FTIR-luminescence mapping of dispersed single-walled carbon nanotubes

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Abstract. We have applied the FTIR-luminescence/FT-Raman technique to map the near-infrared photoluminescence (PL) of water–surfactant dispersions of single-walled carbon nanotubes (SWNTs) in broad excitation (250–1500 nm) and emission (800–1700 nm) ranges. The excitation wavelength was scanned by using the monochromatized light of standard xenon and tungsten halogen lamps. The PL maps are presented for SWNTs with a mean diameter of ~1.3 nm prepared by the pulsed laser vaporization method. When dispersed by powerful ultrasonic agitation and separated by ultracentrifugation, these nanotubes show structured absorption bands and a PL quantum yield as high as ~10^{-3}. This indicates a large fraction of individual nanotubes in the dispersion. Electronic interband transition energies of nanotubes derived from the PL data correspond reasonably to the energies calculated in the modified tight-binding model of Ding \textit{et al.}
1. Introduction

The recently discovered near-infrared bandgap photoluminescence (PL) of dispersed, micelle-isolated semiconducting single-walled carbon nanotubes (SWNTs) has attracted much attention [1]. The luminescence not only provides rich information about electronic properties of SWNTs, but also allows a full characterization of semiconducting tubes in an SWNT sample (at least, its dispersed fraction) regarding both their structures described by the chiral vector indices \((n, m)\) and their relative abundance [2]. The latter opportunity is very important, for example, for a development of methods to selectively separate/modify different \((n, m)\) nanotubes. Very recently, near-infrared photo- and electroluminescence has been observed from individual, surface-deposited SWNTs [3, 4], which may lead to new applications of nanotube-based electronic devices.

The luminescence was first observed for water–surfactant dispersions of SWNTs produced by high-pressure catalytic decomposition of carbon monoxide (the HiPco method) [5]. These tubes have diameters between \(\sim 0.7\) and \(\sim 1.2\) nm and emit in the range of \(\sim 900–1400\) nm with an average quantum yield, \(\varphi_{\text{PL}}\), of \(\sim 10^{-3}\) [1]. We have found that SWNTs with larger diameters (\(\sim 1.0\)–\(1.4\) nm) produced by pulsed laser vaporization (PLV) of Ni/Co/carbon targets show a similar PL with characteristic excitation–emission maxima corresponding to interband electronic transitions between van Hove singularities (vHss) of specific \((n, m)\) nanotubes [6]. Interband transition energies vary roughly inversely with the tube diameter [7], therefore the emission of PLV nanotubes is red-shifted to the range from \(\sim 1200\) up to \(\geq 1700\) nm. In this study of PLV tubes, the overall quantum efficiency of the PL was, however, relatively low (\(\varphi_{\text{PL}} \sim 10^{-3}\)), because the majority of the dispersed nanotubes were apparently still confined in bundles. PL appears to be strongly quenched via interactions with metallic tubes [1].

Recently, we have succeeded in the preparation of highly dispersed PLV SWNTs that show a fine structure in the absorption bands and emit with an average quantum efficiency as high as \(\sim 10^{-3}\), i.e. similar to that of the HiPco tubes. Another major improvement was the use of the FTIR-luminescence/FT-Raman technique for sensitive detection of the near-infrared emission of nanotubes. An FT-Raman spectrometer was combined with a monochromatic light source with xenon and tungsten lamps in order to continuously map the PL of nanotubes in the broad excitation range.
range 250–1500 nm and in the emission range 800–1700 nm. In this paper we present FTIR-luminescence maps for PLV nanotubes. The interband transition energies of SWNTs derived from the experimental data are compared to those calculated in the modified tight-binding (TB) model of Ding et al [8]. For the \((n, m)\) assignment of nanotubes we have used the empirical relations of Weisman et al [2].

