Polarization effects in surface-enhanced resonant Raman scattering of single-wall carbon nanotubes on colloidal silver clusters

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Polarization effects are studied in surface-enhanced resonant Raman scattering (SERRS) experiments on single-wall carbon nanotubes (SWNT's) in contact with silver colloidal clusters. For metallic SWNT's the very low depolarization ratio of the G band observed in normal resonant Raman scattering (RRS) is nearly completely preserved in SERRS, and this is ascribed to the strong antenna effect of metallic carbon nanotubes. For semiconducting SWNT's, the depolarization ratio is a factor of 2 larger in SERRS compared to RRS. This is attributed to a lowering of symmetry for the resonant Raman scattering properties of the SWNT's arising from the very large field gradients on the metal colloidal clusters. The polarization directions of the local optical fields, as seen by the SWNT's on metallic clusters, are preserved.

The Raman scattering signal of single-wall carbon nanotubes (SWNT's) can be enhanced by many orders of magnitude when the nanotubes are in contact with silver or gold nanostructures in surface-enhanced Raman scattering (SERS) experiments.[1–4] Effective SERS cross sections on silver colloidal clusters can reach 10^{-16} cm^2, allowing Raman measurements from a small number of nanotubes and, very likely, from only one nanotube.[1] The sharp electronic transitions associated with the van Hove singularities in the one-dimensional (1D) electronic DOS make SWNT's a unique system for studying resonance Raman scattering phenomena. By exploiting this sharp resonance effect, metallic and semiconducting SWNT's can be selectively probed in the Stokes and anti-Stokes spectra.[1,5] The extremely favorable resonance Raman conditions related to 1D systems, together with the high (geometric) density of molecular bonds in the macromolecule, contributing to the same Raman mode, can result in ''normal'' resonant Raman cross sections for SWNT's on the order of 10^{-20} cm^2, which also is shown to be adequate to perform Raman measurements on one isolated SWNT.[6–9]

Polarized Raman measurements provide information on the symmetry assignment of the phonon modes. Recent studies of the polarization behavior of the Raman scattering[10,11] of SWNT's together with theoretical calculations[8,12] have shown that the two principal first-order Raman features of SWNT's, the radial breathing mode (RBM) and the G-band tangential modes, exhibit, respectively, $A(A_{1g})$ symmetry,[10,12] and a superposition of two $A(A_{1g})$, two doubly degenerate $E_1(E_{1g})$, and two doubly degenerate $E_2(E_{2g})$ constituents.[8,11]

In this paper we study polarization effects in surface-enhanced resonant Raman spectroscopy (SERRS) from SWNT's on silver colloidal clusters. We use SWNT's as a model molecule to understand the increase of the depolarization ratios[13] measured in many SERS experiments compared to ''normal'' (resonant) Raman scattering.[14–17] In particular,

aligned carbon nanotubes provide a probe for the polarization directions of the local optical fields in the vicinity of the metallic nanostructures at the position of the nanotube. In this way, experiments performed on ''a few'' aligned tubes allow us to separate effects related to possible changes in the polarization direction of the local fields. A ''corruption of field polarizations'' on metal colloidal clusters had been previously proposed as a possible explanation for the increase in depolarization ratios measured in SER(R)S experiments.[14–17] Our experiment here shows that such an effect is not essential and other effects must be responsible for the large depolarization ratios measured in SER(R)S.

SWNT's ($d_t = 1.49 \pm 0.20$ nm) were synthesized using the electric arc technique and a catalyst with a 4:1 Ni:Y atomic ratio. SERS samples consist of silver colloidal clusters in sizes between hundreds of nanometers up to a few microns, which are in contact with the SWNT's.[1] Raman experiments were performed using a microscope (~ 1 μm spot size), with incident and scattered light polarized either perpendicular (VH) or parallel (VV) to one another. There was also an option to turn the VV polarization relative to the sample. Spectra were measured at the Stokes and anti-Stokes sides of the 830 nm (1.49 eV) laser excitation.

