

## Midgap luminescence centers in single-wall carbon nanotubes created by ultraviolet illumination

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The authors report the effect of ultraviolet (UV) illumination on optical properties of single-wall carbon nanotubes (SWCNTs) isolated using various dispersants. It is demonstrated that even weak UV light ( $\sim 1 \text{ mW/cm}^2$ ) can irreversibly alter the SWCNT structure, thus resulting in the emergence of hitherto unknown, redshifted photoluminescence (PL) peaks with concomitant reduction in some of the original PL peaks. These UV-induced changes are characterized in detail and attributed to the creation of midgap PL centers. © 2006 American Institute of Physics.

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Optoelectronic applications of single-wall carbon nanotubes (SWCNTs) critically hinge on the development of means to design and control relevant properties. One of such important properties is photoluminescence (PL), which is a very sensitive and versatile probe of electronic states of materials. The analysis and tunability of PL from SWCNTs (Ref. 1–5) constitute an essential step leading towards the applications of SWCNTs.

The present letter reports an unprecedented method to shift PL peaks of SWCNTs by a very simple treatment, namely, shining weak ultraviolet (UV) light on dispersant-aided dispersion of SWCNTs. We show that this shift is triggered by the interaction of SWCNTs with UV-excited dispersants which eventually creates one-dimensionally (1D) confined defect states.

SWCNTs (CoMoCAT, purchased from Southwest Nanotechnologies), showing a narrow PL spectrum with fewer peaks, have been chosen as a starting material to facilitate spectral analysis. Note that essentially the same results were obtained for other SWCNTs such as HiPCO (Carbon Nanotechnology Inc.). Sample preparation and measurements were performed at room temperature. Dispersants were dissolved in  $\text{D}_2\text{O}$  to increase IR transparency at a concentration of 10 g/l. As dispersants, sodium carboxymethylcellulose<sup>6</sup> (CMC) and sodium dodecylbenzenesulfonate (SDBS) were mainly used, while several others were also tried. Then SWCNTs were added at a concentration of 0.3 g/l, sonicated for 20 min (20 kHz,  $\sim 130 \text{ W}$ ), and ultracentrifuged for 5 h at  $\sim 150\,000 \text{ g}$ . Films were prepared by casting. Some films were detached from the silica substrates and mechanically stretched tenfold to partially align the SWCNTs.<sup>6,7</sup>

PL spectra were recorded with a custom-made setup, equipped with a diode laser (660 nm, intensity  $\sim 1 \text{ W/cm}^2$ ) and a nitrogen-cooled InGaAs photodiode array. For polarization measurements, the laser was depolarized, and the polarization of PL was analyzed in terms of the “alignment ratio” of PL signals polarized parallel or perpendicular to the stretch direction.<sup>6,7</sup> PL excitation (PLE) maps were obtained using a Fluorolog FL3-2TRIAx spectrofluorometer.

Sample illumination due to PL or absorption measurements did not induce any detectable photochromic changes. Changes were generated by *in situ* UV illumination with a 20 W  $\text{D}_2$  lamp ( $\sim 1 \text{ mW/cm}^2$  at the sample surface). The lamp spectrum is mostly concentrated in the 190–400 nm range peaking at 200 nm (see inset in Fig. 3). Film samples were kept in vacuum ( $\sim 10^{-3} \text{ Torr}$ ) to avoid polymer photo-oxidation. The spot size and sample thickness were chosen so as to produce homogeneous illumination and induce negligible sample heating.

Most representative results were obtained using CMC dispersant, which produces concentrated, stable SWCNT dispersions.<sup>6</sup> All results appeared very similar for solutions and films and will mostly be presented for the film samples unless otherwise mentioned.