### 2. Experimental details

#### 2.1. Materials and preparation

SWNTs having a relatively narrow diameter distribution between \(\sim 1.1 \text{ and } \sim 1.4 \text{ nm} \) were produced by the PLV method [9] and characterized as described elsewhere [10]. The raw material (\(\sim 10 \text{ mg} \)) was dispersed for several hours in 10 ml of \(\text{D}_2\text{O} \) (transparent up to \(\sim 1800 \text{ nm} \)) containing 1 wt\% of sodium dodecyl sulfate (SDS) or 0.5 wt\% of sodium dodecylbenzene sulfonate (SDBS) anionic surfactants using a 200 W ultrasonic dispergator equipped with a titanium tip. Dispersions were then centrifuged at 150 000–180 000 \(g \) for 1–2 h in a Beckman–Coulter Optima-MAX table ultracentrifuge and the upper \(\sim 2/3\) volume was collected. A typical final concentration of nanotubes was roughly estimated to be \(\sim 0.01 \text{ mg ml}^{-1} \) in \(\text{D}_2\text{O}/\text{SDS}\) and \(\sim 0.1 \text{ mg ml}^{-1} \) in \(\text{D}_2\text{O}/\text{SDBS}\) dispersions.

#### 2.2. Spectroscopy

UV–visible–NIR absorption spectra were recorded on a Varian Cary 500 spectrophotometer. PL was measured in the range of \(\sim 800–1700 \text{ nm} \) with a Bruker Equinox 55S/FRA106 FT-Raman spectrometer equipped with a liquid nitrogen cooled germanium detector. A quartz cuvette with a dispersion of SWNTs was placed in front of a 50 mm collecting lens of the spectrometer and irradiated at 90° with an automated monochromatic light source (Jobin Yvon) equipped with a 400 W xenon lamp and a 150 W tungsten halogen lamp for UV–visible and NIR excitation, respectively. The excitation light was focused on the cuvette with a 6:1 elliptical mirror. Since PLV nanotubes emit above \(\sim 1200 \text{ nm} \), an FT-Raman notch filter (1064 nm) was usually retained and a long-pass filter (an antireflex-coated Si plate with a 50% cut-off wavelength \(\lambda_{\text{cut-off}} \sim 1050 \text{ nm} \)) was additionally inserted in order to reject scattered excitation light at a wavelength \(\lambda_{\text{exc}} < \lambda_{\text{cut-off}} \) and thus to improve the signal-to-noise ratio of the FT-luminescence spectra. A typical acquisition time for a PL map such as that shown in figure 2 was 20 h with 8 nm excitation spectral slits, a 3 nm excitation wavelength increment and a 20 cm\(^{-1}\) resolution of the FT-Raman spectrometer. PL maps in the characteristic ‘finger-print’ S2 excitation range (\(\sim 650–1050 \text{ nm} \) for PLV nanotubes) could be measured with a sufficient signal-to-noise ratio in less than one hour with 12 nm excitation spectral slits and a 5 nm excitation wavelength increment.

The presented PL maps were corrected for wavelength-dependent excitation intensity and instrumental response of the FT-Raman spectrometer (both in relative photon flux units). For the first correction, the excitation intensity was recorded with a Si photodiode and a Dexter thermopile in the UV–visible and NIR excitation ranges, respectively. For measurements with the thermopile, chopper light modulation (10 Hz) and a lock-in technique were applied. A correction function for the spectrometer was determined with the aid of a calibrated tungsten halogen lamp (Oriel). The lamp light was guided to the spectrometer via two diffuse-reflecting plates out of a Spectralon (Labsphere) in order to reduce the light intensity.

