect on the basic interaction between the substrate and the molecule. From a chemistry point of view, the reduction process could have two effects: removing certain chemical groups and changing the structure of the basic graphene framework.

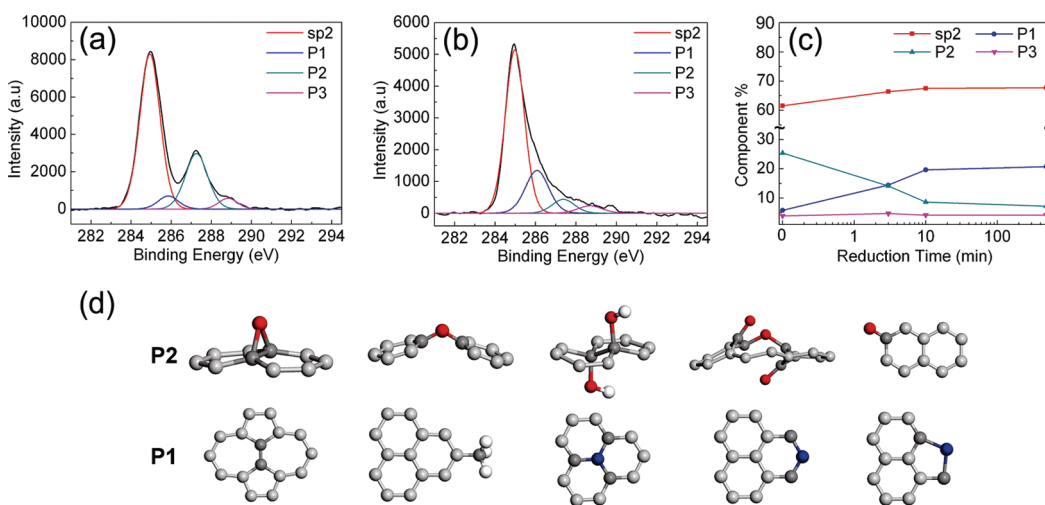


Figure 3. (a) The XPS of as-prepared GO under investigation. The C 1s peak is fitted by four components labeled as sp², P1, P2, and P3. (b) The XPS of 8 h-reduced GO. (c) The evolutions of individual spectral components as functions of the reduction time. (d) Cluster models for the involved oxygen-containing groups mainly responsible for the P2 peak and newly arisen defective carbon structures that contribute to the increase of the P1 carbon. Gray, white, red, and blue spheres, respectively, represent carbon, hydrogen, oxygen, and nitrogen.

From Raman spectra alone, one cannot tell much about what has happened to the substrate during the reduction. To understand the effect of chemical reduction, XPS measurements have been carried out for chemically reduced GO at different reduction times.

One might argue that the chemically reduced GO at different reduction times could have different abilities to adsorb RhB molecules. Fewer molecules might be adsorbed on the sample with a higher degree of reduction, thus resulting in the decrease in Raman signals. To clarify this point, we used XPS to determine the quantities of molecules deposited on the substrates with different reduction levels. By comparing the normalized contents of nitrogen element in the chemically reduced GO substrates with and without RhB adsorption under different reduction stages (the spectra can be found in Figure S3 in the Supporting Information), we found that the RhB contents on the different substrates are almost the same. Moreover, we also used high-vacuum evaporation to deposit RhB of the same thickness on the surfaces of 3 min-, 10 min-, and 8 h-reduced GO. The result also shows that the Raman signals decrease with the increase of the reduction level (Figure S5 in the Supporting Information), which is in good agreement with the result on the soaking-prepared samples. All of these indicate that the difference in the Raman enhancement should be attributed to the intrinsic nature of the substrate and its interaction with the probe molecule. To further study the effect of GO's surface chemistry on the molecular Raman enhancement, XPS on the carbon K-edge is exploited to quantitatively investigate the surface property as well as its evolution at different reduction levels.