Figure 1 shows the Stokes and anti-Stokes resonance Raman scattering (RRS) spectra from a sample of many (non-aligned) SWNT's, measured for the VV and VH scattering configurations. Using 830 nm laser light excitation on this sample, Stokes and anti-Stokes resonant Raman scattering selectively probe semiconducting and metallic SWNT's, respectively.[1] The G-band peaks coming from semiconducting SWNT's were fit with Lorentzian lines (see peak assignments in Fig. 1). Comparing the results in Fig. 1 with previous polarization Raman studies in semiconducting SWNT's,[11] we see that the higher frequency $E_2(E_{2g})$ TO mode[8] is too weak to be seen in the present spectra. This result could be explained if the resonant Raman scattering in Fig. 1 comes mostly from low chiral angle SWNT's, which
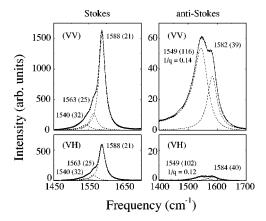
FIG. 1. RRS spectra from a nonoriented SWNT sample ($d_t = 1.49 \pm 0.20$ nm) using $E_l = 830$ nm (1.49 eV) laser excitation. The frequencies (widths) of the Raman peaks are displayed in cm^{-1}.
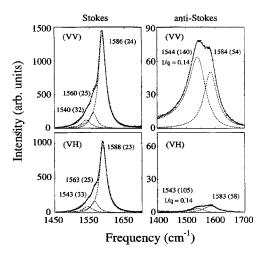

FIG. 2. SERRS spectra from a nonoriented SWNT sample ($d_t = 1.49 \pm 0.20$ nm) using $E_l = 830$ nm (1.49 eV) laser excitation. The frequencies (widths) of the Raman peaks are displayed in cm^{-1}.

is consistent with the low integrated area for the Raman peak at ~ 1560 cm^{-1} (A^{TO}, E_1^{LO}) compared to the integrated area for the ~ 1590 cm^{-1} (A^{LO}, E_1^{TO}) peak.[8] The G-band Raman feature coming from metallic SWNT's was fit using one Lorentzian and one Breit-Wigner-Fano (BWF) peak[18,19] (see peak assignments in Fig. 1). For semiconducting SWNT's, we obtained a scattering power ratio $\delta_{\mathrm{RRS}}(S) = I_{VH}/I_{VV} = 0.36$ for all the Lorentzian components of the G band, in good agreement with previous experiments,[20] and as expected from nonresonant bond-polarization theory for a random ensemble of many SWNT's.[12] For metallic SWNT's measured in the anti-Stokes spectrum, there are only two components, and we obtained the scattering power ratios $\delta_{\mathrm{RRS}}(\mathrm{BWF}) = 0.04$ for the BWF peak, and $\delta_{\mathrm{RRS}}(L) = 0.08$ for the Lorentzian component. These values are much smaller than the value expected from nonresonant theory[12] and can be understood in terms of the ''antenna'' effect in carbon nanotubes,[21] where the absorption and emission is strongly suppressed for light polarized perpendicular to the nanotube axis. The Raman signal from a small bundle or a single tube of metallic nanotubes is strongly suppressed when the light is polarized perpendicular to the nanotube.[9] A similar result was obtained for a fiber of aligned metallic SWNT's, which were partially aligned (within 30°).[22]

Figure 2 shows Stokes and anti-Stokes SERRS spectra when the tubes are in contact with silver fractal colloidal clusters. The anti-Stokes spectra coming from metallic SWNT's show a frequency down-shift for the BWF feature, indicating that the SERS effect is operative.[2] For SERRS, we obtained the scattering power ratios $\delta_{\mathrm{SERRS}}(\mathrm{BWF}) = 0.04$ for the BWF peak, and $\delta_{\mathrm{SERRS}}(L) = 0.17$ for the Lorentzian component. Thus, the δ value is preserved for the BWF component in Fig. 2, but for the Lorentzian component, δ is about a factor of 2 larger than that measured in RRS. In general, the very small depolarization ratio of the metallic nanotubes is preserved in SERRS. This is a new finding for SERS spectra from an ensemble of molecules. SERS typically tends to increase the depolarization ratio substantially relative to normal Raman scattering.[17]

