Ultrafast Ground-State Recovery of Single-Walled Carbon Nanotubes

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The band-edge relaxation dynamics in isolated and bundled single-walled carbon nanotubes (SWNTs) were studied with ultrafast transient absorption spectroscopy. The loss of the excited state population was unexpectedly fast, with $> 90\%$ of the transient absorption signal recovering in a few hundred fs. For isolated SWNTs in resonance with a SWNT electronic transition, a novel relaxation pathway was observed, characterized by a relatively slow signal recovery (> 100 ps). We ascribe this relaxation pathway to the decay of excited electrons from the band-edge.

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Single-walled carbon nanotubes (SWNTs) have attracted much attention recently because of their unique physical properties [1] and potential applications [2–6]. Optical studies, such as resonance Raman scattering [7], absorption [8], and fluorescence [9–11] spectroscopies, have provided insight into various aspects of the electronic structure of this important material. However, many crucial parameters of electronic structure, such as the radiative and nonradiative lifetime of the first excited state, are yet to be determined. These lifetimes fundamentally determine the photoluminescence quantum efficiency and the relative strength of resonant linear and nonlinear optical processes and thus are relevant for potential optoelectronic applications.

Time-resolved nonlinear optical spectroscopy is a powerful method for determining the electronic structure that complements linear optical studies. Despite numerous linear optical studies on SWNTs, time-resolved nonlinear optical studies have been limited. Early measurements of excited-electron dynamics of SWNT bundles found a bi-exponential decay with time constants of 200 fs and a few ps, attributed to thermalization via electron-electron and electron-phonon scattering, respectively [12]. However, due to the use of visible excitation, these results represented dynamics from a complicated continuum of highly excited electronic levels. Carrier dynamics on SWNT bundles with resonant excitation found recovery times of ~ 1 ps [13]. However, complicated effects of intertube coupling [14] prevented hard conclusions about the intrinsic properties of a single nanotube. More recently, saturated absorption (without carrier dynamics) was observed for isolated SWNTs [15] and ultrafast electron-electron interactions were observed in SWNT bundles [16].

Here, we present studies of the ultrafast relaxation of photoexcited electrons in both bundled and isolated SWNTs using transient absorption spectroscopy with resonant infrared excitation of the lowest excited state (E_{11}). Transient absorption spectra of all samples showed absorption saturation. Over 90% of the absorption bleach signal recovered in a few hundred fs and the remainder recovered in a few ps, which is extremely fast. We ascribe this fast signal to intraband relaxation in SWNT bundles. For isolated SWNTs in micelles, an additional signal decay component was observed with a characteristic time > 100 ps, which has not been previously reported. This very slow relaxation, which strongly depended on resonant excitation, is attributed to the lifetime of photoexcited electrons in semiconducting SWNTs.

SWNTs produced by HiPco (H-SWNTs), laser oven (L-SWNTs), and arc discharge (A-SWNTs) processes were purchased from Carbon Nanotechnologies Inc., Tubes@Rice, and BuckyUSA, respectively. Thin-film SWNT bundle (B-SWNTs) samples were prepared by drying 2–3 drops of a dispersion of SWNTs in hexane onto a glass cover slip. Stable SWNT suspensions in D_2O were obtained by isolating individual SWNTs in surfactant micelles using methods described in Ref. [9]. Absorption and fluorescence spectra of SWNTs in micelles (Mic-SWNTs) showed distinct spectral features corresponding to SWNTs with different diameters and chiralities (i.e., different (n, m) values); optical spectra were essentially identical to those previously reported [9,10]. Fluorescence quantum yields (QY) were measured relative to the organic dye IR #26, which has a QY $\sim 5 \times 10^{-3}$ [17]. The average optical density of the Mic-SWNT (B-SWNT) samples was $\sim 0.4(0.6)$ at the first electronic resonance.

Transient absorption data were obtained using a standard pump-probe setup, with excitation provided by a Ti:sapphire regenerative amplifier pumped optical parametric amplifier. Typical peak pump intensities were $I \sim 5$ GW/cm^2 and typical pulse widths were 130 fs. Excitation wavelengths were tuned between 1170 and 1550 nm, in resonance with the lowest electronic transition in SWNTs with diameters between 0.75 and 1.0 nm. For two-color experiments, a white-light continuum served as the probe and a monochromator resolved responses for different probe wavelengths. To improve sensitivity, a portion of the probe beam was split before the sample for a reference.