The carbon K-edge XPS spectrum of GO is given in Figure 3a (the corresponding full spectral survey of XPS is shown in Figure S4, Supporting Information). A recent

first-principles theoretical study has successfully assigned the XPS spectrum of GO, and the spectral positions of different oxygen-containing groups have been fully determined.²⁷ On the basis of previous theoretical and experimental studies,^{28,29} the C 1s spectrum can be fitted by four components, as shown in Figure 3a: a peak of sp² carbon centered at 285 eV, a P1 peak at about 286 eV representing sp³ hybridized carbon, a P2 peak at 287.2 eV, and a P3 peak at 288.8 eV. The observed large intensity of the sp² peak implies that the as-prepared GO is not heavily oxidized. Calculations have shown²⁷ that the P2 peak originates from epoxy, ether, hydroxyl, carbonyl, and carbonyl-edge groups, whereas the P3 peak is mainly contributed by epoxy pair, epoxy–hydroxy pair, and carboxyl. The local structures of the above-mentioned oxygen-containing groups are given in Figure 3d. The areas (namely, the integrated intensities) of these four spectral components as functions of the reduction time are summarized in Figure 3c. It can be seen that, during the reduction, the sp² and the P3 peaks remain almost unchanged, whereas the P2 peak gradually decreases and the P1 peak increases. The contents of the latter two components show clear changes, although with completely opposite trends, and they could be responsible for the observed decrease in the Raman signals with the reduction time. Naturally, we suspect that the groups contributing to the P2 peak are favorable for the Raman enhancement, whereas the structures contributing to the P1 peak are not. It should be mentioned that the removal of P2-type groups could most likely generate fresh defective carbon domains consisting of C–C single bonds, C–N³⁰ (as a result of nitrogen doping on hydrazine hydrate reduced GO), and topological defects, all of which contribute to the increase of the P1 peak. Schematic model structures of the newly

produced defective carbon domains that are possibly responsible for the increase of the P1 peak are given in Figure 3d. Although the total area of the sp^2 domains slightly increases after reduction (which results in the increase of the conductivity and fluorescence quenching), these defective structures could decrease the size of each sp^2 domain, as supported by the increase in the D/G ratio in their Raman spectra (Figure S1, Supporting Information), which severely destroys the π -conjugation of the substrate. The favorable contribution from P2 is understandable because the related oxygen-containing groups shown in Figure 3d possess a strong local dipole moment (μ_{loc}) that can induce a considerable local electric field (E_{loc}) under the laser excitation (E_0). Moreover, the as-prepared GO with larger π -conjugated domains has a larger polarizability (α), which can also contribute an extra local electric field. In this case, the local electric field that interacts with the molecules is determined by a simple relationship: $E_{loc} = E_0 + f(\mu_{loc} + \alpha E_0)$, where f is a geometry-related parameter.³¹ Such an enhanced electric field could naturally result in the enhancement of the Raman signals. However, after the chemical reduction, the local dipole moment will be depressed due to the increased P1 components with on-plane structures, and the polarizability of the substrate also significantly decreases because of the broken π -conjugation. To the best of our knowledge, this is probably a new chemical enhancement mechanism that has been completely overlooked in the past. Besides the evolution of surface structure, our XPS study has also shown that the numbers of RhB molecules adsorbed on the reduced GO at different reduction levels remain almost constant (Figure S3, Supporting Information), but the content of nitrogen atoms in the reduced GO increases monotonically. The involvement of the extra nitrogen atoms in the GO will certainly be responsible for the formation of more in-plane defects and the generation of a P1-type component. However, more sophisticated experimental tools are needed to reveal a more detailed picture of the local structures.

One important parameter that can be used to identify the interaction between the substrate and the molecule is the spectral shift. Stronger interaction should, in principle, lead to larger spectral shift. With this in mind, we have compared the Raman spectrum of RhB deposited on the surface of 3 min-reduced GO with that of a RhB aqueous solution in Figure 4. It should be mentioned that a high concentration of RhB is necessary to obtain detectable Raman signals in its aqueous solution. As marked in Figure 4, the main Raman peaks have been assigned following the literature.^{32,33} It is quite surprising that all the observed spectral features have a one-to-one correspondence between these two samples and show almost no spectral shift. Because the results given in Figure 2 have already shown that there is no observable spectral shift in the Raman spectra of