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The PL maps were not explicitly corrected for the wavelength-dependent absorption of dispersed SWNTs. In the UV–visible excitation range this correction could be ‘avoided’ by measuring PL from a dispersion with a high concentration of nanotubes in a triangular cuvette (∼100% excitation light absorbed independent of \( \lambda_{exc} \)). Diluted dispersions of SWNTs in a rectangular 4 mm cuvette (absorbance \( A \leq 0.5 \) at ∼900 nm) were used for PL mapping in the NIR excitation range in order to minimize reflection/scattering of an excitation light into the FTIR-spectrometer. Under these conditions, the number of excitation photons absorbed is roughly proportional to \( A(\lambda_{exc}) \) (figure 1). A correction of the PL maps for this factor was, however, less important than for the relatively strongly wavelength-dependent excitation intensity and would not significantly change shapes and positions of characteristic features on the PL maps (figures 2 and 3).

The average quantum efficiency of the luminescence of SWNTs, \( \varphi_{PL} \) (the ratio of photons emitted in the whole PL spectrum up to 1700 nm to total photons absorbed), was estimated from a comparison with the phosphorescence of singlet oxygen \( ^1O_2 \) in CCl4 (\( \lambda_{em} = 1275 \text{ nm} \), \( \varphi_{phos} = 1.3 \times 10^{-3} \) [12]) photosensitized by fullerene C70 with a unit quantum efficiency [13]. All measurements were performed at room temperature.

3. Results and discussion

3.1. Dispersions of PLV nanotubes

The characteristic features of a D2O/SDS dispersion of PLV nanotubes after an intense sonication and ultracentrifugation are

(i) a fine structure of the S1–S3 and M1 absorption bands (attributed to optically allowed electronic transitions \( E^{S}_{11}, E^{S}_{22}, E^{S}_{33} \) and \( E^{M}_{11} \) between pairs of vHss in the valence and conduction bands/zones of semiconducting and metallic nanotubes, respectively [7, 14]) and

(ii) a relatively high quantum yield of the NIR PL (figure 1).

This is similar to the observations made for HiPco nanotubes [1] and consistent with a large fraction of individual, micelle-isolated nanotubes in the dispersion. In a film sample [15] in a moderately sonicated dispersion [6] practically all/most of the nanotubes are bundled, therefore the absorption bands are broadened and the PL is entirely quenched/weak (figure 1). Compared to the moderately sonicated dispersion, the absorption (figure 1) and luminescence (cf results below and in [6]) of the well dispersed nanotubes are blue-shifted. This shift suggests a preferential distribution and retention of smaller diameter PLV nanotubes in the intensely sonicated and ultracentrifuged D2O/SDS dispersion.

Dispersions with a relatively high concentration of PLV nanotubes in D2O/SDS (S2-absorbance ≥1 in a 10 mm cuvette) were found to be stable only for several days as indicated by a decrease of PL signals and a broadening of absorption bands. To recover the PL signals, the dispersions had to be repeatedly treated with ultrasound. We have tested several other surfactants and have found, in agreement with results of Islam et al [16], that SDBS is a superior surfactant for preparation of stable, highly concentrated dispersions of PLV nanotubes in water. No significant changes in the absorption and PL spectra have been observed for such dispersions (S2 absorbance ∼5 in a 10 mm cuvette) within two weeks.
Figure 1. Optical absorption spectra and approximate PL quantum yields, $\varphi_{\text{PL}}$, of different samples of SWNTs prepared by PLV: (---) a $\sim$300 nm thick film of SWNTs [16]; (----) a dispersion in D$_2$O/SDS prepared at relatively moderate ultrasonic power and centrifuged at 20,000 g [6]; (-----) a dispersion in D$_2$O/SDS after a high power sonication and centrifugation at 180,000 g. The spectra are vertically offset for convenience as indicated with the short horizontal lines. The S1, S2, S3 and M1 absorption bands correspond to the $E_{S11}$, $E_{S22}$, $E_{S33}$ and $E_{M11}$ electronic transitions in semiconducting and metallic SWNTs, respectively.

