Nonlinear Photoluminescence Spectroscopy of Carbon Nanotubes with Localized Exciton States

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ABSTRACT We report distinctive nonlinear behavior of photoluminescence (PL) intensities from localized exciton states embedded in single-walled carbon nanotubes (SWNTs) at room temperature. We found that PL from the local states exhibits strong nonlinear behavior with increasing continuous-wave excitation power density, whereas free exciton PL shows only weak sublinear behavior. The strong nonlinear behavior was observed regardless of the origin of the local states and found to be nearly independent of the local state density. These results indicate that the strong PL nonlinearity arises from a universal mechanism to SWNTs with sparse local states. The significant nonlinear PL is attributed to rapid ground-state depletion of the local states caused by an efficient accumulation of photogenerated free excitons into the sparse local states through one-dimensional diffusional migration of excitons along the nanotube axis; this mechanism is verified by Monte Carlo simulations of exciton diffusion dynamics.

KEYWORDS: carbon nanotube · nonlinear · photoluminescence · exciton · localized · trapped
detailed exciton photophysics in such hybrid low-dimensional nanostructures.

Here we report on studies of photoluminescence intensities from localized exciton states generated by doping of atomic oxygen and sp\(^3\) defects in SWNTs with increasing continuous-wave (cw) optical excitation power at room temperature. Strong nonlinear behavior of PL intensity from the local states was observed regardless of the origin of the local states, whereas the free exciton PL exhibited only weak sublinear behavior. We also found that the strong nonlinear PL behavior of the local states merely depends on the density of these states in SWNTs. The distinctive difference in the nonlinear PL behavior between localized (0D-like) and free (1D) exciton states can be reproduced by Monte Carlo simulations that consider exciton diffusion dynamics and ground-state depletion (state filling) at 0D-like local states. Comparisons of experimental and simulation results suggest that ground-state depletion, which causes PL saturation of the local states, originates from excitons photogenerated in intrinsic 1D segments being efficiently accumulated into a very small number of local states. The results of the simulations also imply that population inversion necessary for lasing, which has been hampered in intrinsic SWNTs owing to rapid EEA processes, may be achieved by using the luminescent local states in SWNTs even at relatively low-power excitation conditions.

RESULTS AND DISCUSSION

Figure 1a shows a schematic of exciton dynamics in SWNTs with luminescent local 0D-like states. An intrinsic free exciton diffusively moves along the 1D axis of SWNTs. The 0D-like local luminescent states capture free 1D excitons and convert them to 0D-like excitons that emit PL more efficiently than the free 1D excitons. Figure 1b,c shows PL spectra of SWNT ensembles before and after the oxygen- and sp\(^3\)-defect doping treatments to embed local luminescent states in SWNTs according to the procedures originally developed by Ghosh et al. and Piao et al. respectively (see Methods). These PL spectra were measured under low-power cw excitation (1.476 eV), which was low enough to avoid PL saturation. The dominant PL peak at an emission photon energy of \(\sim 1.25 \text{ eV} (E_{11})\) corresponds to radiative recombination of the first sub-band excitons \((X_{11})\) in (6,5) SWNTs. The new PL peaks at the emission photon energy of \(\sim 1.07 \text{ eV} (E_{11}')\) appears after the oxygen- and sp\(^3\)-defect doping treatments (Figure 1b, c). These new peaks have been attributed to PL from neutral excitons trapped by local states generated by oxygen- and sp\(^3\)-defect doping in SWNTs on the basis of calculations using density functional theory. A large Stokes shift induced by oxygen doping has also been predicted for small-diameter SWNTs by \(ab\) \(initio\) many-body perturbation theory considering the local geometric structural change when an exciton is formed. The localized (0D-like) nature of the excitons responsible for the new peaks in oxygen-doped SWNTs has also been verified by temperature-dependent PL studies. Hereafter, we refer to these localized excitonic states as \(X_{11}'\), regardless of their origins.

Figure 2a,b shows the PL spectra of oxygen- and sp\(^3\)-defect-doped SWNTs under cw excitation power densities from 1 to 49 kW/cm\(^2\). PL intensities of each spectrum are divided by the corresponding excitation power density for comparison. The incident photon energy of 1.476 eV used for the measurements is nearly resonant with the \(E_{11}\) phonon sideband of (6,5) SWNTs. The PL intensities from \(X_{11}\) and \(X_{11}'\) states exhibit considerably different nonlinear behavior. The ratio of PL intensities of the intrinsic 1D state \((X_{11})\) and the local state \((X_{11}')\) clearly changes under strong excitation conditions; this indicates much stronger nonlinearity of the PL intensity from local states \((X_{11}')\) than from intrinsic 1D states \((X_{11})\) as the cw excitation power density is increased.

