Defect Induced Photoluminescence from Dark Excitonic States in Individual Single-Walled Carbon Nanotubes

Hayk Harutyunyan, Tobias Gokus, and Achim Hartschuh

1 Dipartimento di Fisica "E. Fermi", Università di Pisa and CNISM, Largo Pontecorvo 3, 56127 Pisa, Italy
2 Department Chemie und Biochemie and CeNS, Ludwig-Maximilians-Universität München, 81377 München, Germany
3 Department of Materials Science and Engineering, Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3108, USA

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We show that new low-energy photoluminescence (PL) bands can be created in semiconducting single-walled carbon nanotubes by intense pulsed excitation. The new bands are attributed to PL from different nominally dark excitons that are "brightened" due to defect-induced mixing of states with different parity and/or spin. Time-resolved PL studies on single nanotubes reveal a significant reduction of the bright exciton lifetime upon brightening of the dark excitons. The lowest energy dark state has longer lifetimes and is not in thermal equilibrium with the bright state.

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Owing to their exceptional electronic properties single-walled carbon nanotubes (SWNTs) are promising candidates for future nanoelectronic and biosensing applications as well as narrow band nanoscale emitting and detecting devices [1, 2, 3, 4]. Excitons are identified to dominate the absorption and PL emission properties of these 1-dimensional systems [3, 6]. Enhanced electron–electron interactions due to the reduced dimensionality lead to exceptionally large binding energies of the excitons that are shown to exist even in metallic SWNTs [7]. Theory predicts a manifold of excitonic states in agreement with theoretical predictions [4, 21].

The direct experimental proof for the existence of dark excitonic states in SWNTs was presented applying two-photon photoluminescence excitation spectroscopy [5, 6] and measurements of magnetic brightening of the SWNT PL [12]. Low-energy forbidden states were also used to explain the dynamics observed in pump–probe experiments [16, 17] and the temperature dependence of PL intensities [18]. In addition, recent results on ensemble [19] and individual nanotube samples [20] have shown low energy satellite peaks in the PL spectra. These peaks were attributed to emission from low lying dark excitonic states while the mechanisms enabling optically forbidden transitions and the interplay between bright and dark excited states remain to be clarified.

In this Letter, we report on the creation of low-energy emission bands in the PL spectra of individual (5, 4) and (6, 4) SWNTs upon high power pulsed laser irradiation at room temperature. The persistence of these bands in subsequent low power measurements indicates that irreversible distortions of the nanotube structure efficiently “brighten” forbidden states via disorder induced mixing of excitonic states in agreement with theoretical predictions [4, 21]. The clear distinction between additional emissive features belonging to a certain nanotube and PL bands from other nanotubes is made possible by observing single nanotube spectra before and after high power irradiation and by recording the polarization dependence of bright and dark emission bands. While the decay times of the allowed transition are in the range of 1 to 40 ps [22], far longer dark state lifetimes of up to 177 ps have been observed. Based on the spectroscopic properties of the lowest dark state emission and its observation upon nanotube exposure to gold that is predicted to create high local spin densities [23, 24], we suggest that low energy emission results from triplet exciton recombination facilitated by magnetic defects and impurities.

Time-correlated single-photon counting (TCSPC) is used in combination with confocal microscopy to perform single SWNT spectroscopy and time–resolved PL measurements [22]. Spatially isolated individual SWNTs were obtained by spin-coating a small volume of micelle-encapsulated CoMoCat material onto a glass cover-slip [25]. Laser excitation was provided by a Ti:Saphire oscillator operated at a photon energy of 1.63 eV and a repetition rate of 76 MHz. The PL spectra were recorded with a CCD camera and a fast avalanche photodiode was used to acquire PL transients.

Fig. 1 shows the generation of low energy satellite PL bands for two individual nanotubes. Initial spectra (solid black lines) acquired at low excitation intensity \(I_0 = 3 \times 10^{13}\) photons \cdot pulse\(^{-1}\)\cdot cm\(^{-2}\) show a single emission peak centered at 1.41 eV (a) and 1.46 eV (b)
assigned to the allowed bright exciton (BE) in (6, 4) and (5, 4) nanotubes, respectively [26]. Irradiation of the nanotubes for 10–100 seconds with an order of magnitude higher pulse intensity $\sim 17 \cdot I_0$ results in some cases in significantly modified spectra (dashed red lines in Fig. 1) with additional redshifted shoulders and new spectral features transferring substantial spectral weight to these satellite peaks. Importantly, no such spectral changes were induced at the corresponding averaged power levels using continuous–wave (cw) excitation suggesting that high power cw excitation, on the other hand, mainly leads to photobleaching and blinking of nanotube PL [27]. Satellite peaks for different (6,4) and (5,4) nanotubes consistently appear at similar energies and can be roughly divided into two groups with redshifts of $\sim 110–190$ meV (DE$_1$) and $\sim 30–60$ meV (DE$_2$) in good agreement with Ref. [20]. The same energy splittings (130 and 40 meV) were predicted for the (6,4) nanotube and attributed to triplet and even parity singlet excitons, respectively [11].

