physica **pss** status solidi **rrl**
www.pss-rapid.com
rapid research letters

...-related trap
...crystal

www.pss-rapid.com

physica **pss** status solidi **c**
www.pss-c.com
current topics in solid state physics

...uted-feedback color center lasers in wide-band gap materials
...ated by a pair of chirped femtosecond pulses
...roboni et al., p. 637)

www.pss-c.com

physica **pss** status solidi **b**
www.pss-b.com
basic solid state physics

Current Trends in Electronic Structure:
...nbedding and Linear Scaling Techniques

...Thomas Beck, and Eduardo Hernández

...real-space discretization techniques
...re calculations (p. 1016)

SPECIAL ISSUE

www.pss-b.com

physica **pss** status solidi **a**
www.pss-a.com
applications and materials science

Editor's Choice
Highly efficient all-nitride phosphor-converted
white light emitting diode
(Regina Mueller-Mach et al., p. 1727)

$h\nu$
$h\nu$
$h\nu$

WILEY-VCH

www.pss-a.com

WILEY-VCH

REPRINT

physica **pss** status solidi **b**

www.pss-b.com

basic solid state physics

Photoluminescence from disorder induced states in individual single-walled carbon nanotubes

Hayk Harutyunyan[*,1]**, Tobias Gokus**[2]**, Alexander A. Green**[3]**, Mark C. Hersam**[3]**, Maria Allegrini**[1]**, and Achim Hartschuh**[*,2]

[1] Dipartimento di Fisica "E. Fermi", Universitá 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, IL 60208-3108, USA

* Corresponding author: e-mail hayk@df.unipi.it, achim.hartschuh@cup.uni-muenchen.de, Phone: +49 89 2180 77515, Fax: +49 89 2180 77188

We report on the generation of new low-energy photoluminescence (PL) bands in the spectra of semiconducting single-walled carbon nanotubes (SWNTs). The new bands, that are brightened because of local modifications of the nanotube structure or the metal adsorption on the SWNT surface, 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. The effect of the created structural disorder on the dynamical properties of the emission is studied by time-resolved PL measurements revealing a significant reduction of the bright exciton lifetime. The lowest energy dark state has a longer lifetime and is not in thermal equilibrium with the bright state.

1 Introduction The unique structure of the graphene lattice combined with the reduced dimensionality of single-walled carbon nanotubes (SWNTs) leads to a manifold of excitonic states with different symmetries and multiplicities that determine all electronic properties of semi conducting carbon nanotubes [1, 2]. Thus, the full understanding of the complex spectral and dynamical properties of the SWNTs is of high importance not only from the fundamental but also pactical point of view. The engineering of the electronic structure of SWNTs, would pave a new way for their future applications as narrow band nanoscale emitting and detecting devices, biosensing, and optoelectronic devices [3]. A pioneering example of the modification of the photoluminescence (PL) and electronic structure of nanotubes by an external action is the magnetic "brightening" of dark, dipole-forbidden excitonic states [4]. In this case the applied strong magnetic field breaks the symmetry of the excitonic bands and relaxes the one photon emission selection rule for a non-emissive excitonic state, thus allowing to tune the PL of SWNTs. A different approach of changing the nanotube's emission properties is to locally change the

structure of the tube and hence the electronic structure associated with it.

In this paper we show that the modification of the SWNT's structure or the local perturbation of it can lead to dramatic changes in PL spectra and in dynamical characteristics of the emission [1, 5]. The irradiation of individual (5,4) and (6,4) chirality SWNTs with intense laser pulses induces new low energy emission bands in addition to the initial single Loretzian peak resulting from recombination of the bright exciton (BE). The persistence of these bands in subsequent low-power measurements indicates that irreversible distortions of the nanotube structure efficiently brightens forbidden states via disorder-induced mixing of excitonic states. 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 [6]. Time-resolved PL measurements show that the decay times of the bright and dark excitons can differ by two orders of magnitude, the later being as slow as ∼170 ps. The observation of similar spectral

changes and dynamical characteristics upon treatment of the individual SWNTs with aqueous solution of gold, suggests that the lowest energy emission band results from triplet exciton recombination facilitated by spin-polarized states induced by structural defects or metal adsorption [7, 8].