The integrated PL intensities \((I_{11}\) and \(I_{11}'\)) from the intrinsic 1D states \((X_{11})\) and local states \((X_{11}')\) in oxygen- and sp\(^3\)-defect-doped SWNTs are plotted as functions of excitation power density in Figure 2c.d. \(I_{11}\) and \(I_{11}'\) were obtained by fits to the respective PL

![Figure 1](image1.png)

Figure 1. (a) Schematic of exciton dynamics in a SWNT with a 0D-like local luminescent state. An intrinsic free 1D exciton diffusively moves along the nanotube axis, converts to a 0D-like exciton at the local state, and emits brighter PL than 1D excitons. (b,c) PL spectra of SWNTs measured with an excitation photon energy of 2.18 eV before (dotted curve) and after (solid curve) the doping of (b) oxygen and (c) sp\(^3\) defects. The dominant peak at \(\sim 1.25 \text{ eV} (E_{11})\) corresponds to PL from the intrinsic first sub-band excitons \((X_{11})\) in (6,5) SWNTs. The new peaks at \(\sim 1.05 – 1.10 \text{ eV} (E_{11}')\) in (b) and (c) are attributed to PL from the 0D-like excitons \((X_{11}')\) trapped at local quantum states embedded in SWNTs.
Figure 2. (a,b) Normalized PL spectra of (a) oxygen-doped and (b) sp$^3$-doped SWNTs taken at selected cw excitation power densities with an excitation photon energy of 1.476 eV. Each spectrum is normalized by the corresponding excitation power density. It is clearly seen that the intensity ratio of $I_{11^*}$ and $I_{11}$ peak heights depends on the excitation power density. (c,d) PL intensities $I_{11}$ and $I_{11^*}$ as functions of cw excitation power density. Both $I_{11}$ and $I_{11^*}$ are normalized by their values at the weak excitation power density of 1 kW/cm$^2$, where the PL intensities are almost linear with respect to excitation density. Dashed black lines show the linear power dependence. Solid circles represent experimental data for the integrated intensities of $X^*$ PL peaks ($I_{11^*}$, red solid circles) and $X_1$ peaks ($I_{11}$, blue solid circles). The integrated intensities were evaluated using peak decomposition procedures, where the weak shoulder peak at the lower energy side of the $X^*$ peak is not included as $I_{11^*}$. Dashed red and blue curves are guides for the eye.

The figure shows that there is a considerable difference between the nonlinear behaviors of $I_{11}$ and $I_{11^*}$ for both oxygen- and sp$^3$-defect-doped SWNTs. A similar effect has been reported for localized excitons in individual SWNTs at cryogenic temperature.$^{53,58,62}$ Note that the nonlinear PL behaviors for $X_1$ and $X_1^*$ excitons in both SWNTs are quite similar to each other regardless of the origin of the local states; this strongly suggests that there is a common physical mechanism for the observed strong PL nonlinearity that is related to unique exciton dynamics in SWNTs with 0D-like local states.

We further examined the nonlinear PL behavior of SWNTs with different local state densities. Figure 3a compares PL spectra of various oxygen-doped SWNTs; each spectrum exhibits a different $I_{11^*}$ intensity that reflects different densities of the local states in the SWNTs (see Methods). These PL spectra were measured in the weak excitation regime (1.3 kW/cm$^2$). Figure 3b compares the nonlinear behaviors of the PL intensities of $I_{11^*}$ in the various oxygen-doped SWNTs as functions of the excitation power density. We found no significant differences in the nonlinear behavior of $I_{11^*}$ in each sample. This suggests that the nonlinear PL behavior is nearly independent of the densities of local states within the range examined in this study.