The polarization analysis of PL emission of the bright exciton BE peak and the newly created satellite DE$_1$ (Fig. 2) show the same $\cos^2 \theta$ behavior proving that the emission bands belong to the same nanotube and indicating that the redshifted emission originates from an intrinsic state of the SWNT. Furthermore, consistent appearance of the new bands in DNA wrapped SWNTs and nanotubes embedded in PMMA matrix (Fig. S1 of the supplementary information [28]) shows that the effect is not due to a chemical reaction specific to sodium cholate surfactant.

To determine the population dynamics of both dark and bright excitonic states and to study the effect of the created disorder we have performed time–resolved PL measurements of the different emission bands before and after creation of emission satellites. Fig. 3 depicts representative PL transients detected from the shaded spectral areas (shown in the insets) for two individual nanotubes of two different chiralities: (6,4) (a) and (5,4) (b). Two important conclusions can be drawn from this data. First, upon creation of the satellite peaks the bright exciton lifetime is decreased (grey curve) compared to the initial decay (black curve), and second, the DE$_1$ emission is...
erogeneities along the nanotube introduced by the defects possibly caused by heterogeneity of the photon flux (about factor 1/20) with fast decay components (8 ps and 2 ps) with far smaller amplitude of phonon replica and bi-excitons can be ruled out based on the present observation. Thus, other origins of the low-energy bands such as population transfer from the newly created states observed here.

Now we discuss the more rapid decay of the bright excitonic state and a good agreement of its emission energy with theoretical predictions [11]. In general, magnetic impurities increasing spin density states created by sidewall modification leading to triplet emission can be assisted by coupling to localized defects, therefore faster decay also serves as an evidence for the mobility of excitons in nanotubes [13, 27, 35]. Population transfer from bright to dark states on the other hand would result in a delayed rise of the DE1 emission with a rise time equal to the decay time of the bright state. Such a delayed rise, that would be detectable in our measurements especially for nanotubes with longer decay times of the BE state of up to 25 ps, was not observed suggesting that a substantial fraction of the dark state population is built up directly upon photoexcitation. Importantly, the fact that the bright exciton maintains a different and finite lifetime in the presence of the dark state DE1 clearly shows that these two states are not in thermal equilibrium.

Based on the longer lifetimes of DE1 state and a good agreement of its emission energy with theoretical predictions [11], we speculate that this PL band is most likely due to triplet state emission. The intersystem crossing leading to triplet emission can be assisted by coupling to high spin density states created by sidewall modification of the nanotube such as vacancy creation [36, 37]. The energy of about 5 eV needed to create a vacancy can be provided through multi-photon excitation processes explaining the high pulse energies required for the creation of DE1. In general, magnetic impurities increasing spin-orbit coupling could also be formed by trace...
amounts of residual catalyst materials explaining the observation of dark state emission in other nanotube materials reported in literature. To test this possibility we treated the SWNTs with a pH neutralized, aqueous solution of gold [28] which induces spin polarized states with significant magnetic moments when adsorbed on SWNT [23] or graphene surface [24]. Covering the sample with a gold solution results in similar changes in the single nanotube PL spectrum without requiring high power pulsed excitation (Figs. S2 and S3 of the supplementary information [28]). The efficiency of brightening of the dark states is especially high when the aqueous SWNTs solution is premixed with the gold solution before deposition thus facilitating the surface adsorption of the metal. In these samples the majority of the (6,4) nanotubes exhibited low energy emission satellites, indicating that the same emissive DE1 state is brightened. This has been further confirmed by time resolved measurements showing a broad distribution of lifetimes in the range of 7 ps to 150 ps, considerably longer than for the BE emission. Importantly, no additional PL bands have been observed in control experiments on single nanotubes deposited on gold films (not shown) as well as near-field optical experiments using sharp gold tips [38] indicating that the new PL bands are not created by metal surface induced electromagnetic field enhancement.

In conclusion, we demonstrated that nominally dark excitonic states in carbon nanotubes can become emissive after exposure to high excitation intensities and by adsorption of gold. We suggest that local defects induce mixing of different excitonic states and relaxation of selection rules via perturbation of the electronic structure. Our single nanotube measurements show that the recombination time of the excitons can be modified by the presence of disorder and that PL from the same nanotube can have decay rates varying by 2 orders of magnitude depending on the detected spectral range. While these findings are relevant for nanotube photophysics, they also indicate possible novel routes for the engineering of SWNT optical properties.

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* Email: hayk@df.unipi.it, achim.hartschuh@cup.uni-muenchen.de