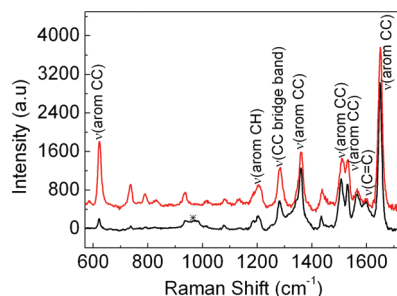


Figure 4. Raman spectrum of RhB molecules in an aqueous solution of 50 mM (red line) and that on the 3 min-reduced MR-GO (black line) deposited by soaking the substrate with 50 μ M RhB aqueous solution. The integration times are both 20 s.

molecules on GO substrates with different reduction levels, this at least shows that the interaction between the RhB and the MR-GO is weak. The fact that such a weak interaction can induce such a large chemical enhancement in SERS is quite unusual, as we discussed above, but it is very useful for practical applications because it can provide clear molecular identification without any complications. We also noted that, in a very recent experimental work,³⁴ specially designed Au particles isolated by an oxide thin shell have been used to eliminate the interference of the adsorbed molecule from the environment as well as any possible undesired reactions between the molecules and the metal particles. Without any need of chemical functionalization, it can be spread on arbitrary substrates to detect the signals of molecules adsorbed on the substrates. Their result significantly expands the applicability of SERS and the high sensitivity as well as high accuracy can be easily achieved even in liquid environments (e.g., the *in situ* studies in wet chemistry and biology), which is impossible to be realized by TERS. It is encouraging that a simple substrate, such as MR-GO studied here, could, in principle, achieve the same goal. Of course, the metal–dielectric core–shell nanostructures can still give much stronger spectral signals because of the involvement of electromagnetic enhancement.

From the spectral assignments, one can see that the strong enhancement seems to be associated with aromatic C–C bonds, suggesting that the aromatic rings in RhB are closely interacting with the substrate, in particular, the P2 components. The π – π stacking and the lone pair electrons in the oxygen-containing groups between the RhB molecule and the MR-GO are the major driving force for the observed large Raman enhancement. Obviously, one cannot completely rule out the contributions from the possible hydrogen bonding.³⁵ In any cases, the performance of the MR-GO substrate is in stark contrast to that of the graphene (MG) substrate, where the charge transfer between the molecule and the substrate was assumed to be the dominant factor that is usually accompanied by large spectral shifts.^{4,5} The different performance could be primarily, if not all, attributed to their different chemical

structures. It is well known that the graphene on the substrate can possess large numbers of delocalized carriers due to unintentional doping from the substrate,^{36,37} whereas in the MR-GO, the presence of oxygen-containing groups breaks the extended π -conjugation network of graphene into small local domains and, consequently, localizes or depletes the free carriers.

CONCLUSION

We have systematically examined the SERS of RhB molecules on chemically reduced GO as a function of reduction time. In combination with XPS spectra, both the important oxygenated groups and the local defects

on the chemically reduced GO substrate that can significantly affect the molecular Raman signals have been identified. It is found that MR-GO can result in the largest Raman enhancement arising from a new chemical enhancing mechanism and hold much better performance than MG. Moreover, a unique property of MR-GO as a SERS substrate has been discovered: it is found that the SERS signals resemble well the native spectrum of the molecules in solution with a negligible frequency shift. The peculiar advantages of high-fidelity, large enhancement, and nondestructive features make MR-GO exceptionally useful for applications of SERS in life science and food safety.