Typical transient absorption responses as a function of probe delay are shown in Fig. 1. All samples showed absorption saturation, as expected for resonant excitation

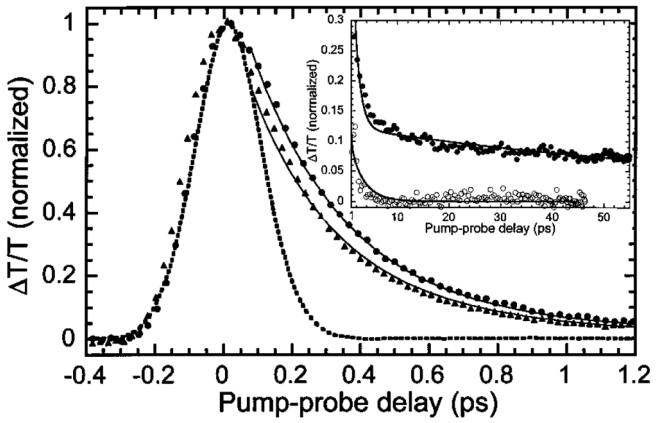

FIG. 1. Normalized one-color transient absorption of B-H-SWNTs (triangles) and Mic-H-SWNTs (circles) with the autocorrelation of the laser pulse (dashed line) with excitation at 1350 nm (nonresonant). The solid lines are curve fits to a bi-exponential function with time constants of 230 fs and 1 ps for the bundle sample and 330 fs and 2 ps for the isolated sample. Inset: Long time response (> 1 ps) of B-H-SWNTs (open circles) and Mic-H-SWNTs (solid circles) with pump and probe at 1250 nm. The solid line is a bi-exponential fit with time constants of 700 fs and 120 ps and 300 fs and 2 ps for Mic-H-SWNTs and B-H-SWNTs, respectively.

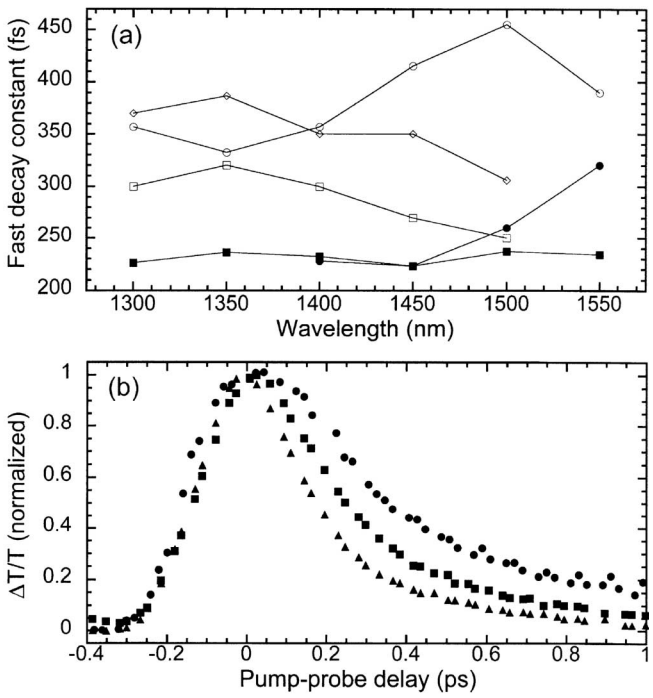

FIG. 2. (a) Subpicosecond decay constant of Mic-H-SWNTs (open squares), B-H-SWNTs (solid squares), Mic-L-SWNTs (open circles), B-L-SWNTs (solid circles) and Mic-A-SWNTs (open diamonds) as function of pump wavelength in one-color experiments. (b) Normalized transient absorption signals for SWNTs pumped and probed at 1500 nm. The circles, squares, and triangles correspond to Mic-L-SWNTs, Mic-A-SWNTs, and Mic-H-SWNTs, respectively.

of a quasi-two-level system. The differential transmission of the probe beam ($\Delta T/T$) ranged from 1% to 8% for Mic-SWNTs and ~10% for B-SWNTs and the signal decayed bi-exponentially. For B-SWNTs, more than 90% of optical bleach disappeared in a few hundred fs, while the remainder completely recovered with a slower time constant of a few ps. For Mic-SWNTs, similar fast responses were obtained when not directly exciting a SWNT electronic state. However, with resonant excitation a slow component was observed (> 100 ps), as shown in the inset of Fig. 1. All decay times were independent of excitation intensity in the range $I = 1$ to 20 GW/cm^2.

Responses from SWNTs prepared by different methods are illustrated in Fig. 2(b), and the respective time constants of the fast component as a function of excitation wavelength are listed in Fig. 2(a). SWNTs prepared by different methods had slightly different temporal responses, but all samples exhibited unusually fast lifetimes between 220 and 420 fs. No clear trend between diameter and fast decay time was found for A-SWNTs or H-SWNTs, and only a slight dependence for L-SWNTs [Fig. 2(a)].