2 Experimental To perform single SWNT spectroscopy and time-resolved PL measurements an inverted confocal microscope in combination with time-correlated single-photon counting electronics is used [9–11]. Spatially isolated individual SWNTs were obtained by spin coating a small volume of surfactant-coated CoMoCat material onto a glass cover-slip [12]. 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 laser beam was focused on the sample through a high numerical aperture objective (NA = 1.3) resulting in a diffraction limited excitation spot of ~400 nm, slightly smaller than the average nanotube length (~550 nm) determined by AFM measurements. The PL spectra were recorded with a CCD camera and a fast avalanche photodiode (full width at half maximum of 27 ps) was used to acquire PL transients.

3 Result and Discussion Figure 1 shows an example of generation of low-energy satellite PL bands for an individual (6,4) nanotube. Initial spectrum (black line) acquired at low excitation intensity shows a single emission peak centered at 1.41 eV, assigned to the allowed BE in (6,4) chirality nanotube [13]. Irradiation of the nanotubes for
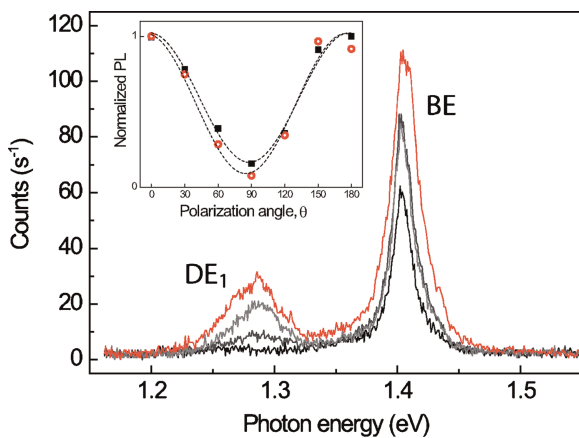

Figure 1 (online color at: www.pss-b.com) Creation of low energy satellite peaks in the PL spectrum of a (6,4) SWNT. Initial spectrum (black line) acquired at low excitation intensity $I_0 = 3 \times 10^{13}$ photons/pulse·cm^2 and considerably modified spectrum (red lines) of the same nanotube acquired after exposure to high excitation intensity $\sim 17 \cdot I_0$. Low energy satellite contributions shifted by ~30–60 meV (DE$_2$) [10] and ~110–190 meV (DE$_1$) with respect to the BE emission are assigned to emission from optically dark states. Gray lines were acquired sequentially between initial and final spectrum at intermediate intensity $\sim 7 \cdot I_0$, illustrating the step-like creation of the additional bands. Inset shows the polarization dependence of the PL emission for the BE (open circles) and the dark exciton DE$_1$ (filled squares) determined from a series of spectra recorded for the same (6,4) nanotube. The dashed lines are $\cos^2\theta$ fits.

10–100 s with an order-of-magnitude-higher pulse intensity results, in some cases, in significantly modified spectra (denoted by the red lines in Fig. 1) with additional red-shifted 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 pulse intensities that initiate multi-photon processes are crucial to induce these modifications. High-power cw excitation, on the other hand, mainly leads to the photobleaching and blinking of nanotube PL [14]. Satellite peaks for different (6,4) and (5,4) nanotubes consistently appear at similar energies and can be roughly divided into two groups [10], with red shifts of ~110–190 meV (DE$_1$) and ~30–60 meV (DE$_2$) in good agreement with Ref. [15]. 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 [16].

The intensities of the original BE peak and the newly created satellite DE$_1$, shown in the inset of Fig. 1, exhibits the same $\cos^2\theta$ behavior, depending on the analyzer angle placed in the detection path, proving that the emission bands belong to the same nanotube and indicating that the red-shifted emission originates from an intrinsic state of the SWNT. Furthermore, the consistent appearance of the new bands in DNA-wrapped SWNTs and nanotubes embedded in a poly(methyl methacrylate) (PMMA) matrix shows that the effect is not due to a chemical reaction that is specific to the sodium cholate surfactant.

Based on these experimental observations, we conclude that, during intense irradiation, the structure of the nanotube is modified by the creation of local defect sites. These defects alter the local symmetry of the nanotube, partially removing restrictions for the population and subsequent emission from intrinsic dark states [5].

