Time-Resolved Fluorescence of Carbon Nanotubes and Its Implication for Radiative Lifetimes

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The temporal evolution of fluorescence from isolated single-wall carbon nanotubes (SWNTs) has been investigated using optical Kerr gating. The fluorescence emission is found to decay on a time scale of 10 ps. This fast relaxation arises from nonradiative processes, the existence of which explains the relatively low observed fluorescence efficiency in isolated SWNTs. From the measured decay rate and a determination of fluorescence quantum efficiency, we deduce a radiative lifetime of 110 ns.

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Since their discovery in 1991 [1], carbon nanotubes have revealed remarkable mechanical [2], thermal [3], and electrical properties [4–6]. With diameters on the order of 1 nm and the existence of both semiconducting and metallic nanotubes, these materials have been of great interest as models for one-dimensional electronic transport, as well as for potential applications in nanoelectronics. Indeed, field-effect transistors have already been fabricated from single nanotubes [7,8] and have shown the ability to sustain current densities in excess of 10^{12} A/m^2 and to exhibit favorable switching characteristics. The interaction of nanotubes with light is also a subject of fundamental importance, and one with equal potential for applications for ultracompact tunable emitters and detectors. Despite the predicted direct-gap character of carbon nanotubes and the strongly peaked joint density of states anticipated for the band edge of one-dimensional systems, for years no measurable light emission could be observed from nanotubes. Recently, however, there have been reports of both band-gap photoluminescence [9] and electroluminescence [10] from isolated single-walled nanotubes (SWNTs). Despite these experimental observations, the radiative and nonradiative relaxation pathways in SWNTs remain poorly understood. In particular, no information is available on the basic parameter of the *radiative lifetime* of excited nanotubes. In addition, the origin of the low fluorescence quantum efficiency ($< 10^{-3}$) reported experimentally [9,11] is uncertain. Does this behavior reflect the weakness of radiative transitions or, conversely, the strength of competing nonradiative relaxation channels?

In this Letter, we present the first experimental determination of the fluorescence lifetime of isolated SWNTs. Our study shows that the decay of the fluorescence of the isolated SWNTs after excitation by a single electron-hole pair occurs on a time scale of 10 ps. Combining this result with a determination of the absolute fluorescence quantum efficiency (QE), we deduce the *radiative lifetime* of an electron-hole pair in SWNTs. A value of $\tau_{\mathrm{rad}} = 110$ ns is obtained. While this lifetime exceeds that of allowed transitions in many molecular systems, it still corresponds to a relatively rapid emission rate compared with that associated with forbidden transitions. A major conclusion of these measurements is thus that the low fluorescence QE observed experimentally reflects the strength of nonradiative decay channels, which we identify as trapping at defects, rather than any inherent weakness of the radiative decay channel. We complement these experimental investigations with a calculation of the expected radiative lifetime for SWNT within the simple tight-binding model of the electronic structure.

A critical aspect of the present experiment is the use of SWNTs that are *isolated* from one another. In most samples, strong intertube van der Waals interactions cause SWNTs to aggregate into bundles. Time-resolved spectroscopy of these nanotube bundles reveals extremely rapid excited-state relaxation (~ 1 ps) [12,13]. This behavior is attributed to intertube energy transfer from the semiconducting to the metallic nanotubes within each bundle [12], followed by rapid nonradiative carrier cooling in the metallic nanotubes [13]. The intertube relaxation processes explain why no measurable fluorescence has been reported from bundled samples. To examine isolated nanotubes, we follow the procedure recently introduced by O'Connell *et al.* [9] to obtain isolated SWNTs encapsulated in micelle-like cases. These nanotubes exhibit distinct absorption and photobleaching [14] features, as well as measurable fluorescence emission. They permit us to probe the *intrinsic* carrier relaxation processes of individual SWNTs, free from the complications of the intertube interactions.

The sample used in our measurements consisted of a suspension of isolated SWNTs prepared from a stock of nanotubes grown by the high-pressure CO procedure [15,16]. In analogy with Ref. [9], the isolated SWNTs were produced by vigorous sonication in an aqueous solution of poly(acrylic acid) [(PAA), molecular weight $\sim 60\,000$, 1% w/v]. The suspension was centrifuged at an acceleration of 110 000 g and the supernatant was collected. To verify that we had indeed isolated SWNTs, we examined the resulting nanotubes by atomic force microscopy (AFM). Figure 1 shows the

