Instability of 0.4 nm carbon nanotubes in a zeolite template under ultraviolet laser irradiation

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The stability of 0.4 nm carbon nanotubes within a zeolite matrix under laser irradiation has been investigated using photoluminescence (PL) spectroscopy. It was found that in the weak excitation power regime the PL spectra have similar line shapes at different excitation wavelengths. When the excitation power is high for ultraviolet light at 325 nm, the PL spectral shape undergoes an irreversible change. This is in contrast to the case with 488 nm laser irradiation and indicates a permanent chemical change in the sample, probably due to photochemical effects.

Recently, we have reported an observation of strong photoluminescence (PL) from (4,2) and (3,3) single-walled carbon nanotubes, which have a diameter of around 0.4 nm [1]. The visible PL from metallic (3,3) and narrow bandgap semiconducting (4,2) tubes was a surprising result, and it has been suggested that it might be due to reduced non-radiative relaxation channels in the one-dimensional structures or to the finite length of the nanotubes in the zeolite template. The stability of these small diameter carbon nanotubes is an interesting and important issue, for both free-standing tubes and tubes within a zeolite matrix. The stability of an isolated single-walled nanotube (SWNT) is determined mainly by the competition between the strain energy introduced by rolling up a planar graphene strip to form the tube and the decrease in edge energy resulting from elimination of the dangling bonds along the edges of the strip. The strain energy is inversely proportional to the square of the radius, while the edge energy is inversely proportional to the radius of the nanotube [2-5]. Hence, as the radius decreases the strain energy for a SWNT increases more rapidly than the edge energy of the corresponding planar graphene strip, which makes small-radius SWNTs unstable. First principles calculations [5] as well as molecular dynamics simulations [3] have shown that the smallest energetically stable SWNTs have a diameter of about 0.4 nm, close to the diameter of the tubes produced in zeolite channels. In this Letter, we report our investigation of the stability of 0.4 nm nanotubes within zeolite channels in response to laser irradiation at different laser wavelengths, using PL as a monitoring tool.

The 0.4 nm carbon nanotubes were grown by pyrolysis of tripropylamine ($((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}$, TPA) in the channels of the host single crystalline aluminophosphate $\text{AlPO}_4\text{-5}$ (AFI) zeolite [6,7]. Carbon nanotubes thus formed are mono-sized and parallel in alignment. They offer the opportunity to study the intrinsic anisotropic physical properties of 1D single-walled nanotubes in the form of macroscopic samples [1]. High-resolution transmission electron microscopy [8] and Raman scattering measurements [7,9] show these SWNTs to have a diameter of 0.4 nm, which can only

occur with three possible structures: (5,0), (3,3) and (4,2). The sample used in this study contained all of these three types of nanotubes and was fabricated by pyrolysis of TPA-loaded AFI crystals at 580°C without pumping out from the reaction chamber the hydrocarbon radicals such as CH₃ and C₂H₅ that were decomposed from the TPA molecules.

The AFI crystal containing 0.4 nm nanotubes used in this work was about 100 μm in diameter and about 400 μm long and was uniform in color. To ensure the same sample spot was used for PL measurements at different excitation laser wavelengths and laser powers, the experiments were performed with a near-field scanning optical microscope (NSOM). The excitation laser beams at different wavelengths, from either a cw He-Cd laser, an Argon ion laser, a He-Ne laser, or a Ti:Sapphire laser, were coupled into an ultraviolet grade optical fiber each at a time and directed to a tapered tip with controlled output power. With a blunt fiber tip, the spot size illuminated on the sample was ~1 μm. The emitted light was collected in the far field by an objective lens and directed to a 1/4 meter monochromator equipped with a charge coupled detector. To eliminate the wavelength-dependent throughput of the detection system, a quartz-tungsten-halogen irradiation source was used to calibrate the detection sensitivities at different wavelengths [10]. Since the optical fiber used did not preserve polarization, the polarization of the excitation light at the fiber tip was elliptical and its major axis was aligned along the nanotubes. The polarization of the emission light was known to be mainly polarized along the nanotubes, and only the nanotube-parallel component of the emission was collected. All the measurements reported here were performed at room temperature.

Figure 1 plots the PL spectra of the SWNTs for excitation laser wavelengths of 325, 488, 632, 720, 762, and 790 nm. All the spectra have been rescaled so that their PL intensities in the long

wavelength region (>700 nm) coincide. Because of different absorption, the scaling factor is not just proportional to the excitation laser power. A broad and intense emission band is observed centered at ~ 700 nm (1.78 eV), a wavelength somewhat shorter than that reported previously in the far field PL measurements (~ 730 nm) [1]. The peak wavelength and intensity are slightly dependent on the excitation wavelength. The fact that the PL spectra at longer excitation wavelengths collapse with those at shorter excitation wavelengths indicates that the sample is inhomogeneously broadened. Interestingly, the energy bands (levels) responsible for the PL emission at long wavelengths (>700 nm) seem to be independent of the excitation laser wavelength, implying the existence of relaxation channels to the same set of electronic states in the carbon nanotubes no matter to what level the electrons and holes are excited initially. As one goes to shorter excitation wavelengths, the PL line shapes are quite similar, but with more and more emissions at shorter wavelengths, again an indication of inhomogeneous broadening. The inhomogeneous broadening may arise from non-uniform N-doping and the large Stokes shift associated with energy transfer from the pure carbon part to N-doped part of the tubes. This would occur if the PL mechanism were dominated by N-doping in the (4,2) tubes. Or, it could arise from the length distribution of the carbon nanotubes if the tube end states control the PL mechanism [1]. At this stage, we are not able to discriminate which PL mechanism is responsible.

