Bundle Effects of Single-Wall Carbon Nanotubes

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Abstract. To see the bundle effects on the electronic and the vibrational properties of single-wall carbon nanotubes (SWNTs), we have measured the resonance Raman scattering of isolated SWNTs and thick bundles. For the measurements of the isolated SWNTs, we used an evacuated sample after bromine doping. A broad and asymmetric tangential mode band, which is a sign of the resonance of the metallic SWNTs and can be fitted by a Fano line shape, is not observed in the isolated SWNTs. This suggests the inter-tube interactions play an important role to the Fano interference. On the other hand, the purified sample shows very thick acquired bundles. We observed 4% higher breathing mode frequencies than in the pristine sample. Further, in the case of multi-wall nanotubes, we observed 5% higher breathing mode frequencies than the SWNTs. These results can be explained by the interlayer interactions.

INTRODUCTION

Pristine arc samples contain many isolated single-wall carbon nanotubes (SWNTs) as well as bundles. (1) Thus, in greater or less degree, measured optical responses are regarded as mixtures of signals from the isolated SWNTs and the bundles. If it is possible to wipe off the signal from the bundles, we can get information about optical properties of the isolated SWNTs. To realize this, we used bromine doped SWNTs. If the isolated SWNTs do not have any stable site for bromine molecules, the evacuation can remove the bromine molecules surrounding isolated SWNTs. Recently, Kazaoui *et al*. have shown that the bromine doped SWNTs do not show any absorption band below 1.8 eV. (2) If we measure the Raman spectra of the evacuated sample by excitations lower than 1.8 eV, we will obtain the Raman spectra only of the isolated SWNTs. Since the charge transfer suppresses the optical transitions in bundles, the Raman signals from the bundles can be wiped off.

Some theoretical works predicted the radial breathing mode (RBM) frequencies are strongly modified by the bundle effects.(3–5) We know that highly purified samples show very thick bundles. The bundle effects should be observed more clearly in the purified sample than in the pristine ones. Further, it is expected that the interlayer interactions in multi-wall nanotubes should be stronger than the inter-tube interactions in SWNT bundles. We will discuss about these results.

EXPERIMENTAL

Samples for a doping were prepared by a conventional electric arc method using NiY catalyst.(6) HRTEM revealed that a considerable amount of isolated SWNTs are existing in the sample. To avoid a doping inside SWNTs, pristine soot was installed into a quartz ampoule without any purification. Saturated bromine vapour was introduced to the ampoule at room temperature. After keeping one hour, the ampoule was evacuated by a rotary pump. Then the ampoule was sealed off.

Thick bundles of SWNTs were prepared by the purification of a SWNT sample fabricated by the laser ablation method using NiCo catalyst.(7) The purification was done by 15% H_2O_2 reflux for six hours.(8) Multi-wall nanotube sample was prepared by the carbon arc in hydrogen gas.

Raman spectra were measured using a JOBIN YVON U1000 double monochromator and HAMAMATSU PHOTONICS photon counting system interfaced to a personal computer. Ar^+, dye and Ti-sapphire lasers were used for the excitation.

RESULTS AND DISCUSSION

For 488 nm excitation, the fully bromine doped SWNTs show only one RBM band at 260 cm^{-1}, which is consistent with the result by Rao *et al.*(9) After the evacuation, we observe two RBM bands at 180 and 240 cm^{-1}. We confirmed that the two-band structure is stable up to 200 °C in vacuum. The band at 180 cm^{-1} is nearly the same to the RBM of the pristine sample and can be observed by any excitation energies in contrast with the 240 cm^{-1} band which has no intensity for excitations lower than 1.8 eV. This means that the sample consists of two kinds of SWNTs. One has stable

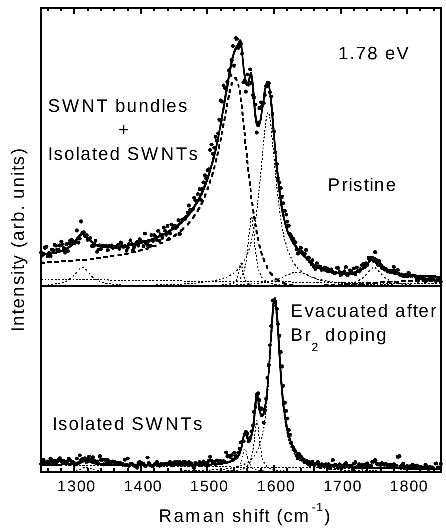

FIGURE 1. Near infrared Raman spectra of pristine and bromine doped SWNTs. Dashed curve indicates the fitted Fano line shape. Here, ω_0 = 1548 cm^{-1}, 1/q = –0.25 and Γ = 27 cm^{-1}.

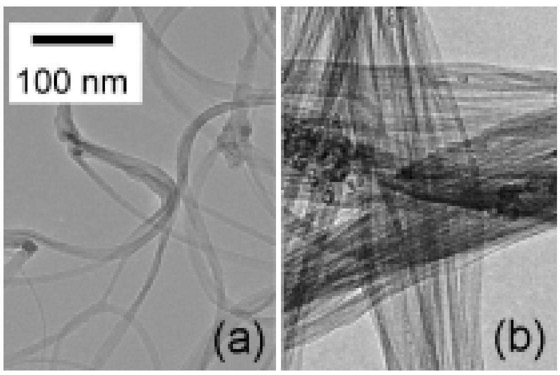

FIGURE 2. TEM images of (a) pristine and (b) purified SWNTs fabricated by the laser ablation method using NiCo catalyst.

bromine sites, and the other one does not have. We think the former should be the bundles and the latter the isolated SWNTs. We conclude that the 240 cm^{-1} band is the RBM of the partially doped SWNT bundles and the 180 cm^{-1} band is that of de-doped portions in the sample namely, the isolated SWNTs.