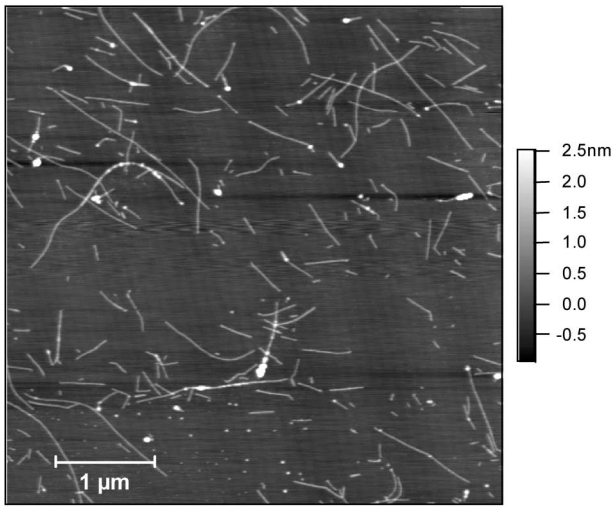

FIG. 1. AFM image of isolated nanotubes deposited on mica. The nanotubes are ~1 nm in height, as expected for isolated SWNTs.

image of the nanotubes obtained after dispersing them on mica. The nanotubes have a height of ~1 nm, as expected for individual (unbundled) SWNTs. Recently, simultaneous Raman and fluorescence spectra at the single nanotube level were obtained from similarly prepared SWNTs [17]. From their findings, the authors concluded that the micelle samples do in fact consist of individual SWNTs. AFM measurement of lengths of 175 nanotubes shows that most of them are between 100–500 nm long (~ 70%), with an average length of 380 nm.

The absorption and fluorescence spectra of our sample are shown in Fig. 2. Signatures of both the metallic and semiconducting nanotubes are clearly seen in the absorption spectra. The peaks in the 900–1400 nm and 600–900 nm regions correspond, respectively, to E_{11} and E_{22} transitions in semiconducting nanotubes [18,19]. The features between 400–600 nm arise, on the other hand, from the first Van Hove singularity of metallic nanotubes, as well as the absorption tail of the π-plasmon resonance [13]. The fluorescence appears in the 900–1400 nm range, the region corresponding to the band-edge E_{11} transitions in our semiconducting nanotubes. In the spectra, eight fluorescence peaks can be identified, with the largest contributions arising from SWNTs with (n, m) values of (7, 6), (12, 1), and (11, 3), according to the assignments made by Bachilo *et al.* [20]. Raman spectra of the sample were also obtained. They show strong radial breathing modes with Raman shifts corresponding to nanotubes of ~1 nm diameter. We also observed a weak D-band peak (2% of the strength of the G-mode feature) associated with defects in the nanotubes.

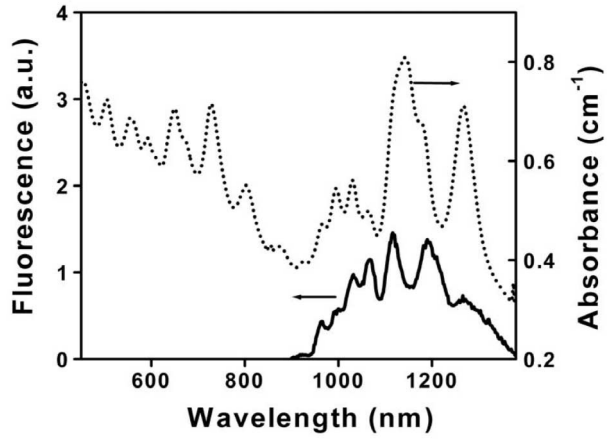

FIG. 2. Absorption (dotted curve) and fluorescence (solid curve; excitation wavelength 785 nm) spectra of isolated SWNTs suspended in PAA micelles in water.

Temporal decay of the fluorescence of the sample of isolated SWNTs was measured using excitation by ultrashort laser pulses in conjunction with optical Kerr gating [21,22]. The laser source for these measurements was an amplified mode-locked Ti:sapphire system, which delivers pulses of approximately 150-fs duration at a wavelength of 810 nm and a repetition rate of 1 kHz. The Kerr medium was a 3-mm-thick cell of CS_2 and an InGaAs photodiode was used as the detector. Our measurements were made at excitation fluences not exceeding 20 mJ/m^2. Using an estimate of the nanotube absorption cross section [19], this corresponds to an average of less than one excitation per (0.4 μm long) SWNT. The absolute quantum efficiency of the luminescence was $\eta = 1.7 \times 10^{-4}$. This value was determined by comparing the current of the calibrated photodetector to the rate of photon absorption from the optical excitation beam, including appropriate corrections for experimental efficiency factors and polarization dependence of the absorption and emission processes (both are predominantly oriented along the carbon nanotubes) [23].

