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## Surface enhanced Raman scattering of aged graphene: Effects of annealing in vacuum

Yingying Wang,<sup>1,a)</sup> Zhenhua Ni,<sup>2,a)</sup> Aizhi Li,<sup>1</sup> Zainab Zafar,<sup>2</sup> Yan Zhang,<sup>3</sup> Zhonghua Ni,<sup>3</sup> Shiliang Qu,<sup>1</sup> Teng Qiu,<sup>2</sup> Ting Yu,<sup>4</sup> and Ze Xiang Shen<sup>4</sup>

<sup>1</sup>Department of Optoelectronic Science, Harbin Institute of Technology at Weihai, Weihai 264209, China

<sup>2</sup>Department of Physics, Southeast University, Nanjing 211189, China

<sup>3</sup>Jiangsu Key Laboratory for Design and Fabrication of Micro-Nano Biomedical Instruments,

School of Mechanical Engineering, Southeast University, Nanjing 211189, China

<sup>4</sup>Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore

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In this paper, we report a simple method to recover the surface enhanced Raman scattering activity of aged graphene. The Raman signals of Rhodamine molecules adsorbed on aged graphene are dramatically increased after vacuum annealing and comparable to those on fresh graphene. Atomic force microscopy measurements indicate that residues on aged graphene surface can efficiently be removed by vacuum annealing, which makes target molecule closely contact with graphene. We also find that the hole doping in graphene will facilitate charge transfer between graphene and molecule. These results confirm the strong Raman enhancement of target molecule adsorbed on graphene is due to the charge transfer mechanism. © 2011 American Institute of Physics. [doi:10.1063/1.3665624]

Graphene is a planar atomic layer of carbon with atoms arranged in hexagonal structures.<sup>1</sup> Investigation of this material became one of the hottest research areas owing to graphene's unique electrical, mechanical, optical, and thermal properties.<sup>1–5</sup> In addition, using graphene as a substrate for probing vibrational information from molecules has been paid more attention recently.<sup>6–8</sup> Molecules adsorbed on graphene have Raman intensity  $\sim 17$  times as that of on SiO<sub>2</sub> substrate under visible light excitation.<sup>7</sup> Graphene can be used as a surface enhanced Raman scattering (SERS) substrate. The Raman enhancement of graphene is most probably due to charge transfer between molecule and graphene induced chemical mechanism.<sup>6–8</sup> This charge transfer process requires the close contact of graphene with molecule. We have studied SERS activity of many graphene samples and found the SERS activity varies a lot among those samples. For graphene samples exposed in ambient for a period (several month or more), i.e., aged graphene, the SERS activities are vanished and no vibrational information of adsorbed molecule can be detected. An easily, quickly performed method to recover the SERS activity of aged graphene is highly demanded.

The graphene samples fabricated by micromechanical cleavage were transferred to SiO<sub>2</sub> (300 nm)/Si substrates. SLG was identified by Raman spectroscopy<sup>9</sup> and white light spectroscopy.<sup>10</sup> The Raman scattering measurements were performed by a HORIBA Jobin Yvon Raman system using excitation energy of 514.5 nm (2.41 eV) from an Ar<sup>+</sup> laser. The laser power at the sample was kept below 0.5 mW to avoid laser induced sample heating.<sup>4</sup>

Figure 1(a) shows Raman spectra of single layer graphene (SLG), Rhodamine 6G (R6G) molecules adsorbed on

