PD Research Report for the 2016 year

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Research Theme Tip-enhanced Raman scattering spectroscopy of nanostructured graphene

Research Period April, 2016 ~ November, 2016

Research Results（about 2,500 characters in Japanese, about 65 lines times 90 characters in English）

The origin of unique features of nanomaterials is in their nanostructures. For example, nanostructures on graphene sheet can drastically alter the properties of graphene. Therefore, characterization techniques which can reveal the true nature of nanomaterials must have nanoscale spatial resolution. Raman spectroscopy is an established characterization method for wide ranges of material because its ability to provide rich molecular information from vibrational modes. However, spatial resolution of Raman spectroscopy is limited by diffraction limit of light (around 300 nm). The resolution in Z axis within polymer is even worse, as it might be larger than 10μm, due to the diffraction at air-polymer interface. These limits prevent the individual characterization of nanostructures in nanomaterials. We demonstrated the use of tip-enhanced Raman spectroscopy (TERS) to overcome these limits. TERS employs near-field plasmonic enhancement at the apex of metallic nanotips. Since the enhancement is confined to small area of less than 100 nm, TERS can archives resolution surpassing diffraction limit. We used TERS to characterize nanostructures on epitaxial graphene. The results show that TERS can reveal the compressive strain relaxation on graphene nanoridges and decreased graphene content on nanocrack, which cannot be measured using conventional Raman spectroscopy. The strain relaxation is the solid evidence to the long-suspected mechanism of ridge forming by compressive strain. By analyzing nanoridges on graphene microisland, we can also rule out the possibility of alternative mechanism of ridge formation by silicon vapor trapping.

The TERS measurement of nanostructures revealed that each kind of nanostructures uniquely affects graphene properties. Nanostep does not affect strain at all, since it is the inherent structure of SiC substrate rather than graphene itseft. Nanoridge shows a relaxation in compressive strain compared to neighbor areas. This is shown in Figure 1. Nanocrack shows a missing of graphene content.

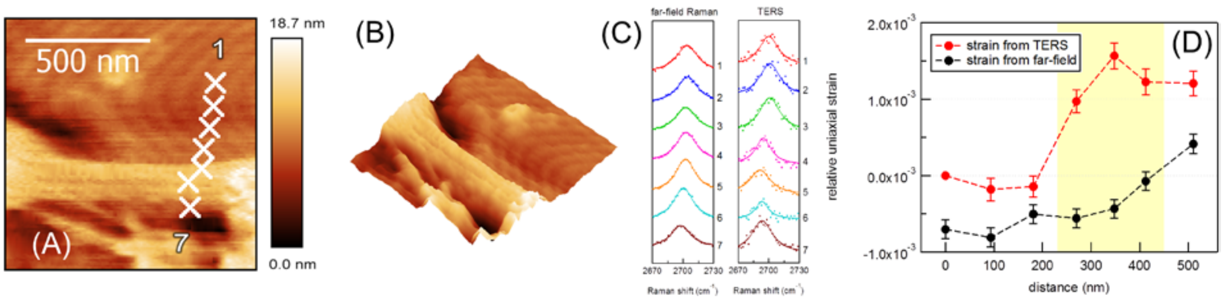

Figure 1. (a) AFM topology of graphene nanoridge. (b) 3D image of (a). (c) G' band in Raman and TERS spectra from each measurement point in (a). (d) graph of strains calculated from band position in (c)

Addition to TERS research, I also conducted 3D surface-enhanced Raman spectroscopy (SERS) research.

This three-dimensional SERS imaging allows the characterization of obscure inhomogeneity of the sample. This work is published in Angewandte Chemie International Edition in May, 2016.

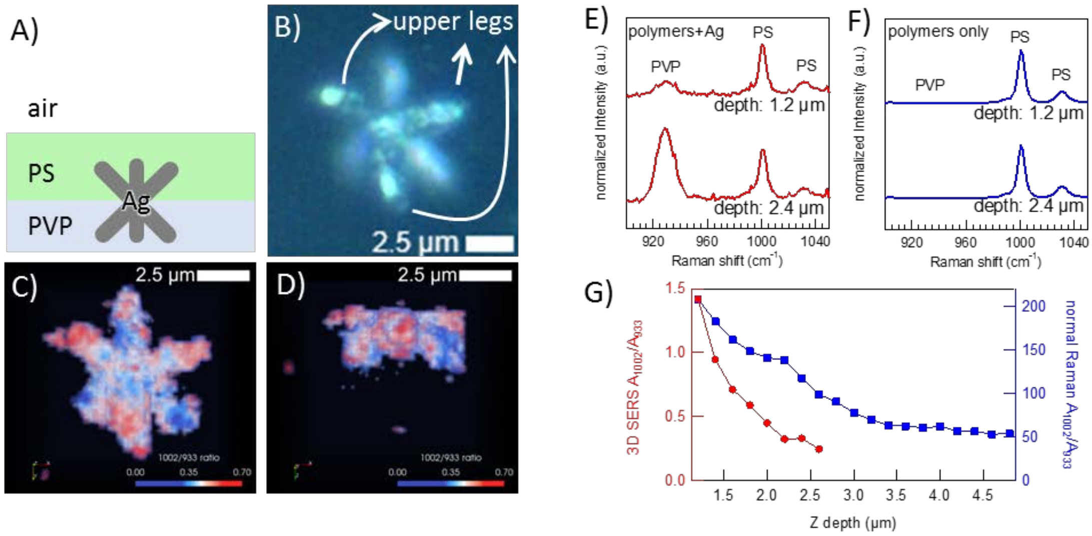

Figure 2. A) A SERS spectrum of PATP from the center of a hexapod silver microstructure. B) Optical microscope image of the particle. C),D) Top and diagonal views 3D SERS images constructed by PATP a1 mode at 1074 cm-1, using the same particle as B). E) Examples of 2D slices in the Z axis of B). Only one in five slices (corresponding to 1.5 µm distance) are shown. Noted that C), D) and E) use the same color scale.

Publication list (during postdoctoral period):

(1) Vantasin, S.; Ji, W.; Tanaka, Y.; Kitahama, Y.; Wang, M.; Wongravee, K.; Gatemala, H.; Ekgasit, S.; Ozaki, Y. 3D SERS Imaging Using Chemically Synthesized Highly Symmetric Nanoporous Silver Microparticles. *Angew. Chem. Int. Ed.* **2016**, *55* (29), 8391–8395.

Conference list (during postdoctoral period):

1. 26th IUPAC International Symposium on Photochemistry, April 3–8, 2016, Osaka, Japan
2. Nanoimaging and Nanospectroscopy IV, August 28 – September 1, 2016, San Diego, CA, USA
3. The 10th Annual Meeting of Japan Society for Molecular Science, September 13-15, 2016, Kobe, Japan
4. SCIX 2016, September 18-23, 2016, Minneapolis, MN, USA