Raman spectra and thermal stability analysis of 0.4 nm freestanding single-walled carbon nanotubes

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The thermal stability of ultrasmall 0.4 nm single-walled carbon nanotubes (SWNTs) are studied by means of Raman-scattering measurements under a vacuum. The 0.4 nm SWNTs are very stable when they are confined inside the channels of the $\text{AlPO}_4\text{-5}$ zeolite crystal. When these SWNTs are extracted from the channels into free space, however, they become thermally unstable because of the strong curvature effect. The *in situ* Raman-scattering measurement under 1×10^{-5} mbar shows all three structures of the 0.4-nm-sized SWNTs are destroyed between 730 to 790 K, a temperature range much lower than that of large-sized SWNTs. The (5,0) tube is only destroyed after the temperature reaches 790 K and seems slightly more stable than the other two structures: the (3,3) and (4,2) tubes. A reference measurement under UHV conditions confirms that the 0.4 nm SWNTs are destroyed after the same thermal treatment indicating that the structural degradation is determined by the curvature effect other than oxidation.

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Recently there has been significant progress in producing ultrasmall carbon nanotubes with diameters in a range of 0.3–0.5 nm. These nanotubes have been found either as the central shell of a multiwalled carbon nanotube,^{1–3} or as the single-walled carbon nanotubes (SWNTs) present in the channels of a porous zeolite crystal,^{4,5} or they branch perpendicularly anchored to the surface of larger nanotubes.⁶ In particular, the aligned 0.4 nm SWNTs in the zeolite channels allow us to perform more controlled characterizations for the electronic system, such as the measurements of polarized absorption,⁷ polarized Raman spectra,^{8,9} and electric transport properties.^{10,11}

In comparison with large-sized nanotubes, the ultrasmall carbon nanotubes are especially interesting because of the strong curvature effect, which leads to a significant hybridization between the σ^* and π^* orbitals.¹² The curvature effect in small SWNTs not only redistributes the energy in the electronic states, which endows nanotubes with much richer electronic properties, but also opens new electron-phonon scattering channels that enhance the electron-phonon coupling and leads to special transport properties such as superconductivity.^{11,13,14} On the other hand, however, the strong curvature effect makes nanotubes unstable. Considering a SWNT of diameter d constructed by rolling up a graphitic sheet within the continuum elasticity scheme, the curvature strain due to bond-bending increases the system energy in proportion to $1/d^2$. Meanwhile, the energy is reduced in proportion to $1/d$ due to the elimination of the dangling bonds on the edge of graphitic ribbon wrapping into a tube.¹⁵ As the energy increase is faster than the energy decrease with the decrease of d , eventually a SWNT becomes marginally stable when its size decreases to a critical diameter d_c . Several theoretical models have been proposed for studying the stability of SWNTs and for predicting how small a stable SWNT can be.^{16–18} It has been shown that 0.4 nm is at or close to the lower limit of a stable SWNT. A 0.4 nm SWNT is thermodynamically unstable,¹⁹ though en-

ergetically it is more favorable than its corresponding graphitic ribbon structure.¹⁷ Experimentally, however, what is lacking is a report on the stability of SWNTs with such a small diameter.

In this paper we report the thermal stability of freestanding 0.4 nm SWNTs by means of Raman-scattering measurements. These ultrasmall SWNTs are synthesized by pyrolysis of tripropylamine (TPA) molecules in the channels of zeolite $\text{AlPO}_4\text{-5}$ (structure type code: AFI) crystals.^{4,5} The SWNTs formed inside the AFI channels (SWNTs@AFI) are monosized and isolated by the AFI framework. The existence of 0.4 nm SWNTs has been confirmed by high-resolution transmission electron microscope (TEM) observation,^{4,20,21} x-ray diffraction,²² optical absorption spectra⁷ as well as radial-breathing Raman modes (RBMs).^{8,9} The zeolite framework can be removed by the following process: the AFI crystals containing SWNTs are ground into a fine powder in an amber mortar, then the powder is etched using hydrochloric acid (18%). There exist two layers in the solution, a black layer with SWNTs on the top and a transparent layer on the bottom. The black layer is then picked out and dispersed into a dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) solvent. The SWNTs in dichloroethane are light brownish in color. Several drops of the nanotube solution are dipped onto a gold substrate. After evaporating the solvent, freestanding 0.4 nm SWNTs are exposed for characterization. The sample is then put onto a heating stage and pumped to a vacuum of 1×10^{-5} mbar. Raman spectra are measured using a micro-Raman system (Jobin Yvon T64000) with the 632.8 nm line of a He-Ne laser as the excitation source. A $50\times$ microscope objective is used to focus the laser beam and collect the backscattered light.