Figure 1 outlines a summary of the PL changes induced in a CMC/CoMoCAT film by  $\text{D}_2$  lamp: illumination reduces PL intensity by approximately ninety percent in a time scale  $\tau \sim 15 \text{ min}$  followed by saturation of changes. While PL intensity decreased, no significant spectral changes could be detected after such short-term processing. Besides, interrupting illumination at this stage resulted in *full recovery* of PL (and absorption, *vide infra*) within 1 h. However, longer

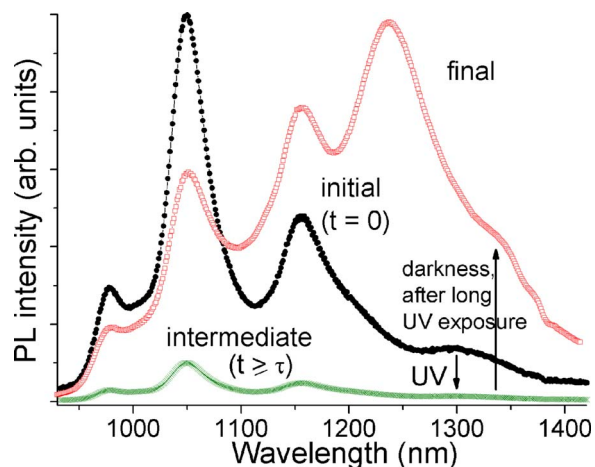


FIG. 1. (Color online) Summary of variations in PL spectrum (660 nm excitation) from a CMC/CoMoCAT film induced by 20 W  $\text{D}_2$  lamp illumination. No extra peaks were detected in the 1450–1640 nm range.

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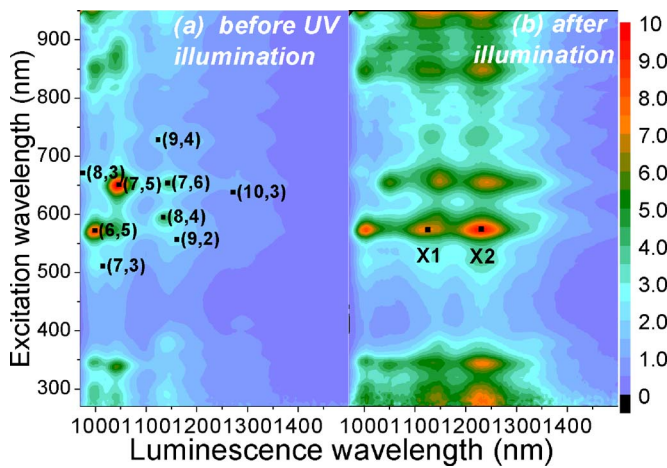


FIG. 2. (Color online) PLE maps from a CMC/CoMoCAT film before (a) and after (b) UV illumination.

(>2 h) illumination induced significant *irreversible* alterations, as shown by the “final” spectrum in Fig. 1: the peaks at 980, 1050, and 1150 nm weaken, and an additional strong signal appears at  $\sim 1235$  nm. Note that these changes could only be observed *a few hours after* turning off  $D_2$  lamp, but not during or immediately after illumination; they were stable for at least 6 months and could not be reversed by annealing (100–250 °C, 1 h).

More detailed and important information on the described changes was obtained by measuring PLE maps before [Fig. 2(a)] and after [Fig. 2(b)] UV illumination. These maps are generally interpreted as follows: PL peaks ( $X$  scale) correspond to the  $S_{11}$  transitions between the first pairs of the van Hove singularities; the PLE peaks ( $Y$  scale) in the range 800–1000 nm have been assigned to the phonon-assisted  $S_{11}$  transitions,<sup>8</sup> while those in the ranges 450–770 and 270–400 nm are attributed to the  $S_{22}$  and  $S_{33}$  transitions, respectively. The  $S_{22}/S_{11}$  pairs identify<sup>9</sup> the SWCNT chirality numbers as indicated in parentheses in Fig. 2(a). Here it is important to note that all the PL peaks in the unilluminated sample [Fig. 2(a)] exhibit *different* PLE spectra.