A typical fluorescence decay curve for the sample of isolated SWNTs is displayed as the solid line in Fig. 3. It shows a dominant decay with a time constant of $\tau = 7$ ps, together with a weaker tail lasting several tens of picoseconds. We attribute the multiexponential nature of the decay to inhomogeneity of the nanotube sample. It should be stressed that the observed decay differs significantly from the more rapid decay in *nanotube bundles* [13], an effect attributed to intertube energy transfer.

From the results of the fast decay rate of the fluorescence, it is already apparent that the low fluorescence quantum yield originates from the presence of a process that rapidly quenches the fluorescence, rather than from the inherent weakness of the radiative transitions. While the data do not in themselves provide an unambiguous determination of the mechanism of this quenching effect, the evidence points towards the role of structural defects. To understand what might happen in the observed 7 ps time scale for fluorescence quenching, we determine the distance that a thermal electron in the conduction band of

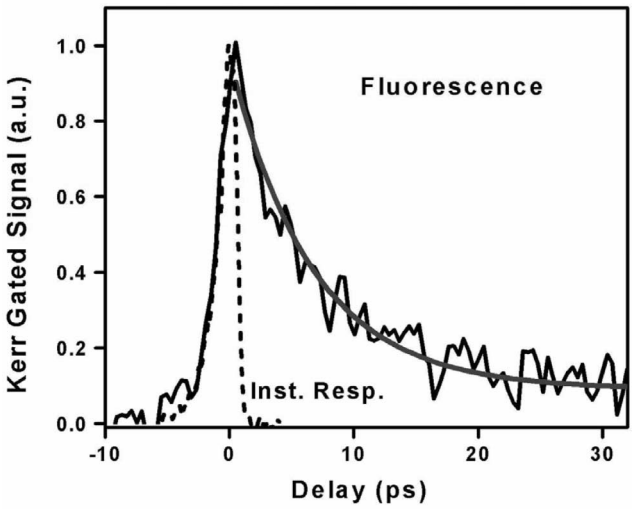

FIG. 3. Fluorescence decay of SWNTs (solid curve) as measured by the Kerr gating technique. The smooth solid line is a fit to a 7-ps exponential decay, with a weaker and slower tail. The dashed curve shows the response function of Kerr medium, as characterized by a spectrally filtered fs white light pulse introduced at time $t = 0$.

a nanotube (mass m $\approx 0.1 m_e$) would travel. We find that at room temperature the electron travels a distance of 2 μm, some 5 times the average length of the nanotubes in our sample. While this estimate neglects scattering, it indicates that it is likely that an electron will be able to find a defect site within the required time and the experimental decay rate can be understood unless the trapping probability is extremely low. The defects in our sample may arise during the growth process or may be introduced by the vigorous sonication. Indeed the weak *D*-band peak in the Raman spectra, as mentioned above, is a signature of the presence of defects. Defects in SWNTs were also seen in earlier studies by other approaches [24,25].

A direct experimental proof of the existence of trapping in an excited nonradiative state is provided by our complementary femtosecond time-resolved measurements of photoinduced bleaching. In these investigations, the same pump excitation was applied as in the time-resolved fluorescence measurements, but the band-edge absorption was recorded as a function of time delay in a standard pump-probe scheme. The results show a decay of the band-edge photoinduced bleaching at the same rate as seen in the time-resolved fluorescence data. In contrast to the latter, however, the photoinduced bleaching signal drops only to about half of its peak value. This result indicates that the carriers in the excited nanotubes undergo a rapid trapping process, which decouples them from the radiation field, but the system does not return to its *ground state*.

The lifetime for radiative emission from carbon nanotubes is one of the key parameters in understanding both the photophysics of these materials and in assessing possible applications in photonics and optoelectronics. Our experiment permits us to obtain this important information. In analyzing the data, we assume a constant radiative relaxation rate of $\gamma_{\mathrm{rad}} = (\tau_{\mathrm{rad}})^{-1}$ in all the nanotubes. We then write the rate of photon emission following initial excitation at time $t = 0$ as $\phi(t) = \gamma_{\mathrm{rad}} N_0 s(t)$, where $s(t)$, which represents the fraction of excited nanotubes that remain in the emissive state at time t, can be determined from the form of the measured fluorescence decay curve. It follows immediately that the radiative relaxation rate is given by $\gamma_{\mathrm{rad}} = \eta/\langle\tau_{\mathrm{exc}}\rangle$, where $\eta = (1/N_0)\int_0^\infty \phi(t)dt$ is the overall fluorescence QE, and $\langle\tau_{\mathrm{exc}}\rangle \equiv \int_0^\infty s(t)dt$ is the lifetime of the nanotubes in the radiative excited state. We use the experimental value of $\eta = 1.7 \times 10^{-4}$ and $\langle\tau_{\mathrm{exc}}\rangle = 18$ ps, the determination of which is discussed below. We thus obtain $\tau_{\mathrm{rad}} = 110$ ns for the radiative lifetime of our SWNTs.