To understand the mechanism of the strong nonlinear behavior of $I_{11^*}$ from 0D-like local states in SWNTs regardless of the origin and density of the local states, we conducted computational simulations of exciton diffusion dynamics in SWNTs with 0D-like local states (see Methods). One of the important implications obtained from the simulation is the very small density of the luminescent local states in the 1D SWNTs. Figure 4 shows simulation results (solid curves) for various densities of local states ($N_q$) plotted together with typical experimental data for the nonlinear behavior of $I_{11^*}$ in oxygen-doped SWNTs. Inset of Figure 4 shows the calculated result for $I_{11}$ (only data for $N_q = 2.7 \mu m^{-1}$ are plotted for clarity; see also Supporting Information S1 for all the $N_q$ values calculated in this study). We found that the calculated nonlinear behaviors of both $I_{11}$ and $I_{11^*}$ for small $N_q (\sim 5 \mu m^{-1})$ are very similar to each other, whereas the calculations for larger $N_q (\sim 10 \mu m^{-1})$ deviate considerably from the experimental values. The calculated $N_q$-dependent change in the nonlinear behavior is reasonable because the average exciton quenching site distance $1/n_q$ that corresponds to the effective nanotube length $L^*$ in the simulation is $\sim 150$ nm (see Methods), and $N_q < 5 \mu m^{-1}$ corresponds to less than one local state in $L^*$. In this case, the probability of having two or more local states in $L^*$ is very small. Therefore, exciton dynamics near local states are nearly independent of $N_q$. In contrast, for $N_q$ greater than
excitons at the local sites (local states, and convert to localized (0D-like) \( \mu \) excitons. In addition, the population decay of \( 11^\ast \) excitons at the local states in SWNTs is understood as follows. First, incident photons are initially absorbed predominantly by intrinsic 1D SWNTs, and \( 11 \) excitons are generated. Then, the \( 11 \) excitons diffusively migrate along the intrinsic 1D parts of the SWNTs, efficiently accumulate into sparsely distributed local states, and convert to localized (0D-like) \( 11^\ast \) excitons. In addition, the population decay of \( 11^\ast \) excitons at the local sites (\( \sim 10^{-7} \) ps\(^{-1}\)) is slower than the diffusion-limited feed rate of \( 11 \) excitons to the \( 11^\ast \) states (\( \sim 10^{-7} \) ps\(^{-1}\)). Consequently, ground-state depletion (state filling) of 0D-like \( 11^\ast \) local states easily occurs; this results in the strong nonlinear behavior of the PL intensities from the \( 11^\ast \) states.

The simulations further predict that local quantum states in SWNTs have quite favorable characteristics for optical applications. We found that the time-averaged number density of \( 11^\ast \) excitons can exceed \( N_\mu/2 \) at a \( 11 \) exciton cw photogeneration rate of less than 200 ns\(^{-1}\) \( \mu \) m\(^{-1}\); this corresponds to a low cw excitation power density of less than 40 kW/cm\(^2\) when \( 11 \) excitons are resonantly excited. The \( 11^\ast \) exciton number density of more than \( N_\mu/2 \) indicates that the number of excited states exceeds that of the ground state; namely, population inversions necessary for laser operations could occur at these local states. The optical gain threshold of individually dispersed SWNTs in a thin film has been previously reported to be \( 55 \) mJ/cm\(^2\) by a 2 ns pulsed excitation at \( E_{22}^\ast \) this corresponds to an effective cw excitation density of \( \sim 3 \times 10^4 \) kW/cm\(^2\) for the pulse duration. Hence, an excitation density of 40 kW/cm\(^2\) is surprisingly low. The availability of population inversion, even at low cw excitation conditions, originates from the same mechanism as that for strong nonlinear PL from the local states, namely, the efficient accumulation of excitons into local states. In contrast, at this low cw excitation condition, the time-averaged number density of intrinsic \( E_1 \) excitons on a SWNT is found to be less than 0.3 ns\(^{-1}\) \( \mu \) m\(^{-1}\), and most of the intrinsic part of the SWNT is in its ground state because of the extremely efficient nonradiative decay of excitons through EEA processes. The results of the simulations thus imply that lasing operations using SWNTs as gain media, which were heretofore hampered by very efficient EEA processes for the intrinsic 1D excitons in SWNTs, can be enabled using the local excitonic states embedded in SWNTs.

**CONCLUSION**

We have reported significant nonlinear behavior of the PL intensities from local electronic states generated by oxygen- and sp\(^3\)-defect doping in SWNTs. The nonlinear behavior was found to be nearly independent of the origin and density of the local states. Computational simulations of the 1D exciton diffusion dynamics reproduce the experimental observations very well. The simulations suggest that the significant nonlinear behavior is dominated by ground-state depletion of local states, which originates from the efficient delivery of intrinsic 1D excitons into the small number of local states. This universal exciton dynamics in SWNTs with sparse 0D-like local states is predicted to enable population inversion necessary for lasing in the local states in the relatively low-power cw optical excitation regime. These findings shed light on the possibility of novel optical applications of the local quantum states embedded in SWNTs, as well as the emergence of unique exciton photophysics in 1D–0D hybrid nanostructures.

