Auger-Assisted Ultrafast Fluorescence Measurement of Semiconductor Single-Walled Carbon Nanotubes

Fengrui Hu,† Zengle Cao,† Zheng Hua,† Qinfeng Xu,†∥ Ming Zheng,‡ Chunfeng Zhang,† Xiaoyong Wang,*† and Min Xiao*†§

†National Laboratory of Solid State Microstructures and School of Physics, Nanjing University, Nanjing 210093, China
‡Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States
§Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, United States
∥Department of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China

Supporting Information

ABSTRACT: In the Auger process of a semiconductor nanostructure, the recombination energy of higher-order excitons would be nonradiatively transferred to the lower-order ones, and only the last exciton left could emit a photon. Here we show that this exciton−exciton annihilation effect can be positively employed to develop a novel optical technique for ultrafast fluorescence measurement. Upon excitation with two laser pulse trains continuously delayed in time, the fluorescence intensity of semiconductor single-walled carbon nanotubes increases accordingly, with two lifetime components of several and tens to hundreds of picoseconds being clearly resolved.

KEYWORDS: Auger effect, exciton−exciton annihilation, ultrafast fluorescence, two-pulse excitation, single-walled carbon nanotubes

Optical studies of carrier decay dynamics in semiconductors can not only reveal the fundamental electronic properties of their energy level structures but also provide great guidance to their device applications, such as in lasers, photodetectors, optical switches, solar cells, and high-speed transistors. After about half a century of research efforts, several optical techniques have emerged and become mature to be used routinely in studying the transient absorption and emission properties of bulk semiconductors.1,2 With the size of semiconductors now being reduced to the nanometer scale in the quantum confinement regime, these optical techniques are naturally applied to the resulting nanostructures, mainly including pump−probe,4,6 time-correlated single-photon counting,4,6 optical Kerr gating,7 fluorescence upconversion,8 four-wave mixing, and excitation correlation (EC).10,11 Only at the single-nanostructure level have two other ultrafast techniques been borrowed from the field of atomic physics for antibunching12 and quantum interference13 characterizations. It would be interesting and of practical importance to see whether novel ultrafast optical techniques can be developed from any intrinsic optoelectronic property of semiconductor nanostructures that is not possessed by their bulk counterparts.

The Auger effect describes a unique and intriguing electronic decay process in semiconductor nanostructures whereby the exciton recombination energy can be nonradiatively transferred to other excitons or extra charges.1 To date, this effect has been the origin of various undesirable optical phenomena in semiconductor nanostructures, such as photoluminescence (PL) saturation10,14 and blinking15 and its subnanosecond lifetime also sets a stringent time limit within which one can operate with multiple excitons in solar cell16,17 and laser device4 applications. Here we show that the exciton−exciton annihilation effect in an Auger process can be positively employed to develop a novel optical technique for the ultrafast fluorescence measurement of semiconductor nanostructures. Upon excitation with two laser pulse trains continuously delayed in time, the fluorescence intensity of semiconductor single-walled carbon nanotubes (SWCNTs) increases accordingly, with two lifetime components of several and tens to hundreds of picoseconds being clearly resolved.

RESULTS AND DISCUSSION

Figure 1 presents schematic diagrams showing the interactions between the exciton energy levels of a single semiconductor nanostructure and two laser pulses with a time separation Δt. When Δt is much smaller than the exciton lifetime τexciton (Figure 1a), two excitons are prepared simultaneously in the semiconductor nanostructure right after the two-pulse excitation. The biexciton transfers its energy to the single exciton, and the exciton transfers its energy to the single exciton, leading to a nonradiative decay of the exciton.