3.2. Photoluminescence maps

Figure 2 shows a two-dimensional FTIR-luminescence contour map of PLV nanotubes dispersed in D$_2$O/SDS and excited in a broad UV–visible–NIR range from 250 nm up to 1500 nm. This range corresponds to the excitation energy varying from approximately $E_{S44}^S$ down to $E_{S11}^S$. The luminescence maxima (spots) on the PL map are related to $E_{Sii}^S$, $i = 1–4$ (excitation), and $E_{S11}^S$ (emission) electronic transitions of specific $(n, m)$ tubes. They form characteristic patterns along the excitation axis corresponding to different $E_{Sii}^S$ regions similar to the PL map reported for HiPco nanotubes [2]. The spots observed in the ‘finger-print’ S2 excitation region ($\lambda_{\text{exc}} \sim 650–1050$ nm) provide pairs of $E_{S11}^S/E_{S22}^S$ energies and can be reliably assigned to specific $(n, m)$ nanotubes by using the empirical relations of Weisman et al [2].

Compared to the dispersion in D$_2$O/SDS, many additional emitting nanotubes have been observed in the PL map of PLV nanotubes dispersed in D$_2$O/SDBS (figure 3, the S2 excitation region). In particular, large diameter PLV nanotubes appear to have been more efficiently dispersed from the raw material and micelle isolated in D$_2$O/SDBS in comparison to D$_2$O/SDS. The positions of the PL spots observed for both dispersions coincide within the experimental error, but their relative intensities are different (figures 2 and 3). The $E_{S11}^S$ and $E_{S22}^S$ energies and structural $(n, m)$ assignment of the observed PLV nanotubes are listed in table 1.

In agreement with previous observations for HiPco and PLV nanotubes [2, 6], the majority of brightly emitting $(n, m)$ nanotubes (marked in blue in table 1) have a large chiral angle between 20° and 30°, i.e. close to $(n, n)$ ‘armchair’ nanotubes. This might suggest a preferential production of these tubes by the PLV method and their abundance in the raw material. However,
Figure 2. Two-dimensional FTIR-luminescence contour map (luminescence intensity versus excitation and emission wavelengths) of PLV nanotubes dispersed in D$_2$O/SDS. The map is combined from two parts measured separately in the UV–visible and NIR excitation ranges, respectively (see experimental details). The intensity scales of the two parts were roughly normalized to each other by using the overlap at $\lambda_{\text{exc}} = 750$ nm. The dashed lines denote vibronic features related to the G ($\sim 1600$ cm$^{-1}$) and G' ($\sim 2600$ cm$^{-1}$) vibration modes of SWNTs.
Figure 3. FTIR-luminescence contour map of PLV nanotubes dispersed in D_{2}O/SDBS and excited in the S2 (E_{S2}^{2}) region. The structural indices (n, m) of the observed nanotubes are listed in table 1. A bright spot at the upper right corner of the map is likely an artefact due to the spectrometer response correction of the FTIR-luminescence spectra with a strong scattered excitation light component (λ_{exc} ≥ λ_{cut-off} of the long-pass filter used) and an increased noise background.

The PL map in figure 2 shows practically no features in the excitation range of ~500–650 nm. It corresponds to the E_{11}^{M} electronic transitions in metallic (non-luminescent) PLV nanotubes and to weak, off-vHs-resonance transitions in semiconducting nanotubes. Below λ_{exc} ~ 500 nm, a rich pattern of PL peaks corresponding to the E_{33}^{S} and E_{44}^{S} excitations is observed (figure 2). Their assignment is in progress and will be presented elsewhere. Note that the E_{33}^{S}/E_{44}^{S} excitations are difficult/practically impossible to distinguish in the absorption spectrum of nanotubes (figure 1) because of a strong π-plasmon background, increasing to the shorter wavelengths [11]. Therefore, PL is an advantageous method to obtain information about the high energy electronic transitions in SWNTs.