The population dynamics of both dark and bright excitonic states and the effect of the created disorder are studied by time-resolved PL measurements of the different emission bands before and after the creation of emission satellites. Fig. 2 depicts representative PL transients detected from the shaded spectral areas (shown in the inset) for an individual (5,4) nanotube. Two important conclusions can be drawn from these data. First, upon creation of the satellite peaks, the BE lifetime is decreased (gray curve), compared to the initial decay (black curve); second, the DE$_1$ emission has a much longer decay time. Monoexponential fits (represented by dashed lines in Fig. 2) to these transients give the lifetimes of the main emission peaks before and after the creation of the red-shifted band 13 and 2 ps for the (5,4) tube, in the range of the lifetimes usually observed for the BE peak [9]. The decay of dark exciton DE$_1$ is dominated by much longer time constants, 177 ps in the present example. Thus, other origins of the low-energy bands, such as biexcitons and phonon replica of the BE, can be excluded, based on this slow decay dynamics. In addition, we observed a fast decay component (2 ps) with a much-smaller photon flux (by a factor of ~1/20). This component is either due to

Phys. Status Solidi B **246** No. 11–12 (2009)   2681
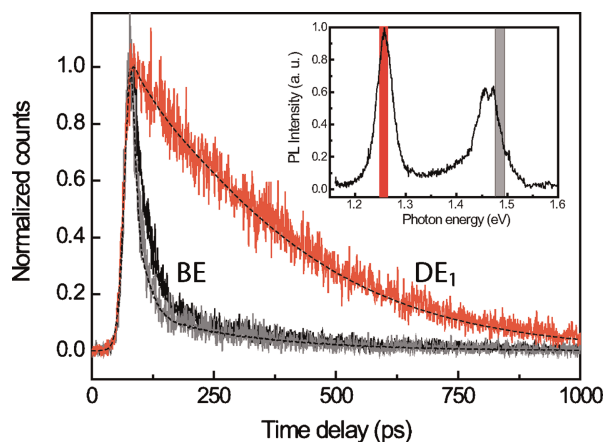
Original
Paper

Figure 2 (online color at: www.pss-b.com) PL transients visualizing the decay dynamics of different emission peaks in the spectra of individual SWNTs (insets) for a (5,4) tube. Black curve shows the decay of the BE state detected in the gray shaded spectral range in the inset before creation of the low energy satellites. After creation of the dark state emission, the decay rate of the BE is increased significantly (gray line). The decay of the dark excitonic state DE_1, shifted by 190 meV with respect to the BE, is substantially slower (red curve). Dashed lines are exponential fits to the data (see text).

Figure 3 (online color at: www.pss-b.com) The lifetime of the DE_1 state depends on the energy splitting between the dark and BEs indicating thermally activated depopulation of the dark state. The solid black line is a reproduction of the dependence, assuming two-

transitions from DE_1 to BE or to other dark excitonic states within the DE_1 manifold. Generally, the decay dynamics of DE_1 is expected to be complex and difficult to assess, because the defects responsible for the brightening will be localized, presumably affecting only finite-length nanotube sections on the order of the exciton's diffusional range (∼110 nm) [14, 17]. Because of the large separation of the emission peaks and the detected spectral windows (shaded areas in insets in Fig. 3), overlapping emission contributions from the BE state are not sufficient to explain this decay component. Measurements on several other (6,4) and (5,4) SWNTs consistently show the same effects with DE_1 lifetimes ranging up to 177 ps. Decay times derived from time-resolved PL and pump-probe data in the range of 50–300 ps with small relative amplitudes have been reported previously from ensemble samples as part of the multiexponential decay [18, 19]. We speculate that these decay times could originate from the newly created states observed here.