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Δt ≪ τ_{exciton} at most one photon is emitted. If Δt ≫ τ_{exciton} (Figure 1b), the exciton generated by the first pulse has already decayed to its ground state by the time when the second pulse arrives, so that up to two photons can be registered. In other cases where Δt is comparable to τ_{exciton}, the probability of the presence of the first exciton and consequently for the Auger interaction decreases as Δt is continuously delayed, leading to a gradual increase in the total number of emitted photons from one to two. Thus, monitoring the fluorescence enhancement induced by the second pulse as a function of Δt would enable the radiative/nonradiative decay dynamics of the first exciton to be reliably mapped.

Figure 1. Schematic of the Auger-assisted ultrafast fluorescence measurement. (a) When the two laser pulses are incident on a single semiconductor nanostructure simultaneously or at a time separation Δt much smaller than the exciton lifetime τ_{exciton} at most one photon is emitted. (b) When Δt ≫ τ_{exciton} up to two photons can be emitted after these two laser pulses.

To test the validity of the above proposal for Auger-assisted ultrafast fluorescence (AUF) measurement at room temperature, we chose SWCNT as a representative semiconductor nanostructure whose Auger recombination of multiple excitons has already been documented in the literature.\[1,15,19\] The CoMoCAT SWCNTs were dispersed in single-stranded DNA using previously published methods\[20\] or alternatively processed to be highly enriched in the (6,5) chirality,\[21\] but similar ultrafast optical results were obtained from the above two samples.

Figure 2a shows the PL spectrum of a solid film of ensemble SWCNTs excited at 800 nm, and the two PL peaks at ~913 and ~995 nm can be assigned to the (9,1) and (6,5) chiralities, respectively.\[20\] The PL spectrum of the (9,1) SWCNTs was distorted to some degree by the 900 nm long-pass filter used in our experiment for signal detection. In the following, we will focus on the SWCNTs with (6,5) chirality, whose PL excitation (PLE) spectrum monitored at 995 nm is displayed in Figure 2b. The PLE peak at ~850 nm is ~0.2 eV in energy above the PL one and originates from an exciton–phonon bound state involving tangential vibrations of optical LO phonons.\[22,23\] When the excitation wavelength was set at 850 nm, the PL intensity of (6,5) SWCNTs showed saturation behavior with increasing single-pulse laser power (Figure 2c) due to the Auger-induced exciton–exciton annihilation effect.\[14\] On the basis of Figure 2c, the number of excitons generated per pulse in an individual SWCNT at a specific laser power can be calculated, as can be seen in Figure S1 in the Supporting Information. Similar PL saturation behavior was observed in (6,5) SWCNTs excited at other wavelengths (e.g., 800 and 820 nm) although the PL intensities were relatively lower than that from the 850 nm excitation with the same laser power. As shown in Figure S2 in the Supporting Information, no significant changes were observed in the SWCNT PL peak and spectral line shape with increasing laser power since they are dominated by the recombination of single excitons.

Next, we split the 850 nm pulsed laser into two beams and attempted the AUF measurement for the (6,5) SWCNTs. The PL spectra measured at several specific time delays between the two laser pulses are shown in Figure S3 in the Supporting Information for a representative laser power of 30 mW at each beam. The spectrally integrated PL intensity calculated from the PL spectrum measured at each time delay is shown in Figure 3 for two representative laser powers of 30 and 50 mW at each beam. When the two pulse trains were positively or negatively delayed from the zero point, the PL intensity of SWCNTs increased accordingly, which can be interpreted in terms of the simplifying AUF scheme shown in Figure 1. As fitted in Figure 3, the PL intensity I(t) can be best described by the biexponential function\[I(t) = I(\infty) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}\]

where I(\infty) is the PL intensity at infinite time delay and \(\tau_1\) (\(\tau_2\)) and \(A_1\) (\(A_2\)) are the lifetime and amplitude of the fast (slow) decay component, respectively. The fitted I(\infty) value is almost twice that of the SWCNT PL intensity measured with single-pulse excitation. Both the fast and slow lifetime components showed up as the laser power of each pulse train was set even