The PLE map of Fig. 2(a) is drastically altered by  $D_2$  lamp illumination: for the 573 nm excitation of the (6, 5) tube, Fig. 2(b) reveals that two additional PL peaks, labeled as X1 and X2, appear at 1125 and 1230 nm. These two peaks exhibit *similar* PLE spectra that also resemble that of the original 1000 nm PL peak. A similar change occurs for the 650 nm excitation of the (7, 5) tube. Two peaks emerge at the longer wavelengths; however, the original 1050 nm peak considerably decreases here, apparently indicating PL intensity transfer from the latter to the former peaks. Remarkably, all the PLE features have comparable linewidth, but the width of PL lines is larger for the UV-induced than for the “original” PL peaks, thus resulting in the oval-shaped features in Fig. 2(b).

PL spectra similar to those in Fig. 1 [mainly due to (7, 5) tubes] were also recorded from stretched CMC/SWCNT films in which SWCNTs are partially aligned in the stretch direction (not shown). The whole PL spectrum of the unilluminated samples showed an alignment ratio  $\sim 5$ , in accordance with our previous results<sup>6,7</sup> obtained for HiPCO SWCNTs. Remarkably, a similar alignment ratio  $\sim 5$  was observed for the UV-induced 1150 and 1240 nm peaks as well. This result means that both the UV-induced and the

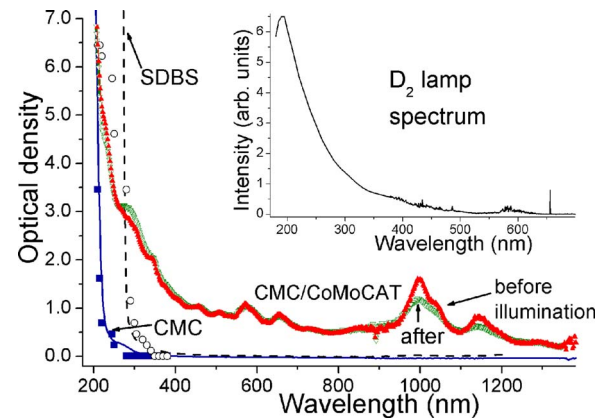


FIG. 3. (Color online) Absorption spectra of a CMC/CoMoCAT film before (solid triangles) and after (open triangles) UV illumination. No extra SWCNT-related peaks could be detected in the range 1400–3200 nm. Solid and dashed lines present absorption spectra from 10 g/l  $D_2O$  solutions of pure CMC and SDBS, respectively. Solid squares and open circles show PL quenching spectra in a CMC/CoMoCAT film and a SDBS/CoMoCAT solution, respectively. The inset presents the  $D_2$  lamp spectrum.

original electronic states have a similar anisotropic nature, implying electronic delocalization along the tube axis.

The absorption spectra from the CMC/SWCNT sample used for Figs. 1 and 2, before and after UV illumination, are presented in Fig. 3. Right after  $D_2$  lamp illumination for 15–180 min, the  $S_{11}$  peaks, appearing in the range 900–1400 nm, but not the  $S_{22}$  and  $S_{33}$  peaks, are reduced by half. However, contrary to the irreversible PL changes occurring after >2 h illumination, the absorption changes always did recover within a few hours.

In contrast to PL, PLE, and absorption results, no detectable UV-induced changes were observed in Raman spectra (not shown), excited at 632.8 nm, in the breathing,  $G$  or  $D$  modes.

In the previous paragraphs, the UV illumination effects were presented for CMC/SWCNT films. However, similar alterations could also be produced when CoMoCAT (or HiPCO) SWCNTs were dispersed with other agents (hydroxyethylcellulose,<sup>6</sup> SDBS, sodium dodecylsulfate, etc.). On the contrary, no PL changes could be detected when the dispersant was removed before UV illumination, showing that the dispersant plays an essential role in this phenomenon. It is worthwhile to note that the response time  $\tau$  and the position of the UV-induced PL peaks varied significantly depending on the dispersant (by a few tens of nanometer).