To investigate the stability of the 0.4 nm carbon nanotubes in the zeolite matrix when exposed to laser irradiation, we performed the PL measurement at 488 nm and 325 nm excitation and varied the incident laser power on the sample. Figure 2 shows the resulting PL spectra for various incident powers. After rescaled by the incident laser power, all the spectra excited at 488 nm (Fig. 2(a)) exhibit nearly identical line shapes for powers up to 6 μ W. This implies that the sample

response was quite linear. When the incident laser power further increases to $10\text{ }\mu\text{W}$ ($\sim 1.3\text{ kW/cm}^2$), the line shape starts to deviate slightly, indicating some nonlinearity. In contrast, the PL line shape depends strongly on the excitation power at 325 nm, as shown in Fig. 2(b). For very low excitation powers ($<0.36\text{ }\mu\text{W}$), the observed PL intensity over the entire spectral range is linear with the incident laser power as indicated by the collapse of the data into a single curve after rescaling. For high excitation powers ($>0.4\text{ }\mu\text{W}$), however, extra PL intensity starts to emerge in the short wavelength region, showing a superlinear relation with the excitation power. When the incident laser power exceeds $1.7\text{ }\mu\text{W}$, an extra PL peak at $\sim 450\text{ nm}$ begins to show up. Since the PL spectra at incident power higher than $0.4\text{ }\mu\text{W}$ have been multiplied by different factors (as labeled in Fig. 2(b)) in order to force the curves to coincide in the long wavelength region ($>700\text{ nm}$), the emergence of the PL peak at 450 nm is at the expense of PL at long wavelengths. **This observation is well reproducible when a new sample is used.**

To understand the nature of the superlinearity in the PL spectra when excited at 325 nm, the PL spectra excited at 488 nm from the same sample spot were compared before and after UV irradiation. This spot can be located to better than $0.1\text{ }\mu\text{m}$ precision using NSOM positioning. As shown in Fig. 3, the PL spectrum after UV irradiation had a drastically altered spectral line shape, with significantly more PL intensity in the shorter wavelength region. This result indicates that the superlinearity of PL spectra in respect to 325 nm excitation is not due to an intrinsic nonlinear effect, rather, it is due to irreversible changes in the materials in response to UV irradiation.

The two PL peaks in Fig. 2(b), one at 450 nm and the other at 700 nm , have previously been shown to correspond to emissions from (3,3) and (4,2) nanotubes, respectively [1]. Since the sample contained both (3,3) and (4,2) nanotubes to start with, one may expect that (3,3) nanotubes would

emit light even at low excitation power at 325 nm. The fact that we do not detect this emission is perhaps due to re-absorption by the (4,2) tubes in the sample. High power UV irradiation could result in break-up of the (4,2) tubes, which have the highest density per unit length among the three types of nanotubes, (5,0), (3,3), and (4,2). This is consistent with the decreasing PL intensity at >700 nm, evident in Fig. 2(b), and thus a decreasing content of (4,2) tubes. With some (4,2) tubes burnt away, the emission from (3,3) tubes would escape to be detected without significant re-absorption. Another possible mode of sample change would be that the (4,2) tubes have been transformed into (3,3) tubes under UV irradiation. At this stage, it is difficult to experimentally discriminate one mechanism from the other. Considering that the mechanical stability of 0.4 nm nanotubes is marginal, break-up of (4,2) tubes at high UV irradiation power seems to be more likely than the transformation of (4,2) tubes into (3,3) tubes.

The irradiation wavelength dependence of the irreversible sample change could be a result of photochemical effects. It is reasonable to assume that thermal effects dominate under 488 nm irradiation. Since the absorption coefficient at 325 nm is only ~ 1.5 -2 times that at 488 nm [11], to reach similar temperatures at a sample spot, and thus similar PL spectral changes to those induced by irradiation at 488 nm at $10\text{ }\mu\text{W}$ would require ~ 5 -6.7 μW at 325 nm for a purely thermal effect. Figure 2(b) clearly shows that a much weaker irradiation power of only $\sim 0.4\text{ }\mu\text{W}$ at 325 nm is already sufficient to cause changes in the PL spectra similar to that at 488 nm at $10\text{ }\mu\text{W}$. Thus, the majority of the changes in the PL spectra at 325 nm must be non-thermal in origin. Since high photon energies are required to effect changes in PL spectra, a photochemical effect must prevail. The observed deterioration of carbon nanotubes in vacuum only at ~ 480 K seems to also support this line of reasoning.

In summary, we have observed instability of 0.4 nm carbon nanotubes in a zeolite matrix when exposed to UV laser irradiation. The irreversible sample change is evident in the PL spectra when excited at 325 nm and 488 nm. It is probable that a photochemical effect plays an important role in causing the sample changes induced by UV irradiation.

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Figure Captions

Figure 1 PL spectra from a SWNT sample at room temperature when excited at various laser wavelengths. For comparison, all the PL spectra have been scaled so that their peak intensities are of comparable magnitude.

Figure 2 (a) PL spectra from a SWNT sample for a various excitation laser powers at wavelength 488 nm. All the PL spectra have been scaled by the excitation power. (b) Similar to (a) but with an excitation wavelength of 325 nm. While all the spectra with excitation power less than 0.4 μW have been scaled by the power, those with higher excitation powers have been first scaled by the power, and then multiplied by different factors as labeled in the figure in order to force their spectra at $\lambda > 700$ nm to coincide.

Figure 3 PL spectra from the same sample spot before and after UV laser irradiation at 6 μW . The two spectra have been rescaled to force data collapse at $\lambda > 700$ nm and clearly indicate a change in PL line shape. The excitation laser wavelength was 488 nm.

Figure 1

Figure 2

Figure 3