Raman spectra (a) and (b) shown in Fig. 1 are measured at room temperature for the freestanding SWNTs and the SWNTs@AFI, respectively. Detailed structures of the RBMs are shown in the inset for both samples. The three RBMs of the SWNTs@AFI, located at 510, 550, and 580 cm^{-1} , are

FIG. 1. (Color online) (a) Raman spectra of freestanding SWNTs (b) SWNTs confined inside AFI crystals at 300 K. The inset shows the magnified spectra of RBMs for the freestanding SWNTs (a) and the confined SWNTs (b). The RBMs are fitted by three Lorentzian peaks at 499, 538, and 576 cm^{-1} for the freestanding tubes and at 510, 550, and 580 cm^{-1} for confined SWNTs, respectively.

attributed to the (4,2), (5,0), and (3,3) tubes, respectively.²³ The Raman feature at around 450 cm^{-1} can be attributed to the RBM of a 0.5 nm-sized SWNT such as a (6,0) tube. The general features of the spectrum of the freestanding SWNTs are similar to those of the SWNTs@AFI, but with a few notable differences: (1) The RBMs are slightly shifted to lower frequency for freestanding tubes with respect to the SWNTs@AFI by 12 cm^{-1} for the (5,0) tube, 11 cm^{-1} for the (4,2) tube, and 4 cm^{-1} for the (3,3) tube, respectively. According to an *ab initio* first-principle calculation, the energy-relaxed diameter is 0.408 nm for the bare (5,0) nanotube, and 0.406 nm for the (5,0) tube present in the AFI channels.²⁴ The redshift of the RBMs can be understood as the slight expansion of the SWNTs in diameter when they are released from the channel to free space. Another possibility for the RBM downshift is the change of force constant. For SWNTs in a bundle, the RBM vibrations are affected by the interaction between SWNTs. The RBM shows upshift with respect to that of an individual tube which is similar to the confinement effect of AFI zeolite.²⁵ (2) The relative intensity of the disorder-induced D band is significantly increased in the spectrum of freestanding SWNTs. The D band phonon modes are not Raman active until the defect on the graphitic sheet breaks the translational symmetry of SWNTs. The strong D band can originate from a higher defects rate or from a significant bending of bonds in small tubes because of the curvature effect. If the strong D band solely originated from the curvature effect, there should be no significant difference in the D-band feature for the freestanding SWNTs and SWNTs@AFI. It is more reasonable to attribute the increase of Raman intensity in the D-band region to defect-induced feature for the freestanding nanotubes. The strong D band implies that a much higher defect density exists in the freestanding SWNTs. When the tubes are confined inside the restricted channels, the spread of defects formed during the

FIG. 2. (Color online) Raman spectra in a RBM region at temperature range from 300 to 870 K. Three distinguishable RBM peaks are fitted by Lorentzian components at 499 cm^{-1} , 538 cm^{-1} , and 576 cm^{-1} from 300 to 670 K. RBM components of (4,2) and (3,3) tubes merge into the tails of the RBM component of the (5,0) tube at 730 K. No distinguishable RBM exists at a temperature higher than 790 K.

fabrication process is depressed. When the tubes are released into free space, however, these defects are expected to grow vigorously due to the serious bond bending in small tubes, leading to a deterioration of structural integrity in the free-standing tubes.

With elevating temperature, the intensity of the RBM Raman signals is decreased significantly and the linewidth is broadened as shown in Fig. 2. At 730 K, the RBMs at 499 cm^{-1} and 576 cm^{-1} are blurred. The main feature of the spectra is the broad band at 538 cm^{-1} which survived up to 790 K. The spectra measured above 800 K are weak and featureless. These results suggest that among the three types of the 0.4 nm SWNTs, the (5,0) tube with zigzag structure is more stable than the other two structures. The tubule structure of the (4,2) and (3,3) tubes are damaged at around 730 K, while the (5,0) tube is still stable up to 790 K. However, all three structures collapse at a temperature higher than 800 K.