METHODS

The GO was produced by oxidation treatment of graphite (high purity, 99.9999%, 200 mesh, Alfa-Aesar) based on the modified Hummer method.³⁸ After the pretreatment, the dried powder was inserted into a hot furnace of 750 °C under a protective gas flow (Ar/H₂ with 5% H₂ in volume ratio) and held in this temperature for 10 s. The thermally expanded graphite then underwent the rest of the oxidation treatment. After being washed clean with water and multiple centrifugations, the oxidized product exfoliated to GO nanosheets and formed a uniform aqueous solution of GO under stirring. By this approach, large single-layer GO nanosheets with lateral sizes up to tens of micrometers can be obtained and the π -conjugation carbon network can be kept away from severe destruction due to the milder oxidation treatment. Then, it was diluted to a stable 0.01% aqueous dispersion for the deposition of GO without further treatment. The water used in all of this work is deionized with a resistivity as large as 18.2 M Ω . The GO was deposited on the surface of the SiO₂/Si substrate with the oxide thickness of 300 nm *via* drop-casting. Before the GO deposition, the substrate was washed with acetone, ethanol, and water in turn. The MR-GO was then prepared by chemically reducing the GO nanosheets through controlling the exposure to hydrazine hydrate vapor. In a typical process, the drop-casted samples were loosely sealed in a small chamber together with adequate hydrazine hydrate (85 wt % in water) and reduced for 3 min, 10 min, and 8 h. The temperature of the cell was kept at 80 °C during the reduction. After the reduction, the reduced samples were rinsed and blown to dry. We distinguished the single-layer graphene by the contrast in the optical microscope images and confirmed it by atomic force microscopy (AFM).

RhB purchased from Sigma-Aldrich (R6626, 95%) was used as the probe molecule. Soaking was used to deposit the molecule on the surfaces of MR-GO and the control samples. A series of RhB aqueous solutions with different concentrations (5×10^{-5} M, 5×10^{-7} M, 5×10^{-8} M) diluted from the same original solution were used for the soaking. The soaking time was 30 min for all the cases. After soaking, the samples were repeatedly rinsed with plenty of water to remove the unadsorbed molecules and were then dried for the SERS experiment.

Raman spectra were obtained using a LABRAM-HR Raman spectrometer with an excitation wavelength of 514.5 nm generated by an Ar⁺ laser. For the need of experiments, different integration times have been used, which can be found in the context. The focused laser spot is about 10 μ m with a constant on-sample power of \sim 1 mW. For all of the Raman spectra, the baselines have already been subtracted. The AFM images were collected under a dynamic force microscope mode with an SPA 300HV microscope (Seiko Instruments, Inc.). The XPS measurements were performed using an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatic Al K α radiation ($h\nu = 1486.6$ eV).

Acknowledgment. We acknowledge support from the National Natural Science Foundation of China (50721091, 10874165, 90921013, and 20925311) and the Major State Basic Research Development Programs of China (2010CB923300 and 2011CB921403). We also thank Professor Jian Zuo of USTC for helpful discussions and experimental support.

Supporting Information Available: Morphological information of GO and chemically reduced GO, XPS analysis for RhB adsorption on the surfaces of GO and chemically reduced GO, Raman spectra of RhB deposited on GO and chemically reduced GO using vacuum evaporation, Raman spectra of RhB on MG as well as the morphological information of MG, and calculation of the Raman enhancement factor. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Wu, J. S.; Pisula, W.; Mullen, K. Graphenes as Potential Material for Electronics. *Chem. Rev.* **2007**, *107*, 718–747.
- Verma, V. P.; Das, S.; Lahiri, I.; Choi, W. Large-Area Graphene on Polymer Film for Flexible and Transparent Anode in Field Emission Device. *Appl. Phys. Lett.* **2010**, *96*, 203108.
- Bunch, J. S.; van der Zande, A. M.; Verbridge, S. S.; Frank, I. W.; Tanenbaum, D. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. Electromechanical Resonators from Graphene Sheets. *Science* **2007**, *315*, 490–493.
- Ling, X.; Xie, L. M.; Fang, Y.; Xu, H.; Zhang, H. L.; Kong, J.; Dresselhaus, M. S.; Zhang, J.; Liu, Z. F. Can Graphene Be Used as a Substrate for Raman Enhancement? *Nano Lett.* **2010**, *10*, 553–561.
- Xie, L. M.; Ling, X.; Fang, Y.; Zhang, J.; Liu, Z. F. Graphene as a Substrate To Suppress Fluorescence in Resonance Raman Spectroscopy. *J. Am. Chem. Soc.* **2009**, *131*, 9890–9891.
- Sun, Y. H.; Liu, K.; Miao, J.; Wang, Z. Y.; Tian, B. Z.; Zhang, L. N.; Li, Q. Q.; Fan, S. S.; Jiang, K. L. Highly Sensitive Surface-Enhanced Raman Scattering Substrate Made from Superaligned Carbon Nanotubes. *Nano Lett.* **2010**, *10*, 1747–1753.
- Shen, X. S.; Wang, G. Z.; Hong, X.; Zhu, W. Nanospheres of Silver Nanoparticles: Agglomeration, Surface Morphology Control and Application as SERS Substrates. *Phys. Chem. Chem. Phys.* **2009**, *11*, 7450–7454.
- Nielsen, P.; Hassing, S.; Albrektsen, O.; Foghmoes, S.; Morgen, P. Fabrication of Large-Area Self-Organizing Gold Nanostructures with Sub-10 nm Gaps on a Porous Al₂O₃ Template for Application as a SERS-Substrate. *J. Phys. Chem. C* **2009**, *113*, 14165–14171.
- Stiles, P. L.; Dieringer, J. A.; Shah, N. C.; Van Duyne, R. R. Surface-Enhanced Raman Spectroscopy. *Annu. Rev. Anal. Chem.* **2008**, *1*, 601–626.
- Polavarapu, L.; Xu, Q. H. Water-Soluble Conjugated Polymer-Induced Self-Assembly of Gold Nanoparticles and Its Application to SERS. *Langmuir* **2008**, *24*, 10608–10611.