To reveal which spectral component of the UV light induces the PL changes, the  $D_2$  lamp was filtered with long-pass filters, whose cut-off wavelength was progressively decreased. The thus obtained “PL quenching spectra” are presented by squares and circles in Fig. 3 for two representative samples: a CMC/SWCNT film and an SDBS/SWCNT solution. These spectra exhibit abrupt thresholds at  $\sim 250$  and 300 nm, which match the absorption thresholds of CMC and SDBS, respectively (lines in Fig. 3). Here the PL quenching is defined as  $I(0)/I(\tau) - 1$ , where  $I(t)$  is time-dependent PL intensity, which corresponds to the “reversible” part of the PL change.

The data summarized above allow us to build a phenomenological description of the UV-induced changes as follows.

- (1) The alterations in PL from SWCNTs are triggered by the UV excitation of the dispersant. This conclusion origi-

nates from the close match between the excitation spectra of the PL quenching and the absorption spectra of the dispersant (Fig. 3), and from the lack of PL changes in the absence of dispersant. This result unambiguously manifests electronic interaction between the SWCNTs and UV-excited dispersants.

- (2) The time evolution of the UV-induced changes occurs in two steps: (i) PL quenching ( $t \sim \tau$ ) and (ii) modification of PL spectra ( $t \gg \tau$ ). The first step is fully reversible. The concomitant reduction in  $S_{11}$  absorption suggests UV-induced electron injection into the conduction bands (or hole injection into the valence bands) of SWCNTs. We assume that these doping-induced, “metallic” states induce PL quenching by providing additional excitation relaxation channels. Once UV illumination is terminated, reverse charge transfer occurs, fully restoring the original absorption and PL. The larger reduction of PL than of absorption signals could be explained by the stronger dependence of the PL on the relaxation process.
- (3) When UV illumination time exceeds  $\tau$ , the irreversible, second step comes into effect. We suggest that this process originates from the UV-induced, doped states, eventually creating hitherto unknown luminescent defects. The PL peaks originating from these defects are not observable immediately after the termination of this prolonged UV illumination, possibly because PL quenching by the doping-induced metallic states remains operative. As these metallic states disappear, the UV-induced PL peaks emerge gradually (Fig. 1).
- (4) The redshift of the PL peaks implies that these UV-induced defects have luminescent states in the forbidden gap of SWCNTs. The aforementioned polarization dependence of PL reveals strong anisotropy of the defects along the film stretching direction, indicating 1D delocalized, rather than dotlike nature of these states. Note that these UV-induced features appear broader than the parent peaks (see Fig. 2), possibly due to the defect-related disorder, in agreement with the proposed the defect-related origin.
- (5) The fact that no UV-induced features could be detected in absorption (Fig. 3), PLE (Fig. 2), and Raman spectra (not shown) suggests that the SWCNT’s structure remains mostly intact and that the density of the created defects is low. Nonetheless, the UV-induced PL peaks

dominate over the original ones, probably because excitons migrating along 1D SWCNT can be very efficiently trapped by these sparse defects.

The present results have established the creation and existence of midgap luminescent states in SWCNTs. While a UV-induced change in PL from 0.4 nm thick SWCNTs grown in zeolite has been reported before,<sup>10</sup> the range of UV intensity used ( $\sim 100$  W/cm<sup>2</sup>), the way PL changes, and the underlying mechanism seem completely different from those observed here. It is rather surprising that relatively weak UV illumination ( $\sim 1$  mW/cm<sup>2</sup>) can induce such drastic PL changes, provided that SWCNTs coexist with a dispersant. This observation suggests necessity for precaution against SWCNT degradation when handling dispersed SWCNT samples. On the positive side, however, these results could be of technological importance as they provide unprecedented means to tune the emission wavelength of SWCNTs, as we indeed found that different dispersants resulted in differently shifted PL peaks.

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