Another interesting group of features on the PL map in figure 2 is broad spots at λ_{exc} ~ 1100–1250 nm. Their excitation positions are shifted relative to the emission by the characteristic Raman frequency of SWNTs hω ~ 1600 cm^{-1} (G-band) as denoted by a dashed line in figure 2. We also observe a group of weaker features with hω ~ 2600 cm^{-1} (Raman G’-band). Their origin is not yet clear. Since all of these features clearly correlate with the bright PL spots at the same emission wavelength (E_{11}^{S}), we attribute them to vibronic transitions E_{11}^{S} + hω in the
Table 1. PL maxima of PLV nanotubes dispersed in D$_2$O/SDBS (SDS) and their $(n, m)$ assignment according to Weisman et al [2]. The last two columns indicate the diameter, $d$, and chiral angle, $\alpha$, of the assigned nanotubes.

| $E_{11}^S$ (nm)$^a$ | $E_{22}^S$ (nm)$^a$ | $E_{11}^S$ (eV) | $E_{22}^S$ (eV) | $(n, m)$ | $d$ (nm)$^b$ | $\alpha$ (grad) |
|----------------------|----------------------|-----------------|-----------------|-----------|-------------|----------------|
| 1172                 | 791                  | 1.058           | 1.568           | (12, 1)   | 0.995       | 4.0            |
| 1172                 | 714.5                | 1.058           | 1.736           | (8, 6)$^c$| 0.966       | 25.3           |
| 1198                 | 789                  | 1.035           | 1.572           | (11, 3)   | 1.014       | 11.7           |
| 1244                 | 671                  | 0.997           | 1.848           | (9, 5)    | 0.976       | 20.6           |
| 1250                 | 784                  | 0.992           | 1.582           | (10, 5)   | 1.050       | 19.1           |
| 1267                 | 726                  | 0.979           | 1.708           | (8, 7)    | 1.032       | 27.8           |
| 1306                 | 856                  | 0.949           | 1.449           | (13, 2)   | 1.120       | 7.1            |
| 1322                 | 788                  | 0.938           | 1.574           | (9, 7)    | 1.103       | 25.9           |
| 1344                 | 852                  | 0.923           | 1.455           | (12, 4)   | 1.145       | 13.9           |
| 1382                 | 753                  | 0.897           | 1.647           | (10, 6)   | 1.111       | 21.8           |
| 1399                 | 852                  | 0.886           | 1.455           | (11, 6)   | 1.186       | 20.4           |
| 1416                 | 806.5                | 0.876           | 1.538           | (9, 8)    | 1.170       | 28.1           |
| 1429                 | 921                  | 0.868           | 1.346           | (15, 1)   | 1.232       | 3.2            |
| 1448                 | 919                  | 0.856           | 1.349           | (14, 3)   | 1.248       | 9.5            |
| 1474                 | 864                  | 0.841           | 1.436           | (10, 8)$^c$| 1.240       | 26.3           |
| 1489                 | 921                  | 0.833           | 1.346           | (13, 5)$^c$| 1.278       | 15.6           |
| 1496                 | 797                  | 0.829           | 1.556           | (12, 5)   | 1.201       | 16.6           |
| 1523                 | 837                  | 0.814           | 1.481           | (11, 7)   | 1.248       | 22.7           |
| 1549                 | 927                  | 0.801           | 1.338           | (12, 7)$^c$| 1.321       | 21.4           |
| 1559                 | 984                  | 0.795           | 1.260           | (16, 2)$^c$| 1.357       | 5.8            |
| 1562                 | 885                  | 0.794           | 1.401           | (10, 9)$^c$| 1.307       | 28.3           |
| 1591                 | 988                  | 0.779           | 1.255           | (15, 4)   | 1.377       | 11.5           |
| 1623                 | 942                  | 0.764           | 1.316           | (11, 9)$^c$| 1.377       | 26.7           |
| 1625                 | 843                  | 0.763           | 1.471           | (14, 4)   | 1.300       | 12.2           |
| 1634                 | 876                  | 0.759           | 1.416           | (13, 6)   | 1.336       | 18.0           |
| 1639                 | 995                  | 0.757           | 1.246           | (14, 6)   | 1.411       | 17.0           |
| 1666                 | 918                  | 0.744           | 1.351           | (12, 8)   | 1.384       | 23.4           |

$^a$ Luminescence emission and excitation wavelengths (energies) were determined to an accuracy of ±0.2%.