fresh SLG and on SiO<sub>2</sub>. There are two major Raman features of SLG, the G band ( $\sim 1580\text{ cm}^{-1}$ ), and 2D band ( $\sim 2680\text{ cm}^{-1}$ ).<sup>11</sup> The fresh SLG samples were soaked in R6G solution (5  $\mu\text{M}$  in water) for 30 min. For R6G adsorbed on SiO<sub>2</sub>, only fluorescence back ground of R6G is observed. The low concentration of R6G is the reason why no Raman signals from the molecules can be detected. On the other hand, due to graphene induced fluorescence quenching<sup>6</sup> and charge transfer between graphene and adsorbed molecule induced chemical enhancement,<sup>7,8</sup> the Raman scattering intensity of R6G adsorbed on graphene is enhanced and clearly observed. Fig. 1(b) gives the optical conductivity spectra of SLG as well as R6G adsorbed on SLG. The conductivity spectra are obtained from the contrast spectra whose derivation can be found in Ref. 12. In the detection range, graphene exhibits universal optical conductivity,<sup>3,12</sup> while for R6G adsorbed SLG, there is an absorption band located at  $\sim 575\text{ nm}$  (2.16 eV), which is red shift relative to the electronic transition from HOMO to LUMO of R6G ( $\sim 540\text{ nm}$  (2.3 eV)).<sup>7</sup> The similar atomic structure of R6G with that of graphene make R6G easily lies parallel to the surface of graphene, and the  $\pi$ - $\pi$  stacking would induce red shift of absorption bands of R6G as what has happened for other molecules.<sup>13,14</sup>

We have carried out SERS activity studies of many SLG samples and found there was a large difference between fresh and aged samples. The latter exhibits rarely SERS activities. In order to recover the SERS activity of aged SLG, the samples were annealed at 900 °C for 30 min, in vacuum of 0.5 Pa. The vacuum annealed SLG samples as well as aged samples were soaked into R6G solution (5  $\mu\text{M}$  in water) for 30 min for comparison.

Figure 2 shows the Raman spectra of R6G adsorbed on aged and annealed SLG samples. For aged SLG, it exhibits no SERS activity. However, after heat treatment at 900 °C,

<sup>a)</sup>Authors to whom correspondence should be addressed. Electronic addresses: zhni@seu.edu.cn and yywanghit@yahoo.com.cn.

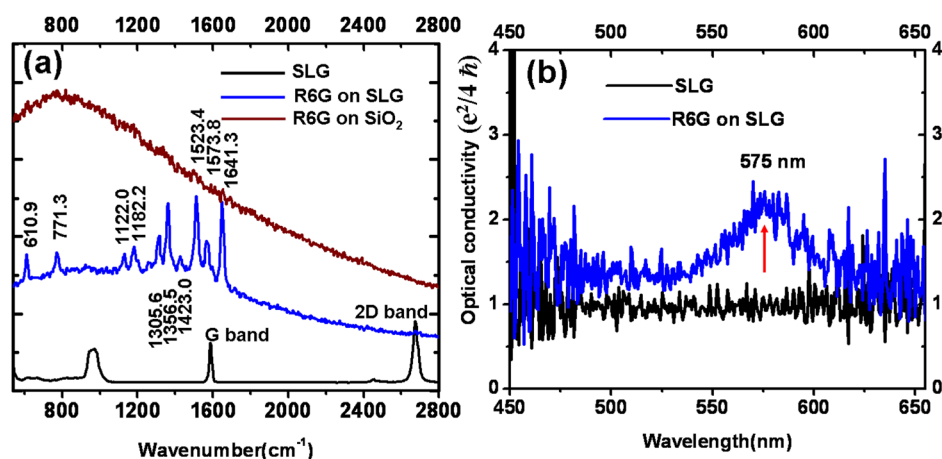


FIG. 1. (Color online) (a) Raman spectra of SLG, R6G molecules adsorbed on SLG and on SiO<sub>2</sub> substrate. (b) Optical conductivity spectra of SLG as well as that of R6G on SLG.

the Raman bands of R6G on SLG are clearly observed. In order to confirm our observation, up to ten different SLG samples annealed at 900 °C are studied, and all of them show good SERS activity. On the other side, up to ten different aged SLG samples are also studied, and all of them exhibit no SERS activity, (results not shown). Similarly, the SERS activities of SLG samples annealed at lower temperatures (700 °C, 500 °C, 300 °C, and 200 °C) are also recovered, even when the annealing temperature is as low as 100 °C.