11. Wang, L. F.; Yang, F. H.; Yang, R. T.; Miller, M. A. Effect of Surface Oxygen Groups in Carbons on Hydrogen Storage by Spillover. *Ind. Eng. Chem. Res.* **2009**, *48*, 2920–2926.
12. Goncalves, G.; Marques, P. A. A. P.; Granadeiro, C. M.; Nogueira, H. I. S.; Singh, M. K.; Gracio, J. Surface Modification of Graphene Nanosheets with Gold Nanoparticles: The Role of Oxygen Moieties at Graphene Surface on Gold Nucleation and Growth. *Chem. Mater.* **2009**, *21*, 4796–4802.
13. Lu, C. H.; Yang, H. H.; Zhu, C. L.; Chen, X.; Chen, G. N. A Graphene Platform for Sensing Biomolecules. *Angew. Chem., Int. Ed.* **2009**, *48*, 4785–4787.
14. Liu, Z.; Robinson, J. T.; Sun, X. M.; Dai, H. J. PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs. *J. Am. Chem. Soc.* **2008**, *130*, 10876–10877.
15. Wang, L.; Lee, K.; Sun, Y. Y.; Lucking, M.; Chen, Z. F.; Zhao, J. J.; Zhang, S. B. Graphene Oxide as an Ideal Substrate for Hydrogen Storage. *ACS Nano* **2009**, *3*, 2995–3000.
16. Hu, Z. L.; Aizawa, M.; Wang, Z. M.; Yoshizawa, N.; Hatori, H. Synthesis and Characteristics of Graphene Oxide-Derived Carbon Nanosheet–Pd Nanosized Particle Composites. *Langmuir* **2010**, *26*, 6681–6688.
17. Otto, A. The “Chemical” (Electronic) Contribution to Surface-Enhanced Raman Scattering. *J. Raman Spectrosc.* **2005**, *36*, 497–509.
18. Jensen, L.; Aikens, C. M.; Schatz, G. C. Electronic Structure Methods for Studying Surface-Enhanced Raman Scattering. *Chem. Soc. Rev.* **2008**, *37*, 1061–1073.
19. Lombardi, J. R.; Birke, R. L. A Unified Approach to Surface-Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2008**, *112*, 5605–5617.
20. Eda, G.; Lin, Y. Y.; Mattevi, C.; Yamaguchi, H.; Chen, H. A.; Chen, I. S.; Chen, C. W.; Chhowalla, M. Blue Photoluminescence from Chemically Derived Graphene Oxide. *Adv. Mater.* **2010**, *22*, 505–509.
21. Luo, Z. T.; Lu, Y.; Somers, L. A.; Johnson, A. T. C. High Yield Preparation of Macroscopic Graphene Oxide Membranes. *J. Am. Chem. Soc.* **2009**, *131*, 898–899.
22. Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S. The Chemistry of Graphene Oxide. *Chem. Soc. Rev.* **2010**, *39*, 228–240.
23. Si, Y.; Samulski, E. T. Synthesis of Water Soluble Graphene. *Nano Lett.* **2008**, *8*, 1679–1682.
24. Gomez-Navarro, C.; Weitz, R. T.; Bittner, A. M.; Scolari, M.; Mews, A.; Burghard, M.; Kern, K. Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets. *Nano Lett.* **2007**, *7*, 3499–3503.