Assuming Mic-SWNTs are comprised of solely individual nanotubes in micelles, the loss of electrons from the optically pumped state was unexpectedly fast, since the simplest thinking suggests that an ideal semiconducting nanotube should have no efficient nonradiative pathway. Films of pure C_{60} (which also has a well defined energy gap) have decay times of ~30 ps [18]. By contrast, for SWNTs the fast decay time was only ~100 fs longer than lifetimes for electrons pumped into a continuum of excited states well above the band edge [12]. Thus, the origin of this fast decay, for both Mic-SWNTs and B-SWNTs, is likely intraband nonradiative processes [12].

To further investigate why intraband nonradiative processes dominate the response of Mic-SWNTs, we performed two-color pump-probe experiments, shown in Fig. 3. The pump wavelength was set to 1250 nm, directly populating the E_{11} state for (10, 3) and (10, 5) SWNTs. For all probe wavelengths longer than 1250 nm, the maximum in $\Delta T/T$ occurred at zero pump-probe delay, and the initial subpicosecond component was basically unchanged from the one-color experiments. However, probing directly on resonance, an additional long-lived decay was observed with a characteristic time > 100 ps that accounted for ~20% of photobleaching signal. Further, this decay time became significantly faster when the probe was tuned away from resonance. For example, the long-lived decay was ~120 ps with the probe wavelength at 1250 nm, it became as short as 10 ps at 1280 nm, and most interestingly it became slow (~ 120 ps) again when the probe was resonant with E_{11} for (13, 2) SWNTs (~ 1300 nm). In addition to the decay time itself, the relative percentage of the bleach signal associated with the longer decay time decreased when off resonance. We observed similar behavior of this

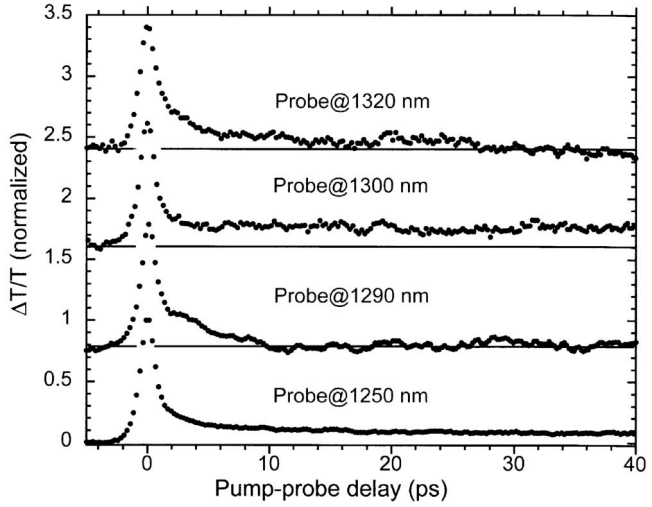

FIG. 3. Two-color transient absorption spectra for Mic-H-SWNTs with pump wavelength = 1250 nm.

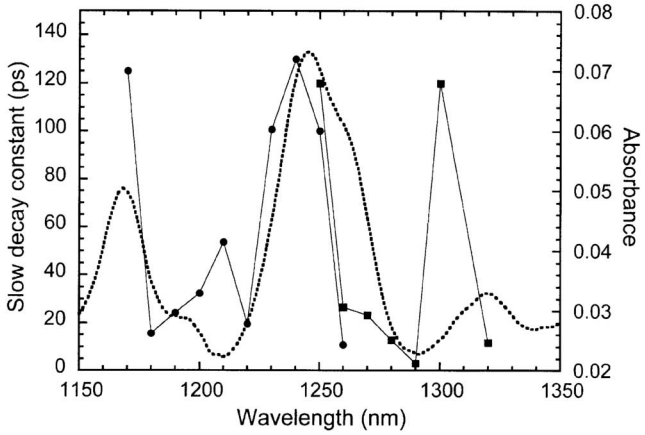

FIG. 4. Absorption spectrum (dashed line) and slow decay constant of Mic-H-SWNTs as a function of probe wavelength (solid line). The circles and squares correspond to pump at 1170 nm and 1250 nm, respectively.

long-lived signal component for excitation at 1170 nm (Fig. 4). Although we found generally good agreement between both the relative magnitude and decay time of the long-lived signal component and the Mic-SWNT absorption spectrum, for some nanotube structures [such as the (11, 3) nanotube resonant at 1200 nm] we did not observe any very slow decay. We attribute these few discrepancies to the relatively low concentration of these particular SWNTs in our samples.