Figure 2. (a) PL spectrum of CoMoCAT SWCNTs excited at 800 nm. The two peaks at ~913 and ~995 nm can be assigned to the (9,1) and (6,5) chiralities, respectively. (b) PLE spectrum monitored at the 995 nm emission peak of (6,5) SWCNTs. (c) Laser power dependence of the spectrally integrated PL intensity of (6,5) SWCNTs showing the saturation effect.
below the PL saturation point. The changes in $t_1$ and $t_2$ have no significant trend with increasing laser power, with average values around $\sim 3.5$ ps (Figure 4a) and $\sim 100$ ps (Figure 4b), respectively, but their amplitude ratio $A_1/A_2$ is $\sim 2.5$ at low power and approaches a constant value of $\sim 4.0$ at high power (Figure 4c).

From the AUF curves in Figure 3, we can define a parameter of intensity depth as the difference between the PL intensities measured at infinite and zero time delays, i.e., $I(\infty) - I(0) = A_1 + A_2$, as can be derived from the biexponential fitting function. When the exciton number $\alpha$ prepared by each pulse in a single SWCNT is less than 1, a proportion $\beta$ of it is dissipated nonradiatively at zero time delay as a result of the finite biexciton generation probability even at low laser power. This fractional exciton number $\alpha$, which would be recovered gradually with increasing time delay, is proportional to the intensity depth or, alternatively, the enhanced fluorescence contributed from the second pulse. When the laser power is increased, so are $\alpha$ and $\beta$, and the associated intensity depth, which would stay at a constant value after the condition of $\alpha \approx 1$ is achieved since the second pulse can provide at most one fluorescent exciton. This transient saturation behavior predicted from the AUF scheme in Figure 1 is shown in Figure 4d, where the intensity depth is plotted as a function of the laser power at each beam.

Using the traditional pump–probe technique, we measured the transient absorption (TA) dynamics of solution (6,5) SWCNTs at pump and probe laser wavelengths of 800 and 990 nm, respectively. The laser power was set such that the average number of excitons generated per pulse within each SWCNT was less than $\sim 0.1$. As shown in the inset of Figure 3 by a biexponential fit of the TA curve, two decay components of $\sim 1$ and $\sim 83$ ps were detected with an amplitude ratio of $\sim 5.4$. Since the $\sim 3.5$ ps decay component resolved from the AUF curves in Figure 3 is close to the laser pulse width of $\sim 3.3$ ps, we can verify that the newly developed AUF method and the traditional pump–probe technique yielded similar exciton decay dynamics.

As a result of the extremely low fluorescence quantum efficiency and both the transient absorption and emission curves of semiconductor SWCNTs are dominated by nonradiative decays, $5^{-7,25-27}$ and two lifetime components of several to hundreds of picoseconds have normally been reported from the ensemble studies. $7,25-27$ As might be applicable to our AUF results, the fast component of several picoseconds can be assigned to the intertube exciton transfer due to the presence of small residual bundles, while the tens to hundreds of picoseconds lifetime is due to the intratube nonradiative decay of excitons into defect sites. $25,26$ The as-prepared DNA-wrapped SWCNTs were previously characterized by atomic force microscopy (AFM), $21$ where the helical pitch and height could be structurally determined. Although an individual SWCNT is contained in a majority of the hybrid structures, it is still possible to have several SWCNTs bundled inside DNA molecules that are hardly resolved from the AFM measurement. $25$ Electron or exciton transfer from semiconductor SWCNTs to the neighboring metallic SWCNTs in such a bundle has been proposed as a possible origin of the fast decay component of $\sim 1$ ps observed in previous TA measurements. $26$ Meanwhile, there exist defect sites to trap photoexcited carriers in a DNA-wrapped individual SWCNT, leading to the low fluorescence quantum efficiency associated with a relatively slow PL decay lifetime of tens to hundreds of picoseconds. Although the Auger lifetime of multiple excitons in SWCNTs was reported to be on the time scale of $1-3$ ps, $18,19$ we can still exclude it as the possible origin for the fast decay component observed here from the AUF measurement. First, this fast component appears in the TA curve in the inset of Figure 3 from the pump–probe measurement at a low pump fluence. Second, the amplitude ratio $A_1/A_2$ for the fast and slow decay components in Figure 4c approaches a constant value at high laser power, which is more reasonably explained as the saturation of intertube exciton transfer $18$ inside a limited number of residual SWCNT bundles.