Figure 3 shows the Raman spectra in the region of the D- and G-like bands for the freestanding SWNTs at different temperatures. With increasing temperature, the G band at 1589 cm^{-1} and D band at 1239 cm^{-1} show collective downshifting by 8 cm^{-1} and 13 cm^{-1} , respectively. The tempera-

FIG. 3. (Color online) Variation of Raman spectra of SWNTs from 300–870 K. The inset shows the enlarged G band at different temperatures. The dot and arrow denote the peak position of two components in the asymmetric G band showing downshift and broadening with elevating temperature. The two components merge into a single symmetric peak at a temperature higher than 670 K.

ture coefficient of the shift for the G band is $-0.0246 \text{ cm}^{-1}/\text{K}$, which is comparable to SWNTs with a larger diameter of 1.3–1.4 nm.²⁶ Since the G band is related to the tangential vibration of the tube, the diameter of the tube does not affect the vibration prominently. In contrast, the temperature coefficient of the Raman shift for the D bands is $-0.0235 \text{ cm}^{-1}/\text{K}$, which is larger than that of large-sized tubes.^{27,28} We noticed that the shift of the D band is comparable to that of the G band in these ultrasmall SWNTs. Due to the large frequency splitting of the G -mode vibration along the tube direction (G^+ mode) and along the circumferential direction (G^- mode),^{29,30} the G^- band in these ultrasmall carbon nanotubes are overlapped with the D band. The large shift in the D -band region is determined by a combination of the temperature coefficient of the D and the G^- bands.

Isotherm Raman spectra in Fig. 4(a) are measured by keeping the temperature at 870 K for different heating times. With increasing heating duration, the Raman spectrum became weaker and broader. Under isothermal condition for 30 min, the SWNTs completely change into amorphous carbon characterized by the broad Raman bands centered around 1300 cm^{-1} and 1580 cm^{-1} . The spectrum shown on the bottom of Fig. 4(a) is measured when the temperature is cooled back to the room temperature from 870 K. The spectrum is keeping an amorphouslike feature; no nanotube modes are observable. This fact indicates that the nanotube structure is permanently destroyed by heating at 870 K. As a

FIG. 4. (Color online) (a) Spectra change under an isotherm condition at 870 K for different heating durations. Spectrum at 300 K after the temperature is cooled down is at the bottom. (b) Spectra of SWNTs@AFI at 870 K (top) and at 300 K (bottom) after heating at 870 K under a vacuum of 1×10^{-5} mbar. (c) Spectra at 300 K of freestanding SWNTs before (above) and after (below) heating at 870 K under a vacuum of 1×10^{-10} mbar.

reference, in panel (b) we show the Raman spectra of the SWNTs@AFI measured at 870 K as well as measured when the temperature is cooled back to 300 K. The typical nanotube signal at the RBM and G^+ mode regions are clearly seen at both spectra, indicating that the SWNTs are very stable even at 870 K when they are confined inside the channels. The zeolite channels play a crucial role in maintaining the nanotube structural integrity. The thermal stability of these freestanding 0.4 nm SWNTs is much weaker than that of large-size SWNTs, which are reported to be thermally stable up to the graphite instability temperature of around

4000 K.³¹ The thermal damage temperature observed for the 0.4 nm SWNTs is even lower than that predicted for the 0.33 nm SWNTs using tight-binding molecular-dynamics simulations.⁶ The results indicate that for SWNTs with such a small diameter, the strong curvature effect significantly affects the stability of the SWNTs. The defects which exist in the dissolved SWNTs might also play a significant role in lowering the thermal stable temperature.

It is worth pointing out that the vacuum of 1×10^{-5} mbar used in the experiment discussed above is not high enough to exclude the oxidation effect. One question may arise as to whether the oxygen residue facilitates the structural damage of the 0.4 nm freestanding SWNTs. In order to evaluate the degree of influence of the oxygen residue, we heat the freestanding 0.4 nm SWNTs in an ultrahigh-vacuum (UHV) chamber of 1×10^{-10} mbar at the same temperature. The Raman spectra of the freestanding SWNTs measured before and after heating in the UHV chamber are shown by the top and bottom curves in Fig. 4(c), respec-

tively. It is seen that, even in the oxygen-free environment, the irreversible structural change is also observed, implying that the thermal instability plays a key role in destroying the freestanding SWNTs and the oxidation effect is negligible even at a 10^{-5} mbar vacuum environment.

In summary, we have studied the thermal stability of free-standing 0.4 nm SWNTs by the *in situ* measurement of Raman scattering as a function of temperature. The extreme curvature effect makes these ultras-small SWNTs marginally stable. The structural degradation starts at a temperature around 730 K and the SWNT structures are completely changed into amorphous-carbon-like species at 870 K.

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