Because of the close association between a nanotube electronic resonance and the emergence of the slowly recovering signal component, we propose that the long-lived portion of the signal corresponds to the lifetime of photoexcited carriers at the band edge of isolated semiconducting SWNTs, ~120 ps. This value agrees with an estimate of the excited state lifetime (~ 100 ps) obtained using Fourier-transform infrared photoluminescence [19] and is also consistent with an upper bound for the fluorescence lifetime of 1.2 ns using time-correlated photon counting spectroscopy in the infrared (excitation at 1030 nm and fluorescence energies ranging from 1050 to 1280 nm).

Surprisingly, the SWNT nonlinear optical response was instantaneous for all probe wavelengths. This can be explained by the suggestion that Mic-SWNT samples actually contain a relatively large fraction of bundled nanotubes. For example, for B-SWNTs electronic state coupling between the various SWNTs [14] would result in instantaneous excitation at energies relatively far away from the direct pump wavelength. The suggestion that Mic-SWNT samples contain a large fraction of B-SWNTs is also consistent with many other observations. First, the fluorescence QYs for H-SWNTs and A-SWNTs are minute (QY $\sim 6 \times 10^{-4}$ and 8×10^{-4}), and the QY for H-SWNTs agrees with previous estimates (QY $\sim 10^{-3}$) [9]. However, despite the QY being 1000 times smaller than for typical organic fluorophores, photoluminescence from single nanotubes has been observed with a comparable signal to noise ratio [11]. Second, the fast decays for Mic-SWNT samples are hardly different from those for B-SWNTs. Third, two-color pump-probe data acquired approximately two months after preparation of a Mic-SWNT sample resulted in no evidence of a long decay component because the micelles likely coalesced to form B-SWNTs. An alternative possibility is that isolated SWNTs have a significant density of weakly absorbing electronic levels that mediate efficient nonradiative decay, in addition to the strongly absorbing van Hove transitions. However, such a possibility would imply that, when probing to the red of the excitation, the saturated absorption maximum would occur for a finite pump-probe delay, which was not observed.

The differential transmission signal can be used to determine the magnitude of the nonlinear absorption coefficient β and the imaginary part of the third-order nonlinear susceptibility $\mathrm{Im}[\chi^{(3)}]$. By fitting the pump-probe spectra to $\beta = \frac{\mathrm{Ln}(1+\Delta T/T)}{dI}$, and $\mathrm{Im}[\chi^{(3)}] = (c^2 n_0^2 \varepsilon_0/\omega)\beta$, where d is the optical path length, I is the excitation intensity, c is speed of light, n_0 is the weak-field refractive index, ε_0 is the permittivity of free space, and ω is excitation frequency [20,21], we obtained $\beta \sim 0.1$ cm/GW and $|\mathrm{Im}[\chi^{(3)}]| \sim 3 \times 10^{-12}$ esu for Mic-SWNTs. By comparison, a typical highly nonlinear semiconductor has $|\chi^{(3)}| \sim 10^{-13}$–$10^{-11}$ [22,23]. Although fairly large, the value for $|\mathrm{Im}[\chi^{(3)}]|$ is much smaller than what is expected based on calculations [$\chi^{(3)} \sim 10^{-9}$] [24]. This discrepancy is due in part to the relatively small percentage of semiconductor SWNTs, compared with metallic SWNTs and other graphitic particles that contribute to linear absorption but have a very weak nonlinear absorption. In addition, femtosecond pulses have a large bandwidth, which produces an averaged

nonlinear response over the highly frequency dependent $\chi^{(3)}$ [25].

The large resonant $\chi^{(3)}$ at wavelengths important to telecommunications combined with the ultrafast electronic response of SWNTs make this material potentially desirable for photonics applications such as THz optical switching. SWNTs are especially attractive because, unlike typical nonlinear optical materials, they not only have a fast "on" response, but their short excited state lifetime allows for the system to have a fast "off" response as well.

In summary, we have performed studies of ultrafast band-edge relaxation dynamics of Mic-SWNTs and B-SWNTs using both one-color and two-color pump-probe spectroscopy with resonant excitation. A new relaxation pathway with time constant longer than 100 ps was observed exclusively for Mic-SWNTs. The characteristic time of this relaxation had strong resonance dependence and is interpreted as the lifetime of photoexcited electrons in isolated semiconducting SWNTs.

Since our initial submission, similar observations have also been found through transient absorption spectroscopy (Ref. [26]) and photoluminescence lifetime measurements (Refs. [27,28]).

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