Figure 2(b) shows the 2D band of fresh SLG and aged SLG before and after vacuum annealing. The position shift of Raman bands of SLG could be used to monitor dopants,<sup>15,16</sup> effect of substrate,<sup>17</sup> and local temperature variation in graphene.<sup>4</sup> For annealed SLG, there is a blue shift of 2D band due to hole doping in graphene induced by the adsorption of H<sub>2</sub>O and O<sub>2</sub> molecules after annealing.<sup>15</sup> Higher annealing temperature causes higher hole doping in SLG. For SLG annealed at 900 °C, the blue shift of 2D band is  $\sim 18$  cm<sup>-1</sup>, corresponding the down shift of Fermi level of  $\sim 0.5$  eV.<sup>16</sup>

We further study the effect of annealing temperature on the intensity of different Raman bands of R6G adsorbed on SLG. We analyze the Raman results by taking three different kinds of vibrations from R6G. Each data point presented in Figure 3 is the statistical result from ten different samples. The bands appear at 613 cm<sup>-1</sup> and 771.3 cm<sup>-1</sup> are due to C<sub>x</sub>-C<sub>x</sub>-C<sub>x</sub> ring in plane bending.<sup>18</sup> The band at 1423.0 cm<sup>-1</sup> arises due to C<sub>c</sub>-H bending motion,<sup>18</sup> while Raman bands at

1356.5, 1523, and 1641 cm<sup>-1</sup> are due to aromatic C<sub>x</sub>-C<sub>x</sub> stretching modes.<sup>18</sup> (Subscripts x, e represent the xanthene ring, ethylamine group attached to the xanthene ring, individually).<sup>18</sup> From Figure 3, it can be seen that the Raman intensity of R6G adsorbed on aged SLG appears after annealed at 100 °C and increases slightly as the annealing temperature increases. This temperature dependence can be understood by the down shift of Fermi level in graphene. The energy gap between Fermi level of intrinsic graphene (-4.26 eV) and the LUMO (-3.40 eV) of R6G molecule is about 0.86 eV,<sup>7</sup> which is smaller than the energy of incident laser (2.41 eV). For SLG samples annealed at higher temperature, the hole doping in graphene is increased and shifts the Fermi level of graphene further down. The down shift of Fermi level increases the energy difference between graphene and LUMO of R6G, which is closer to the incident laser energy, hence facilitate the charge transfer resonance process.<sup>8</sup>

Figure 4 gives the atomic force microscopy (AFM) image of graphene samples before and after annealing. It can be seen that the surface of graphene becomes much smoother after vacuum annealing at 500 °C for 30 min. Before annealing, the height difference between bi-layer graphene (BLG), SLG, and SiO<sub>2</sub> substrate is  $0.85 \pm 0.21$  nm and  $0.44 \pm 0.16$  nm. After annealing, the height difference becomes  $0.82 \pm 0.13$  nm and  $0.41 \pm 0.10$  nm. These measurements indicate that residues, e.g., dust, adsorbed molecules are

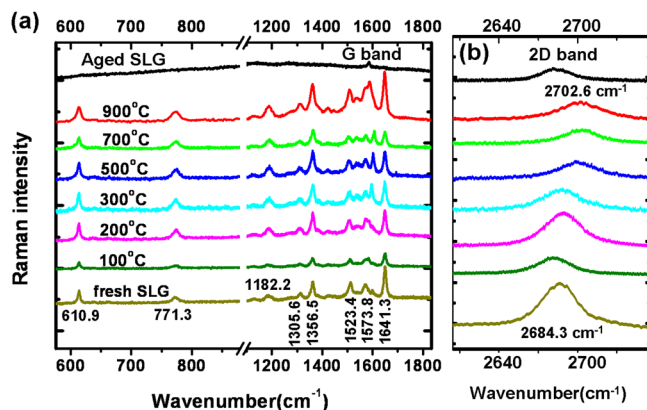


FIG. 2. (Color online) (a) Raman spectra of R6G adsorbed on aged, annealed and fresh SLG samples. (b) 2D bands of aged, annealed and fresh SLG samples.