Figure 3. Spectrally integrated PL intensities of (6,5) SWCNTs measured at laser powers of 30 and 50 mW as functions of the time delay between the two excitation pulses. The solid lines are biexponential fits with fast and slow lifetime components of several and tens to hundreds of picoseconds, respectively. Inset: Transient absorption curve of (6,5) SWCNTs measured by the pump–probe technique with pump and probe laser wavelengths of 800 and 990 nm, respectively. The solid line is a biexponential fit with two decay components of $\sim 1$ and $\sim 83$ ps.

Figure 4. Plots of (a) the fast lifetime component $t_f$, (b) the slow lifetime component $t_s$, (c) the amplitude ratio $A_1/A_2$ for the fast and slow lifetime components, and (d) the PL intensity depth as functions of the excitation laser power at each beam. The dotted lines are just guides to the eye.

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When the (6,5) SWCNTs are excited at 850 nm, an exciton–phonon bound state is formed whose dynamic evolution affects the exciton relaxation process instead of the exciton recombination process discussed above. This exciton–phonon bound state is formed instantaneously after the laser pulse excitation and dissociates on a picosecond time scale as a result of the anharmonic mode coupling between the optical LO phonon and lower-energy phonons. If the relaxation process of the freed exciton is slow enough, it would cause a plateau or even a peak at zero time delay in the AUF curves, which was not observed in our experiment. Therefore, we can conclude that exciton relaxation from the initial exciton–phonon bound state to the final recombination state is too fast to be resolved from the AUF curves measured in our experiment. This is consistent with a previous observation that it took less than 100 fs for the exciton to finish the relaxation process after it was pumped to a higher-lying excited state.  

It should be mentioned that the (9,1) SWCNTs exhibited PL behaviors very similar to those of (6,5) SWCNTs with single- and two-pulse excitations at ~850 nm, as can be seen in Figures S4 and S5 in the Supporting Information. Since the whole AUF scheme in Figure 1 is based on the PL saturation behavior dictated by the exciton–exciton annihilation effect, it reasonably comes to this critical question of how the PL intensity of a bulk semiconductor evolves with the delayed two-pulse excitation. For comparison, a bulk GaAs(100) substrate was optically excited at 800 nm at room temperature, and the corresponding PL spectrum is shown in the inset of Figure 5a. In contrast to the case of SWCNTs, the PL intensity of GaAs has a superlinear dependence on the single-pulse laser power (Figure 5a), implying that the Auger effect can be neglected in bulk semiconductors and that the absorption of multiple photons even favors the fluorescence enhancement. Consistent with the above laser power dependence, the PL intensity of GaAs excited at 800 nm with two-pulse trains acquires a maximum at zero time delay and decreases continuously from that, as shown by the transient PL curve excited with a laser power of 30 mW at each beam (Figure 5b).

To understand this transient PL behavior of bulk GaAs, we turn to previously reported results for bulk semiconductors also excited with two pulse trains in the EC measurement. It was observed that for free excitons whose PL intensity possesses a superlinear dependence on the single-pulse laser power, the transient PL intensity decays exponentially with increasing time delay from the zero point. This was explained by the higher probability of biexciton formation at shorter time delays and the apparent enhancement of the fluorescence efficiency could be attributed to the shorter radiative lifetime of biexcitons relative to that of single excitons. We believe that this biexciton formation mechanism is also relevant to the transient PL behavior of bulk GaAs observed here in our experiment. As can be seen in Figure 5b, when the laser power at each beam was elevated to a higher value of 50 mW, a fast decay component appeared in the transient PL curve with a time constant comparable to the laser pulse width, which might be a signature of stimulated biexciton emission as previously discussed in ref 31. It was also demonstrated from the EC measurement that the transient PL of bound excitons in bulk semiconductors has an intensity dip at zero time delay between the two excitation pulses, which is a direct consequence of the sublinear dependence of the bound exciton PL intensity on the excitation laser power. Since the Auger effect is normally negligible in bulk semiconductors, this PL saturation behavior was attributed to the phase-space-filling effect due to the limited concentration of impurities that can bind free excitons.  

