

## Field localization dependence of SERS from defect-free graphenes

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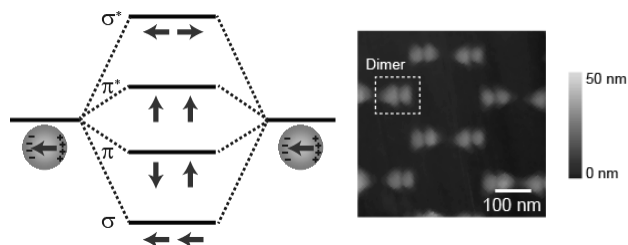
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Resonance Raman spectroscopy is widely utilized to characterize carbon nanomaterials such as graphenes and carbon nanotubes. There appear characteristic bands in Raman spectra: RMB, D, G, and 2D, etc. Especially, the G/D ratio is considered as a quality parameter because activation of D-band is due to defects in graphitic lattices. Carbon nanomaterials are now drawing much attention in various research fields such as energy conversion and electrocatalysis because of their unique chemical, physical, and electronic properties. Therefore, it is essentially important to evaluate the quality of carbon nanostructures.

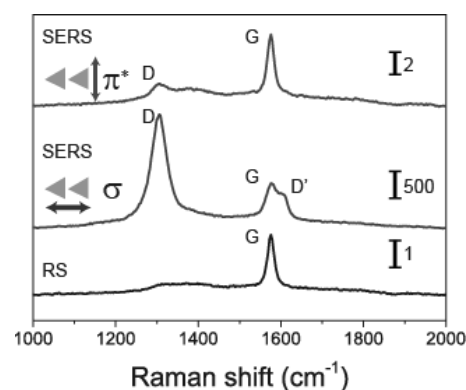
Recently, nanoscale vibrational spectroscopy is becoming possible using tip-enhanced Raman scattering (TERS). For example, it has been demonstrated that this technique visualized diameter distribution in carbon nanotube bundles. To achieve super-resolution beyond the diffraction limit, this technique is based on plasmonic resonances on a metal nanostructure; a metallized AFM tip is scanned on the sample under light illumination. However, such strong field localization yields field gradients. Because the largest wave number present in the localized near field is characterized by the field varies, selection rules for optical transitions may be affected by the field localization. In this work, we demonstrate that D-band is induced in Raman spectra of defect-free graphenes using plasmonic field localization [1].

To control the degree of field localization, gold nano-dimer arrays were utilized in this study, which were fabricated on a glass substrate using Angle-resolved nanosphere lithography (AR-NSL). [2,3] By changing the evaporation angle of gold thin films, the interparticle distance can be controlled on the order of nanometers. Figure 1 right panel shows a typical AFM image of the fabricated dimer arrays; all of the dimers are well aligned on the substrate. Plasmon resonance features on this dimer can be understood by the coupled dipole-dipole model as shown in the left panel of Fig. 1. Among these four hybridized modes,  $\sigma$ - and  $\pi^*$ -modes are optically active. The degree of the field localization is controllable for the  $\sigma$ -mode.



**Figure 1:** Schematic illustration of hybridized plasmon modes in a metal nano-dimer and typical AFM image of gold nano-dimer array on a glass substrate.

Few-layer graphenes were fabricated on a cover slip using Scotch tape method. Raman spectra were measured using a Raman microscope (785-nm excitation, 100x objective) in the absence and presence of the gold nano-dimer arrays. As shown in Fig. 1, the Raman spectrum without the dimer array showed only G-band, indicating the absence of defects in the graphitic lattice. When the dimer array was attached on the sample, however, D- and D'-bands appeared in the SERS spectra. Although the direct contact of the gold surfaces may induce defects to the graphenes, the observed polarization dependence of the spectra strongly supports that this is not due to chemical interactions but due to field localization. Indeed, the relative intensity of these induced modes was dependent on the interparticle distance only when  $\sigma$ -plamons were excited. After the measurements, Raman spectrum without dimers was again measured to confirm any defect was not induced during the experiment; no D- or D'-band was observed. For further confirmation, we also conducted TERS measurements of defect-free graphenes, and a similar tendency was confirmed.



**Figure 2:** Comparison of Raman and SERS spectra of a defect-free graphene without and with gold nano-dimer array.

In general, the activation of D- and D'-bands due to defects is explained by the double resonance mechanism, which works well for explaining characteristic behavior of these bands in Raman spectra. Because these modes with a large momentum can contribute to Raman spectra only when the momentum conservation is satisfied, the excited electron/hole pair must be scattered by defects when graphenes are illuminated by free propagating optical waves. However, highly localized fields on a metal nanostructure with large wave numbers can access to these modes directly. In conclusion, selection rules for Resonance Raman scattering can be controlled by the degree of field localization.

### References:

1. K. Ikeda, M. Takase, N. Hayazawa, S. Kawata, K. Murakoshi, and K. Uosaki, submitted.
2. Y. Sawai, B. Takimoto, H. Nabika, K. Ajito, and K. Murakoshi, *J. Am. Chem. Soc.* 129, 1658 (2007)
3. K. Ikeda, M. Takase, Y. Sawai, H. Nabika, K. Murakoshi, and K. Uosaki, *J. Chem. Phys.* 127, 111103 (2007)