ABSTRACT

The radial breathing mode (RBM) in the Raman spectrum of carbon nanotubes is one of the key spectroscopic signatures for both identification of single-wall carbon nanotubes (SWCNTs) and determination of the chiral indices (n,m). However, if the excitation wavelength is too far away from the resonance condition, it seems not possible to observe the RBM of individual tubes. Here we show by tip-enhanced Raman scattering (TERS) on small bundles that the RBMs are well-visible in near-field, even if they are not observable in far-field. Enhancement factors in TERS greater than 10^4, depending on the thickness of the Au coating of the tip, the sharpness of the tip and the tube sensitivity under the incident excitation were observed. Furthermore, by comparing confocal Raman and TERS spectra, we discuss the local character of different Raman modes in SWCNTs and the strong dependence of the TERS signal on the distance between the tip and the sample.

BACKGROUND AND MOTIVATION

TERS
- metal-coated AFM tip in intermittent contact with the sample surface;
- enhancement of near-field Raman signal generated at nm-sized contact region;
- allows collection of Raman spectra from sub-Å particles (spatial resolution limited to the tip diameter).

TERS on single-wall carbon nanotubes
- identification of Raman features that are not well visible with confocal Raman scattering;
- establishment of the near-field enhancements for different Raman modes;
- discussion of the shifts of the D mode and 2D mode under near-field excitation;
- assignment of the chiral indices (n,m).

RESULTS AND DISCUSSION

Additional chiral configurations of the same bundle were observed in the TERS spectrum, and their heights.

AFM
-XE-100 AFM from Park Systems;
- optical microscope;
  ► located parallel to the Z-scanner;
  ► direct on-axis view of the cantilever in conjunction with the sample area;
- contact-mode Au-coated tips from Veeco;
  ► made from silicon nitride with 60 nm Au-coating;
  ► extra-coating of <20 nm via thermal evaporation;
  ► cast geometry with a triangular shape.

EXPERIMENTAL

RAMAN
- LabRam spectrometer (Horiba Jobin Yvon) combined with a microscope objective for AFM-tip illumination from the side;
- long distance microscope objective (50x);
  ► mounted in a 60° orientation to the surface normal;
  ► N.A. = 0.35;
- Nd:YAG laser (532.2 nm); power on the sample 0.1 mW;
- spectral resolution of 2 cm^{-1};
- Peltier-cooled CCD camera;
- collection of the spectra in backscattering geometry.

CONCLUSIONS

TERS spectra of SWCNTs in small bundles and along a SWCNTs bundle show different enhancement factors of up to 10^4;

For RBMs, the enhancement factor can be considered even larger because they are only visible in the TERS measurements;

The radial breathing mode (RBM) in the Raman spectrum of carbon nanotubes is one of the key spectroscopic signatures for both identification of single-wall carbon nanotubes (SWCNTs) and determination of the chiral indices (n,m). However, if the excitation wavelength is too far away from the resonance condition, it seems not possible to observe the RBM of individual tubes. Here we show by tip-enhanced Raman scattering (TERS) on small bundles that the RBMs are well-visible in near-field, even if they are not observable in far-field. Enhancement factors in TERS greater than 10^4, depending on the thickness of the Au coating of the tip, the sharpness of the tip and the tube sensitivity under the incident excitation were observed. Furthermore, by comparing confocal Raman and TERS spectra, we discuss the local character of different Raman modes in SWCNTs and the strong dependence of the TERS signal on the distance between the tip and the sample.

REFERENCES

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