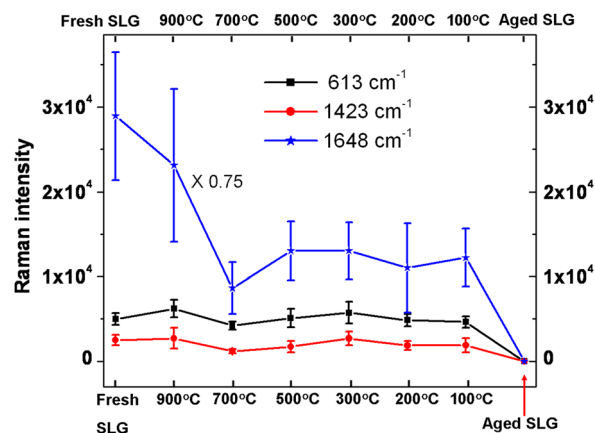


FIG. 3. (Color online) Raman intensity of R6G adsorbed on fresh, annealed and aged SLG samples. Three different vibration bands from R6G on those different substrates are compared. The Raman intensity of 1648 cm<sup>-1</sup> band given in this figure is 75% of the original value.

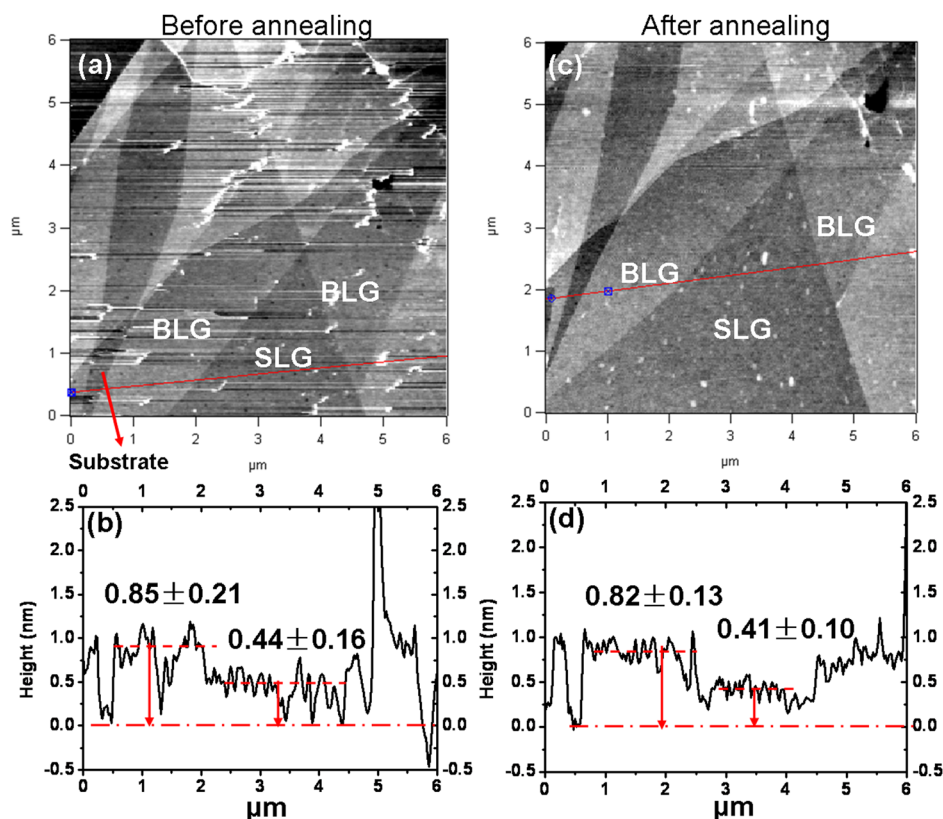


FIG. 4. (Color online) AFM image of graphene samples before annealing (a) and after annealing at 500 °C (c). (b) and (d) are the height distributions of graphene samples along straight lines given in (a) and (c).

removed from graphene surface by annealing process, therefore, making target molecule closely contact with graphene. This further support that the enhanced Raman signals of molecule adsorbed on SLG is due to the charge transfer which requires the close contact of molecule with graphene.<sup>8</sup>

In summary, aged SLG samples were treated by vacuum annealing at different temperature. The SERS activity of aged SLG can be recovered after vacuum annealing and comparable to fresh SLG. AFM image clearly showed that residues on the surface of graphene can be removed and makes close contact of molecule with graphene possible, and hence, recover the charge transfer induced chemical enhancement. Our result provides a simple and effect way to recover the SERS activity of graphene, which helps the application of graphene as a high efficient SERS substrate.

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