Besides the AUF method reported here and the traditional pump–probe technique, there are several other reported ultrafast approaches utilizing two delayed pulse trains for the characterization of carrier decay dynamics in semiconductor nanostructures. In refs 34 and 35, the photocurrent of individual SWCNTs was monitored as a function of the time delay between two excitation pulses to demonstrate the transient optoelectronic behavior of photoexcited charge carriers. In refs 10 and 11, the exciton recombination processes of SWCNTs were resolved from the EC measurement, where each pulse train was differently modulated and the PL signal collected by a photodetector was read out from a lock-in amplifier at either the sum or difference modulation frequency. More recently, the two-pulse excitation scheme was applied to single self-assembled InAs quantum dots to detect their single-exciton and biexciton decay lifetimes based on the phase-space-filling effect. In contrast, the present AUF measurement utilizes the Auger-induced exciton–exciton annihilation effect that, in addition to the SWCNTs studied here, has been observed in a variety of other semiconductor nanostructures, including nanocrystal quantum dots and rods. The application of this AUF technique to semiconductor nanocrystals, with a focus on the subpicosecond characterizations of
exciton Auger recombination and energy transfer processes at the single-particle level, is now being pursued in our laboratory.

**EXPERIMENTAL SECTION**

**Sample Preparations.** To prepare the DNA-wrapped SWCNT sample, approximately 1 mg of CoMoCAT SWCNTs was added to a 1 mg/mL solution of single-stranded DNA in 100 mM NaCl/D$_2$O. After vortexing, homogenization, and probe ultrasonication, the resulting suspension was loaded into capped tubes and spun in a centrifuge at 13 000 rpm for 1 h. The upper 50% of the supernatant was then decanted from the tubes and reserved. As a reference, the CoMoCAT SWCNTs were alternatively processed to be highly enriched in the (6,5) chirality using previously published methods$^{21}$ (see Figure S6 in the Supporting Information for a representative AUF curve measured for this sample). One drop of a very diluted solution of SWCNTs was put on a silica coverslip and allowed to dry to avoid possible photodegradation and photodesorption effects under high-power laser illumination.

**Optical Characterizations.** For the AUF measurement, the laser output of a 76 MHz Ti:sapphire oscillator with a pulse duration of $\sim$3.3 ps was split into two beams collinearly aligned with equal power and perpendicular polarizations. Optical delay between these two beams was introduced by scanning a linear translation stage with a stepping resolution better than 10 fs. The laser beams were focused onto the SWCNT films with a diameter of $\sim$100 μm and at an incident angle of $\sim$45° relative to the surface normal direction. The fluorescence signal was collected vertically from the sample surface by a 50× microscope objective and sent through a 0.5 m spectrometer to the surface normal direction. The fluorescence decay was biexponential with increasing laser powers; AUF curve measured for (9,1) SWCNTs excited and AUF curve of (9,1) SWCNTs; biexponential fitting parameters of the AUF curves for (9,1) SWCNTs excited with increasing laser powers; AUF curve measured for the SWCNT sample highly enriched in the (6,5) chirality (PDF).

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: wxiaoyong@nju.edu.cn.
*E-mail: mxiao@uark.edu.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(38) Bindl, D. J.; Shea, M. J.; Arnold, M. S. Enhancing extraction of photogenerated excitons from semiconducting carbon nanotube films as photocurrent. *Chem. Phys.* 2013, 413, 29–34.