The line shape for the SERRS spectra from semiconducting SWNT's (Stokes side) is basically the same as in the

RRS experiment, indicating that many SWNT's are contributing to the SERRS spectra. The Stokes spectra in Fig. 2, however, yield scattering power ratios $\delta_{\mathrm{SERRS}}(S) = 0.69$ for all Lorentzian components within the G band of semiconducting SWNT's. Thus the depolarization ratio measured in the SERRS spectra from many semiconducting SWNT's is about a factor of 2 larger than that measured in RRS (similar to the result for the Lorentzian peak in metallic SWNT's).

Figure 3 shows the VV and VH Stokes Raman spectra from a highly diluted sample.[23] The Raman signals show smaller linewidths (see Fig. 3) compared to the spectra in Fig. 2, consistent with a reduction in inhomogeneous line broadening, due to a reduction in the number of nanotubes contributing to the spectra. Scattering power ratios $\delta_{\mathrm{SERRS}}(S) = 0.66 \pm 0.10$ were observed at all selected sample spots, in agreement with SERRS results on the ''high density'' sample (Fig. 2).
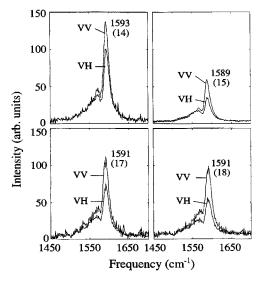

FIG. 3. SERRS Stokes spectra from four different spots where Raman signal from ''invisible'' SWNT's is observed. The frequencies (widths) for the most intense Raman peaks in each spectrum are displayed in cm^{-1}.
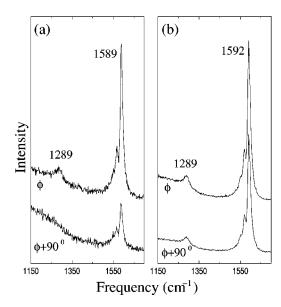
FIG. 4. (a) SERRS spectra from an ''invisible'' bundle of aligned semiconducting SWNT's, for two *VV* polarization directions separated by 90°, where ϕ denotes a relative maximum of the scattering power. (b) Similar RRS measurements performed on a sample containing many unaligned SWNTs. The frequencies for the *D* band and the most intense *G* band Raman peak are displayed in cm^{-1}.

For a selected spot on the SERS target where the linewidth (12 cm^{-1}) of the tangential *G* band of the semiconducting tubes was close to the value attributed to the homogeneous linewidth (~ 9 cm^{-1}),[1,8] it is likely that only ''a few'' nanotubes (of relatively uniform diameter and maybe also aligned) contribute to the spectrum. *VV* SERRS spectra from this spot were measured while turning the field polarization directions by 90° steps relative to the SERS sample starting from a relative maximum in the *VV* signal. The scattered signals from the *G* and the *D* bands (predominantly *A* symmetry)[11,24] follow the same dependence on turning the *VV* polarization direction by several subsequent 90° steps, with large changes in scattering power between the spectra taken from adjacent 90° steps. Figure 4(a) shows two spectra in the region of the *D*- and *G*-band modes measured in subsequent 90° steps. For comparison, Fig. 4(b) shows the results of the same polarization turning experiment, performed in ''normal'' Raman scattering from many nonaligned semiconducting nanotubes, showing that such a strong 90° dependence does not exist in this case.