$^b$ Calculated with a carbon–carbon bond length of 0.142 nm [2].

$^c$ Marked in blue are nanotubes with strong luminescence as compared to the neighbouring $(n, m)$ tubes.

Absorption (which result for some reason in an increased PL efficiency), rather than to vibronic transitions $E_{11}^S - h\omega$ in the emission. However, no corresponding features at $E_{11}^S + h\omega$ could be observed in the absorption spectrum of PLV nanotubes (figure 1).

Excitation directly into the band-gap (S1) is seen on the PL map to give rise to very broad features correlating with PL spots in the S2 region, but strongly obscured by the scattered excitation light (white stripe in figure 2). Nevertheless, one can roughly estimate that the S1-excited PL is at least equally strong as the PL obtained by S2 excitation.

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3.3. Comparison with tight-binding model calculations

A simple TB model has been widely used for theoretical investigations of electronic properties of nanotubes as well as for an interpretation of experimental data [7]. It also provided a basis for the empirically ‘adjusted’ \((n, m)\) assignment relations derived by Weisman \textit{et al} [2] from PL and Raman data for HiPco nanotubes. However, this model, even after considering accurately the trigonal warping effects on the energy dispersion relations [14, 17], describes only qualitatively the optical absorption and PL data \((E_{11}^{S} \text{ and } E_{22}^{S} \text{ energies})\) for SWNTs [2, 6]. To fit to the spectroscopic data, one can in fact adjust only a few parameters: the graphite sheet interaction integral \(\gamma_{0}^{\infty}\) in the TB model and the uniform up-shifts of calculated energies, \(\Delta E_{ii}\). The latter correct empirically for excitonic effects in SWNTs [18, 19], which are expected to be especially pronounced for the first interband transitions, i.e. for \(E_{11}^{S}\) energies [18]. This prediction has been experimentally confirmed by Kataura \textit{et al} and Ichida \textit{et al} for the shifts \(\Delta E_{ii}\) observed in the absorption spectra of solid films prepared from different SWNT materials [14, 20, 21]. A relatively weak dependence of \(\Delta E_{ii}\) on the mean diameter of SWNTs [21] justifies the above approximation of \((n, m)\) independent (constant) values of \(\Delta E_{ii}\).

Recently, Ding \textit{et al} [8] have modified the TB model in a simple and physically clear way in order to take into account the curvature and chirality effects on \(sp^{2}\) hybridization of carbons on a nanotube surface. Remarkably, their approach does not introduce any new parameters. Hagen and Hertel [22] have fitted the modified model to the S1-absorption band structure of dispersed HiPco nanotubes and determined two sets of the optimal parameters \(\gamma_{0}^{\infty}\) and \(\Delta E^{S}\) (for both \(E_{11}^{S}\) and \(E_{22}^{S}\)): (I) \(\gamma_{0}^{\infty} = 3.0\ eV, \Delta E^{S} = +0.135\ eV\); (II) \(\gamma_{0}^{\infty} = 2.63\ eV, \Delta E^{S} = +0.19\ eV\).