**METHODS**

**Sample Preparation.** Local electronic states in SWNTs were prepared by doping of atomic oxygen\(^{60,61}\) or sp\(^3\) defects\(^{59}\) that induce local reduction of the band gap and exciton energy. The oxygen- and the sp\(^3\)-defect-doped SWNTs were, respectively, prepared using the procedure originally developed by Ghosh et al.\(^{60}\) and Piao et al.\(^{69}\) with some modifications in selections of chemicals and experimental parameters as described in ref 54. In short, (6,5)-rich CoMoCAT SWNTs purchased from Southwest Nanotechnologies (or purchased from Sigma-Aldrich) were isolated by dispersion in D\(_2\)O with 0.2% (w/v) sodium dodecyl benzenesulfonate (SDBS), 60 (120) min of moderate bath sonication, 40 min of vigorous sonication with a tip-type sonicator, and centrifugation at an acceleration of 130 000g
for 4 (17) hours for the samples shown in Figures 1 and 2 (Figures 3 and 4). These experimental parameters were optimized for each sample batch of the CoMoCAT SWNTs. Slight differences of the PL spectra and nonlinear behavior shown in Figures 2–4 could be because of the difference of the sample batches. For the oxygen doping, the dispersion of isolated SWNTs was combined with a small amount of D_{2}O that contained dissolved oxygen and was left under the illumination of a desk lamp (∼5 mW/cm²) overnight; this enabled the moderate atomic oxygen doping to generate sparse oxygen-derived local states. For the sp²-defect doping, the dispersion of isolated SWNTs was combined with a small amount of D_{2}O that contained dissolved organic diazonium salts (4-bromobenzene-diazonium tetrafluoroborate)⁵⁶ and left under dark for more than 10 days; this enabled the moderate sp²-defect doping to generate sparse sp²-defect-derived local states.

**Optical Measurements.** The excitation source for measurements of PL nonlinearity was a cw laser (Ti:Al_{2}O_{3}) with an 840 nm wavelength (1.476 eV) focused on the sample in a quartz cell (1 mm light path) with a spot size of 4–6 μm. The PL from the sample was collected by an achromatic lens and passed through a confocal optical arrangement. Finally, the PL was recorded with a liquid-nitrogen-cooled InGaAs 1D array detector. All of the measurements were conducted on the SWNTs ensemble.

**Monte Carlo Simulations of Exciton Dynamics.** We conducted computational simulations of the exciton diffusion dynamics in a hybrid-dimensional exciton system based on the Monte Carlo method. In the Monte Carlo simulations, the motion of an exciton in a SWNT is treated as a random walk. We consider 1D exciton diffusional contact quenching⁶⁵ as the dominant exciton relaxation mechanism in a SWNT: if the exciton reaches nonradiative sites in the SWNT, it instantaneously disappears from the system. Here, nanotube ends are included as nonradiative sites as well as other local exciton quenching sites on the nanotube wall originating from structural defects, electronic impurity, or unintentional chemical attack.⁶⁶–⁷₀ A SWNT with an exciton quenching site density n_{q} (including nanotube ends as exciton quenching sites) corresponds to a nanotube in the simulation with an effective length L_{e} = 1/n_{q}. The length L_{e} (=1/n_{q}) is the substantial length within which excitons can migrate and generally shorter than the actual length of SWNTs and intrinsic exciton diffusion length limited by radiative recombination processes.

At the beginning of a simulation, luminescent local states in SWNTs are randomly prepared so that the average density of the local states becomes N_{0} μm⁻¹. Then, the excitons are stochastically and spatially created according to the probability proportional to the excitation power at each unit time step. In the simulations, the same absorption cross sections per carbon atom at the excitation energy (1.476 eV) were assumed for the 1D part and local states. This assumption is valid as far as the rate constant of photoexcitation of the local states is substantially smaller than that of indirect excitation through diffusion-limited feeding of excitons; the fact that the PL excitation spectra probed at the X₁₁ and X₁₁* emission photon energies are quite similar to each other⁶⁵ suggests that most of the X₁₁* excitons in the local states are generated originally in the 1D part of the SWNTs. In each unit time step δt, an intrinsic exciton randomly walks a characteristic distance δx. Considering the 1D diffusion of a particle with diffusion constant D, we obtain the relationship (δx)² = 2Dδt. The time step δt corresponds to the exciton scattering time and is deduced to be 0.1 ps based on the homogeneous line width of Γ ∼ 13 meV⁻¹ and the relationship δt = 2Γ/k_{B}ΔΓ. Then, considering the relationship between the PL quantum yield η and the dimensionless parameter that determines η, the value L_{e}/δx = 30 is deduced from η ∼ 1% with an exciton radiative lifetime of 1.6 ns.⁷¹ From the previously reported values that are on the order of 10⁻¹⁰ cm² per carbon atom in a single nanotube at E_{22} resonance⁶⁵,⁷⁲ and, thus, supports the validity of the simulation.

**Conflict of Interest:** The authors declare no competing financial interest.

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**Supporting Information Available:** Calculated nonlinear photoluminescence behavior for free 1D excitons, and optical absorption spectra of the samples. This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**


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