25. Albrecht, A. C.; Hutley, M. C. Dependence of Vibrational Raman Intensity on Wavelength of Incident Light. *J. Chem. Phys.* **1971**, *55*, 4438–4443.
26. Sariciftcia, N. S.; Heeger, A. J.; Krasevecb, V.; Venturinib, P.; Mihailovicb, D.; Caoc, Y.; Libertd, J.; Brédasd, J. L. Symmetry-Specific Electron-Phonon Coupling for Electronic States near the Fermi Energy of Metallic Polyaniline: Resonant Raman Scattering. *Synth. Met.* **1994**, *62*, 107–112.
27. Zhang, W. H.; Carravetta, V.; Li, Z. Y.; Luo, Y.; Yang, J. L. Oxidation States of Graphene: Insights from Computational Spectroscopy. *J. Chem. Phys.* **2009**, *131*, 244505.
28. Benayad, A.; Shin, H. J.; Park, H. K.; Yoon, S. M.; Kim, K. K.; Jin, M. H.; Jeong, H. K.; Lee, J. C.; Choi, J. Y.; Lee, Y. H. Controlling Work Function of Reduced Graphite Oxide with Au-Ion Concentration. *Chem. Phys. Lett.* **2009**, *475*, 91–95.
29. Tung, V. C.; Allen, M. J.; Yang, Y.; Kaner, R. B. High-Throughput Solution Processing of Large-Scale Graphene. *Nat. Nanotechnol.* **2009**, *4*, 25–29.
30. Stankovich, S.; Piner, R. D.; Chen, X. Q.; Wu, N. Q.; Nguyen, S. T.; Ruoff, R. S. Stable Aqueous Dispersions of Graphitic Nanoplatelets via the Reduction of Exfoliated Graphite Oxide in the Presence of Poly(sodium 4-styrenesulfonate). *J. Mater. Chem.* **2006**, *16*, 155–158.
31. Böttcher, C. J. F. In *Theory of Electric Polarization*; Böttcher, C. J. F., Ed.; Elsevier: Amsterdam, 1973; pp 17–26.
32. Zhang, J. T.; Li, X. L.; Sun, X. M.; Li, Y. D. Surface Enhanced Raman Scattering Effects of Silver Colloids with Different Shapes. *J. Phys. Chem. B* **2005**, *109*, 12544–12548.
33. Hildebrandt, P.; Stockburger, M. Surface-Enhanced Resonance Raman Spectroscopy of Rhodamine-6G Adsorbed on Colloidal Silver. *J. Phys. Chem.* **1984**, *88*, 5935–5944.
34. Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; Wu, D. Y.; et al. Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy. *Nature* **2010**, *464*, 392–395.
35. Yang, X. Y.; Zhang, X. Y.; Liu, Z. F.; Ma, Y. F.; Huang, Y.; Chen, Y. High-Efficiency Loading and Controlled Release of Doxorubicin Hydrochloride on Graphene Oxide. *J. Phys. Chem. C* **2008**, *112*, 17554–17558.
36. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature* **2005**, *438*, 197–200.
37. 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* **2004**, *306*, 666–669.
38. Gilje, S.; Han, S.; Wang, M.; Wang, K. L.; Kaner, R. B. A Chemical Route to Graphene for Device Applications. *Nano Lett.* **2007**, *7*, 3394–3398.