The emission bands with smaller energy shifts in the range of several tens of millielectron Volts (DE_2), exhibit exactly the same decay behavior as the main peak (data not shown). Dark states a few millielectron Volts below the BE were shown to affect the dynamics of BE PL [11]. The observed slow decay component was attributed to weak coupling of the two states. This study, focusing on highly luminescent and presumably defect-free individual nanotubes, explained the inefficient coupling to be mediated by phonon modes. Assuming that the DE_2 observed here is identical to that of Ref. [11], its similar dynamics with the BE indicates that, because of the defect-induced mixing of the excitonic states, the efficiency of the coupling is significantly increased, leading to faster transition rates and thermal equilibration between the two states.
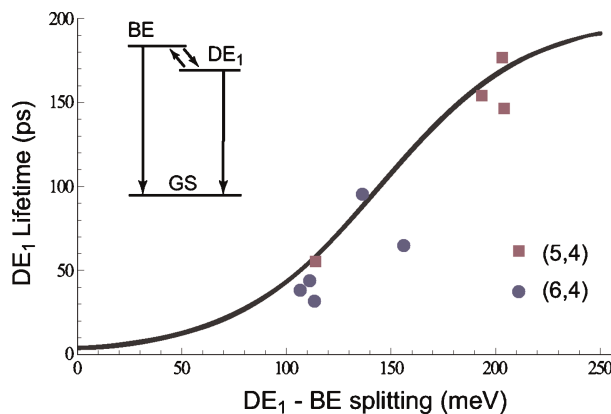
Similarly, if a fast (1 ps) coupling from bright to DE_1 state at 0 K is assumed due to state mixing, it can explain the observed dependence of the BE and DE_1 emission energy splitting on the dark excitonic lifetime, depicted in Fig. 3. In this model (black line in Fig. 3), we assumed two excited levels, BE and DE_1, coupled to the ground state with recombination rates 1/(2 ps) and 1/(200 ps), respectively and a temperature of 400 K. Although it would be a simplification to treat nanotube's excited states as a two-level system neglecting the exciton mobility, the general behavior can be reproduced by employing thermally activated coupling of DE1 to the higher lying excited state via phonon-induced exciton scattering and assuming Bose-Einstein distribution of phonon population at 400 K.

Next, we address the more rapid decay of the BE in the presence of the red-shifted peaks (Fig. 2). Because the amplitude of the BE peak is decreased, we conclude that disorder-inducing defects are responsible for additional radiationless relaxation channels depopulating the bright excitonic state. Two possible competing channels can be distinguished. First, population transfer to the dark state DE_1, mediated by the introduced defects and second, decays to the ground state, facilitated by enhanced exciton–phonon coupling, because of defect-associated local phonon modes [20, 21]. Both relaxation channels require propagation of the BE along the nanotube to enable interaction with localized defects; therefore, faster decay also serves as an evidence for the mobility of excitons in nanotubes [22, 14, 17]. Population transfer from bright states to dark states, on the other hand, would result in a delayed rise of the DE_1 emission with a rise of time that is equal to the decay time of the bright state. Such a delayed rise, which 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 BE maintains a different and finite lifetime in the presence of the dark state DE_1, clearly shows that these two states are not in thermal equilibrium.

The strongly polarized emission of the DE_1 state depicted in Fig. 1 and its regular appearance at similar emission energies for different nanotubes, makes the possibility of simply having luminescent defects unlikely. Recent experimental studies on ensemble samples enriched with (6,5) chirality nanotubes have attributed low-energy emission bands to 160 meV phonon sidebands of K momentum excitons that are higher in energy than the BE [23]. However, the large energy separation of the DE_1 state of ∼190 meV observed in the present work (Fig. 3) also excludes this scenario. On the other hand, the energy separation for the triplet state calculated for the (6,4) chirality in Ref. [16] is in good agreement with our experimental data. The intersystem crossing leading to triplet emission could be assisted by coupling to high spin density states created by sidewall modification of the nanotube, such as vacancy creation [7]. The energy of ∼5 eV needed to create a vacancy [7] could be provided through multiphoton excitation processes, which explains the high pulse energies required for the creation of DE_1. Generally, magnetic impurities that increase spin-orbit coupling could also be formed by trace amounts of residual catalyst materials, which explains the observation of dark state emission in other nanotube materials reported in the literature [15]. The slow PL decay times for the triplet exciton can be explained by the spin-dependent nature of the non-radiative relaxation mechanism.

To test this possibility, we treated the SWNTs with a pH-neutralized aqueous solution of gold that induces spin-polarized states with significant magnetic moments when adsorbed on SWNTs [8]. Strikingly, covering the sample with a gold solution results in similar changes in the single nanotube PL spectrum without requiring high-power pulsed excitation, thus supporting the hypothesis of the triplet state emission [10]. Importantly, no additional PL bands have been observed in control experiments on nanotubes that have been deposited on gold films (not shown) as well as near-field optical experiments using sharp gold tips [24], indicating that the new PL bands are not created by metal-surface-induced electromagnetic field enhancement.