The determination of the average excited-state lifetime $\langle\tau_{\mathrm{exc}}\rangle$ is carried out in two different ways. One is by means of a direct integration of the time-resolved fluorescence over a time interval of several hundred picoseconds. The presence of a long and relatively weak tail of the emission (not shown in Fig. 3) renders this process somewhat difficult, given the limited signal-to-noise ratio at long delay times. Consequently, we independently verified this value by calibrating the absolute sensitivity of the Kerr gate. This measurement permitted us to determine the fraction (40%) of the radiation that was emitted during the initial exponential decay of the fluorescence and to cross-check our result using explicit integration only over the region of time corresponding to the initial exponential decay. A possible concern in this determination might be the presence of a very fast relaxation process that we are unable to resolve fully with our Kerr gating technique. While such an effect cannot be entirely ruled out, the time-resolved photobleaching measurements described above did not indicate the existence of a faster trapping process, even on the 200 fs time scale accessible by this technique.

Can we understand the magnitude of the measured radiative lifetime of $\tau_{\mathrm{rad}} = 110$ ns theoretically? On a qualitative basis, the radiative lifetime is comparable, but somewhat longer, than allowed transitions in most molecular systems, which typically lie in the range of several nanoseconds. To examine this issue from the simplest quantitative standpoint, we treat the SWNTs as rolled-up graphene sheets having electronic states described within the tight-binding model that has been previously applied to the optical properties of nanotubes [26]. In the picture of free carriers at the band edge, the radiative lifetime τ^0_{rad} follows from the usual perturbation theory expression [27] of $\tau^0_{\mathrm{rad}} = n\omega_0^3\mu_{cv}^2/(3\pi\varepsilon_0\hbar c^3)$, where $\hbar\omega_0$ is the transition energy. We assume that the nanotube is embedded in a medium with a refractive index of $n = 1.33$ and evaluate the transition dipole moment μ_{cv} according to Ref. [19]. We then find a radiative

lifetime of $\tau_{\mathrm{rad}}^0 \sim 7$ ns, a value quite comparable to that of an allowed molecular transition. This result is valid in the limit of low temperatures where the electron and hole have identical (zero) momenta. At finite temperatures T, we obtain an increased radiative lifetime of

$$\tau_{\mathrm{rad}} = \sqrt{\frac{\pi k_B T}{2\Delta}}\tau_{\mathrm{rad}}^0, \qquad \left(k_B T \gg \Delta \equiv \frac{\pi^2\hbar^2}{2mL^2}\right), \qquad (1)$$

where Δ denotes the longitudinal quantization energy, m denotes the electron/hole effective mass, and L denotes the nanotube length. For the different tube structures identified in the fluorescence spectra, using average nanotube length ~380 nm, we obtain similar room temperature lifetimes of 180–240 ns.

The semiquantitative agreement with experiment obtained using the simple tight-binding model is somewhat surprising given the severe simplifications of the model compared to state-of-the-art *ab initio* calculations [28,29]. In particular, the tight-binding model entirely omits excitonic effects, which are expected to be very important in quasi-one-dimensional systems [30]. Theoretical investigations have indeed predicted significant *spectral modifications* induced by electron-hole interactions within SWNTs [29,31]. The expected influence of excitonic effects on *radiative lifetime* has not, however, been a focus of study to date. This subject has been considered in detail in the related context of semiconductor quantum wires fabricated by molecular-beam epitaxy [32]. It is hoped that the present experiments will provide an impetus for further theoretical studies on carbon nanotubes.

In conclusion, we have performed a time-resolved fluorescence measurement of isolated SWNTs by means of optical Kerr gating. The fluorescence decay is multiexponential, but exhibits a pronounced initial decay with a time constant of 7 ps. This fast nonradiative relaxation process explains the low quantum efficiency of fluorescence observed experimentally and indicates that significant improvement in the emission properties of nanotubes may be expected with improved synthetic approaches. From the time-resolved measurement and the absolute fluorescence QE, we infer a radiative lifetime of $\tau_{\mathrm{rad}} =$ 110 ns. In addition to serving as a stimulus for further theoretical investigation of the process of light emission for SWNTs, the present investigations should provide basic information needed to evaluate photonic and optoelectronic applications on carbon nanotubes, such as the expected efficiency of recently demonstrated electroluminescent devices [10].

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