To quantify the effect which appears by 90° turning of the parallel field polarizations relative to the sample orientation in SERS and ''normal'' RRS experiments, we compare the average value for the difference between the signals measured at turning angles ϕ and $\phi + 90°$ normalized to the sum of both signals. This value is 0.69 in the SERRS experiment, compared to 0.19 for RRS measurements on a sample with many tubes. Raman spectra from many randomly aligned tubes should not show any dependence of the scattering power on turning the field polarizations relative to the sample. The observed difference as shown in Fig. 4(b) reflects the different throughput of the spectrograph for polar-

ization directions parallel and perpendicular to the slit.[26]

The 90° period in the SERRS signal in Fig. 4(a) very likely reflects polarization directions (nearly) parallel and perpendicular to the nanotube axis. From theory[12] and experimental observations on aligned bundles of carbon nanotubes[11,25] the strongest signal should be related to the polarization direction parallel to the nanotube axis (*Z* direction). The strong polarization dependence indicates that we are measuring SERRS spectra in Fig. 4(a) from mostly parallel aligned nanotubes. The observed ratio between the *G*-band signals measured for field polarization directions perpendicular and parallel to the nanotube axis [see Fig. 4(a)] is $I_{\phi+90°}/I_\phi = 0.24$. This value is in very good agreement with theoretical estimates[12] of $I_{XX}/I_{ZZ} = I_{\phi+90°}/I_\phi = 0.25$, and with experimental results for RRS for SWNT's (Ref. 11) and MWNT's.[25] This strong dependence of the SERRS spectra of aligned semiconducting nanotubes on the polarization direction of the fields, and particularly the good quantitative agreement between the $I_{\phi+90°}/I_\phi$ ratios in RRS and SERRS of aligned nanotubes provides a strong argument against any corruption of field polarization directions in the SERRS experiment.

Interestingly, the effect shown in Fig. 4(a) is ''washed out'' when we do not use an analyzer, indicating that a relatively strong crossed (*ZX* and *XZ*) scattering exists in SERRS, comparable in magnitude to the *ZZ* scattering. This result is different from RRS scattering in aligned semiconducting SWNT's, where $I_{ZX}/I_{ZZ} = I_{XZ}/I_{ZZ} \sim 0.20$. The experimental observation that in SERRS more scattering power goes into the perpendicular polarized field than in RRS can be understood by a lowering of the symmetry of the ''scattering properties'' of nanotubes when they are attached to silver colloidal clusters. The very large *field gradients*, predicted for colloidal clusters,[27] may provide a rationale for such an effect. The changed symmetry for the ''Raman scattering properties'' of SWNT's by RRS does not necessarily mean that the symmetry of the molecule, or the nanotube changes. Rather, the scattering tensor in the case of RRS for SWNT's can be changed by inducing changes in the electronic system, which couples strongly to the phonon system, but generally leaves the symmetry of the phonons unchanged. Changes in the electronic system in SERRS result in stronger scattering, due in part to contributions from off-diagonal elements in the Raman tensor. This effect also explains the increase in the depolarization ratio measured in SERRS from samples containing many semiconducting nanotubes.

In summary, polarization effects in the Raman spectra of *metallic* SWNT's are always, in both RRS and SERRS, determined by the strong antenna effect which favors, in all optical effects, field polarization directions parallel to the nanotube axis. For *semiconducting* nanotubes our experiments show that the larger depolarization ratio measured in SERRS is not related to changes of the field polarization directions by the metal particles themselves, but rather is due to changes in the symmetry of the resonant Raman scattering tensor of the nanotubes arising from the large field gradients on a silver (or gold) cluster surface. This finding implies that resonant SERS experiments (SERRS), do not probe the in-

trinsic resonance Raman tensor of a ''free'' semiconducting nanotube measured in the absence of metal colloidal clusters. This situation may be altered for nonresonant SERS, which should probe the intrinsic nonresonant Raman tensor of a molecule, essentially independent of changes in the electronic levels due to interaction with the silver colloids.

The changed resonant ''Raman scattering properties'' of the molecule in contact with metal colloidal clusters, arising from changes in the electronic system, very likely also explains the increase of depolarization ratios in SERRS experiments on dye molecules.[15,16] The experimental observation that a strong increase in depolarization ratios is not observed for isolated or less aggregated silver colloidal particles[15,16] can be understood in terms of their lower field gradients. In contrast, the increase of the depolarization ratio in nonreso-

nant SERS experiments of ''small'' molecules, such as pyridine, might be related to a lowering of the vibrational symmetry of the molecule geometry, as modified by adsorption to the metal.[17]

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