Tip-enhanced Raman Study of Interwall Interactions in Multi-Walled Carbon Nanotube

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1. Introduction

Multi-walled carbon nanotubes (MWNTs) have unique electronic and physical properties, which originate from the strong interwall interactions between adjacent walls of a MWNT. It is important to investigate these interwall interactions through a suitable and nondestructive technique. Raman spectroscopy allows us to directly fetch information about optical and physical properties of carbon materials. While a similar interlayer interaction in graphene was reported through the intensity ratio of two Raman modes (2D-/G-band) [1], the analysis of the interwall interaction in MWNTs via the 2D-band would become more complicated as the number of walls increases because a MWNT can be visualized as multiple co-axial single-walled carbon nanotubes, which may have different kinds of chiralities and structures. In contrast, the D-band arises from the symmetry breaking of six-carbon-atom rings caused by various defects, such as a structural or a physical defect. We expect that when two neighboring walls of a MWNT interact with each other, the strong interwall interaction influences the molecular vibrations and the symmetry of six-carbon-atom rings might be destroyed. Hence, the D-band should become stronger as the number of walls increases. Since the interwall interactions vary at nanoscale even along the length of an isolated MWNT, it is better to investigate them with tip-enhanced Raman spectroscopy (TERS), which enables to access Raman scattering from a nanometric volume of a sample.

Here, we present TERS analysis of interwall interactions in MWNTs via the D-band and experimentally confirmed that D-band is strongly correlated with the number of walls.

2. Result and discussion

Figure 1(a) shows typical TERS and normal Raman spectra of a MWNT, where a strong D-band together with a G-band can be seen. To correlate the D-band intensity with the number of walls, we investigated its TERS intensity for nanotubes of the various number of walls by performing multiple TERS measurements. Normalized TERS intensities of the D-band are shown by black dots in Fig. 1(b). Further, we calculated the TERS signal intensity from a MWNT by considering the exponential decay of light intensity at the tip apex and the nanometric volume of the MWNT under illumination. Since the light filed is strongly locallized within nanometric volume near the tip apex, the illuminated area of the sample is also limited, which varies as the number of walls varies and hence affects the D-band intensity. Fig. 1 (c) shows the calculation model for TERS measurement of a MWNT and the mathematically described MWNT and the near-field light. By taking the region of the MWNT within the near-field light into account, the illuminated part of the MWNT was numerically calculated and visualized in Fig. 1(c). Because of the exponentially decay of light intensity from the tip apex, near-field Raman scattering from each wall also exponentially decreases. The calculated TERS intensity was obtained by assuming that TERS intensity is proportional to light intensity at the tip apex and the illuminated area. In Fig. 1(b), calculated TERS intensity agreed with the experimental result, which verifies that we successfully evaluated interwall interactions in MWNTs at nanoscale. I will discuss about the detail of both experimental analysis and mathematic calculation of TERS intensity.

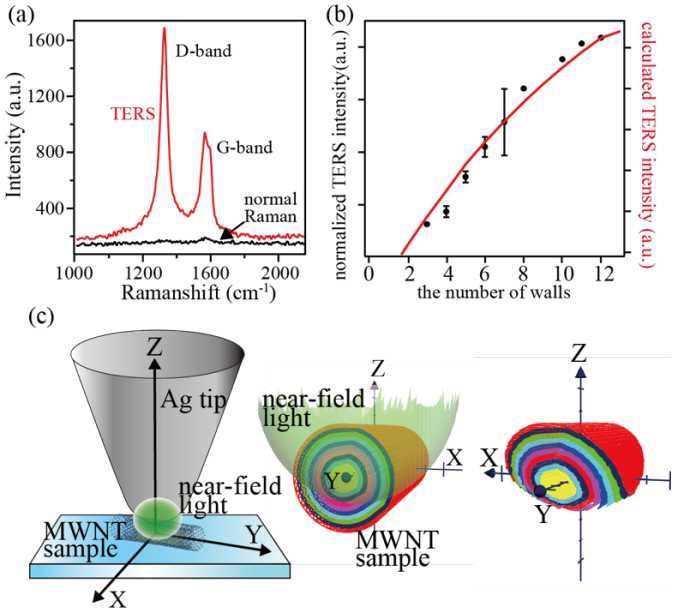

Fig. 1 (a) TERS and normal Raman spectra of a MWNT (b) Normalized TERS intensity at the D-band as a function of the number of walls (black dots). Error bars indicate standard deviation of intensities at the same number of walls. Calculated TERS intensity is shown by the red solid line. (c) The calculation model for TERS measurement of MWNT. The near-field, the MWNT, and the illuminated part of the MWNT were numerically calculated and visualized by a mathematic method.

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References

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