In summary, we showed that new emission bands can be induced in the spectra of individual SWNTs after exposure to high excitation intensities and by adsorption of gold. We suggest that local defects induce the mixing of different excitonic states and the relaxation of selection rules via perturbation of the electronic structure. The presented measurements confirm that non-radiative decay is accelerated by increasing the number of defects and that PL from the same nanotube can have decay rates varying by 2 orders of magnitude, depending on the detected spectral range. These findings are relevant for nanotube photophysics, they also indicate possible novel routes for the manipulation of SWNT optical properties.

References

[1] V. Perebeinos, J. Tersoff, and P. Avouris, Nano Lett. **5**, 2495–2499 (2005).
[2] E. B. Barros, R. B. Capaz, A. Jorio, G. G. Samsonidze, A. G. Souza Filho, S. Ismail-Beigi, C. D. Spataru, S. G. Louie, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **73**, 241406(R) (2006).
[3] A. Jorio, M. S. Dresselhaus, and G. Dresselhaus (Eds.), Carbon Nanotubes. Topics in Applied Physics, Vol. 111 (Springer, Berlin/Heidelberg, 2008).
[4] A. Srivastava, H. Htoon, V. I. Klimov, and J. Kono, Phys. Rev. Lett. **101**, 087402 (2008).
[5] C. D. Spataru, S. Ismail-Beigi, R. B. Capaz, and S. G. Louie, Phys. Rev. Lett. **95**, 247402 (2005).
[6] A. Hartschuh, H. N. Pedrosa, L. Novotny, and T. D. Krauss, Science **301**, 1354–1356 (2003).
[7] P. O. Lehtinen, A. V. Krasheninnikov, A. S. Foster, and R. M. Nieminen, Carbon Based Magnetism (Elsevier, Amsterdam, 2006).
[8] E. Durgun, S. Dag, S. Ciraci, and O. Gulseren, J. Phys. Chem. **108**, 575 (2004).
[9] T. Gokus, H. Harutyunyan, F. Hennrich, A. A. Green, M. C. Hersam, P. T. Araujo, M. Kappes, A. Jorio, M. Allegrini, and A. Hartschuh, Appl. Phys. Lett. **92**, 153116 (2008).
[10] H. Harutyunyan, T. Gokus, A. A. Green, M. C. Hersam, M. Allegrini, and A. Hartschuh, Nano Lett. **9**, 2010 (2009).
[11] S. Berciaud, L. Cognet, and B. Lounis, Phys. Rev. Lett. **101**, 077402 (2008).
[12] A. A. Green and M. C. Hersam, Mater. Today **10**, 59 (2007).
[13] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, and R. B. Weisman, Science **298**, 2361–2366 (2002).
[14] C. Georgi, N. Hartmann, T. Gokus, A. A. Green, M. C. Hersam, and A. Hartschuh, Chem. Phys. Chem. **9**, 1460 (2008).
[15] O. Kiowski, K. Arnold, S. Lebedkin, F. Hennrich, and M. M. Kappes, Phys. Rev. Lett. **99**, 237402 (2007).
[16] E. Chang, D. Prezzi, A. Ruini, E. Molinari, arxiv.cond-mat/0603085v1 [cond-mat.mtrl-sci]
[17] L. Cognet, D. A. Tsyboulski, J. D. R. Rocha, C. D. Doyle, J. M. Tour, and R. B. Weisman, Science **316**, 1465–1468 (2007).
[18] S. Berger, C. Voisin, G. Cassabois, C. Delalande, and P. Roussignol, Nano Lett. **7**, 398–402 (2007).
[19] L. Huang, H. N. Pedrosa, and T. D. Krauss, Phys. Rev. Lett. **93**, 017403 (2004).
[20] B. F. Habenicht, H. Kamisaka, K. Yamashita, and O. V. Prezhdo, Nano Lett. **7**, 3260 (2007).
[21] V. Perebeinos and P. Avouris, Phys. Rev. Lett. **101**, 057401 (2008).
[22] A. Hagen, M. Steiner, M. B. Raschke, C. Lienau, T. Hertel, H. Qian, A. J. Meixner, and A. Hartschuh, Phys. Rev. Lett. **95**, 197401 (2005).
[23] O. N. Torrens, M. Zheng, and J. M. Kikkawa, Phys. Rev. Lett. **101**, 157401 (2008).
[24] H. Qian, P. T. Araujo, C. Georgi, T. Gokus, N. Hartmann, A. A. Green, A. Jorio, M. C. Hersam, L. Novotny, and A. Hartschuh, Nano Lett. **8**, 2706 (2008).