Compared to absorption spectra, PL data are much more informative and characteristic since they provide pairs of \(E_{11}^{S}/E_{22}^{S}\) energies that can be unambiguously assigned to specific \((n, m)\) nanotubes [2]. We have compared the PL data for PLV nanotubes (table 1) with the values of \(E_{11}^{S}/E_{22}^{S}\) calculated in the modified TB model using different parameters \(\gamma_{0}^{\infty}\) and \(\Delta E_{11}^{S}/\Delta E_{22}^{S}\). For this size range and \((n, m)\)-ensemble composition, the best agreement between the modified TB model and the PL data was found for \(\gamma_{0}^{\infty} = 3.15\ eV, \Delta E_{22}^{S} = 0\) and \(\Delta E_{11}^{S} = +0.1\ eV\) (figures 4(a) and (b)). A small (zero) shift \(\Delta E_{22}^{S}\) and a large shift \(\Delta E_{11}^{S}\) are consistent with theoretical predictions of Ando [18]. It is seen from figure 4(b) that in this case the calculated energies \(E_{11}^{S}/E_{22}^{S}\) (black crosses) follow the same pattern as their experimentally observed \((n, m)\) counterparts (blue circles) and deviate less than \(\pm3\%\) from the latter ones for nanotubes with \(E_{11}^{S} \leq 1.0\ eV\). Relatively poor agreement was found for the parameter set II chosen in [22] (figure 4(a)). Note that although some theoretical points (crosses) fit coincidentally to the experimental points (circles) around \(E_{11}^{S} \sim 0.9\ eV\) in figure 4(a), they have ‘wrong’ \((n, m)\) indices.

Although not as accurate as the empirical relations [2], the modified TB model could be used with the above parameters for the \((n, m)\) assignment of PLV nanotubes from PL data (figure 4(b)). Deviations of the calculated energies from the experimentally observed ones may be attributed, among other factors, to \((n, m)\)-dependent excitonic effects in SWNTs.

4. Concluding remarks

We have demonstrated a convenient, sensitive and time-effective technique for mapping the near-infrared PL of dispersed carbon nanotubes in a broad UV–visible–NIR excitation range using an FTIR-luminescence/FT-Raman spectrometer for PL detection and a standard monochromatic lamp light source for PL excitation. Such PL maps provide rich information about characteristic
Figure 4. A comparison of $E_{11}^S/E_{22}^S$ energies of PLV nanotubes (circles) derived from the PL data (table 1) to those calculated in the modified TB model of Ding et al \[8\] (crosses): (a) with parameters of Hagen and Hertel, $\gamma_0^\infty = 2.634$ eV, $\Delta E_{11,22}^S = +0.19$ eV \[22\]; (b) with parameters optimized in this work for the PL data, $\gamma_0^\infty = 3.15$ eV, $\Delta E_{11}^S = +0.1$ eV. Black crosses overlaid on the grey ones denote calculated counterparts for the experimentally observed $(n, m)$ nanotubes.

Electronic transitions in SWNTs and a structural $(n, m)$ assignment of emitting semiconducting nanotubes \[2\].

High intensity sonication followed by ultracentrifugation appear to be crucial for the preparation of water–surfactant dispersions of PLV nanotubes having a large fraction of individual, PL-active nanotubes. The PL quantum efficiency of PLV nanotubes in such dispersions is comparable to that of the smaller diameter HiPco nanotubes ($\sim 10^{-3}$) \[1\]. This indicates a slower decrease of the PL with increasing nanotube diameter than we have proposed previously \[6\]. The interesting question of quantitatively determining PL efficiency as a function of tube diameter and chiral index or indeed of a spectral limit to the (near-)infrared PL of nanotubes remains open.

In contrast to the standard TB model of the electronic structure of SWNTs \[7, 14, 17\], the modified model of Ding \textit{et al} \[8\], which takes into account curvature and chirality effects on $sp^2$ hybridization of a nanotube carbon network, agrees—given its simplicity—very reasonably with the PL data with regard to the interband transition energies $E_{11}^S$ and $E_{22}^S$. These results support strongly the view that curvature effects cannot be neglected—also for SWNTs having moderate to large diameters, such as PLV nanotubes with a mean diameter of $\sim 1.3$ nm.

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