Now we can measure the Raman spectra of the isolated SWNTs by near infrared laser excitations. Figure 1 indicates the high-frequency Raman spectra of the pristine and the isolated SWNTs by the excitation in the metallic window of the sample. (10,11) In the case of the pristine sample, the spectrum can be fitted well by some Lorentzians and a Fano line shape, which is the sign of the resonance of metallic SWNTs. Surprisingly, however, the Fano line shape cannot be observed anymore in the case of the isolated SWNTs. The tangential modes can be fitted simply by three Lorentzians, instead. If the Fano line shape is originating from the metallic bundles and three Lorentzians are from the isolated SWNTs, the both Raman spectra can be explained simply. This result indicates that the Fano interference strongly connects with the inter-tube interactions. Indeed, the coupled phonon mode in the Fano line shape is 45 cm^{-1} lower than the tangential mode of the isolated SWNTs. This frequency shift is the similar value to the inter-tube mode frequency. (3)

To see the bundle effect on the RBM frequencies we measured the resonance Raman spectra of isolated, pristine and purified SWNTs. Typical change in bundle diameter by the purification is indicated in Fig.2. TEM images show typical bundle diameters of the purified sample are larger than 50 nm. Figure 3 shows the low frequency spectra of each sample in the metallic window. Each sample shows similar resonance feature but RBM frequencies of the purified sample are 4% higher than the pristine one. This is consistent with the theoretical predictions of the bundle effect on the RBM frequencies.(3-5) Although the RBM frequencies of the isolated SWNTs are slightly higher than those of the pristine sample, this may be the effect of the bromine

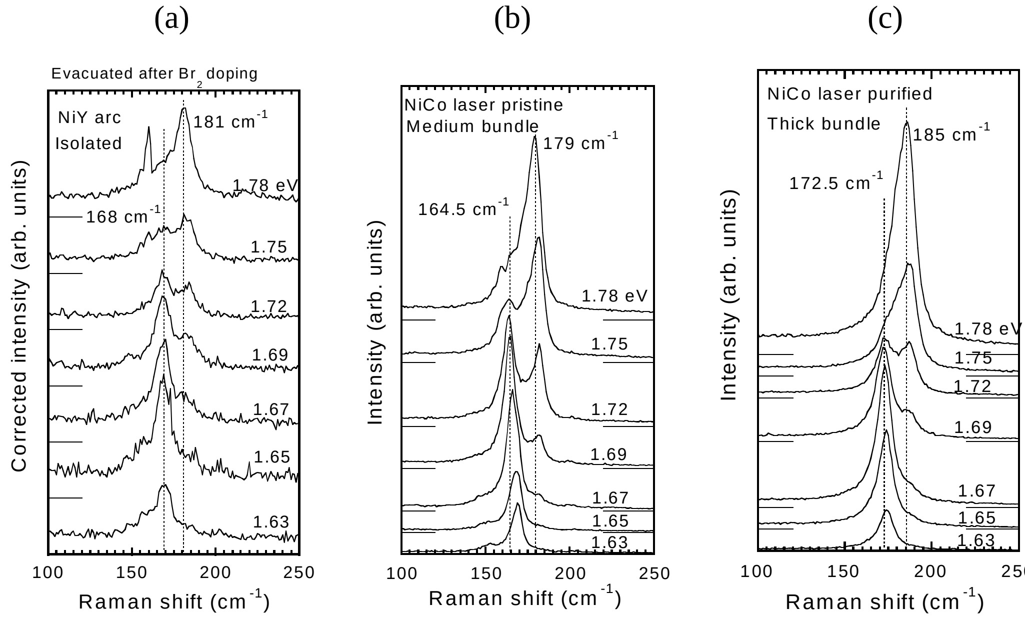

FIGURE 3. Resonance Raman spectra of (a) isolated SWNTs, (b) mixture of isolated SWNTs and medium bundles, and (c) thick bundles of SWNTs.

molecules remaining around the isolated SWNTs. Further, we found a interesting phenomenon. In the cases of the isolated SWNTs and the purified sample, RBM frequencies are independent of the excitation energy. In the case of pristine sample, however, the RBM peak position is strongly depending on the excitation energy. This strange result can be explained by the bundle effects by taking into account the fact that the pristine sample is a mixture of the isolated SWNTs and the bundles. The isolated SWNTs have lower RBM frequencies (3) and narrower electronic bandwidth than the bundles.(12) When the excitation energy is just the energy gap of a certain kind of SWNTs, isolated SWNTs are resonated predominantly. Thus, the RBM peak position locates the lowest frequency with the highest intensity. When the excitation is higher or lower than the energy gap, bundles are mainly resonated due to the broader band feature. Thus, RBM peak shows up-shift with decreasing the intensity. In the case of the purified sample, most of the SWNTs are inside of thick bundles. Consequently, the RBM frequency is stably high. Apparently, there is no cause to move the RBM peak of the isolated SWNTs.

Multi-wall carbon nanotubes produced by carbon arc in hydrogen gas show RBM peaks.(13,14) The peak frequencies are about 5% higher than the corresponding RBMs of SWNTs. Although there is no theoretical calculation about interlayer interaction in MWNTs, it is reasonable that the interlayer interaction in the MWNT is larger than inter-tube interactions in the SWNT bundle.

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