Ultrafast charge photogeneration and dynamics in semiconducting carbon nanotubes

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Abstract: We show that charge-carriers are instantaneously photogenerated in semiconducting carbon nanotubes by identifying their spectral signature in transient absorption. We exploit carbon nanotubes as ideal systems for the study of charge-carriers dynamics in one dimension.
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Single-walled carbon nanotubes (SWNTs) are excellent model systems for the study of photoexcitation dynamics in one-dimensional (1D) quantum confined systems. Theory predicts that Wannier-Mott excitons are the elementary photoexcitations in SWNTs, due to the strong Coulomb interaction caused by the weak screening [1]. Such excitons have peculiar 1D characteristics, such as extraordinary large binding energies, large size and 1D transport. Experimental observations, such as the measured binding energy, typically 0.1-1 eV [2], and the electron-hole correlation length, in the 1-10 nm domain [3] confirm theoretical predictions. The exciton model alone, however, fails to capture the whole dynamics following photoexcitation, and many other photoexcited species have crowded the complex scenario of SWNTs' optical response, ranging from triplets to bi-excitons and trions. Experiments based on photocurrent, transient absorption and THz spectroscopy also point out a non-negligible photogeneration of free charge-carriers. This is in contrast with the excitonic model and the reduced Sommerfeld factor that predicts that excitons should be the only species generated upon photoexcitation. Attempts to solve this discrepancy proposed non-linear processes, such as exciton-exciton annihilation, as a mechanism of charge-carrier photogeneration. However, there is solid experimental evidence that charge-carrier photogeneration is linear with the pump fluence.

Here we apply broadband ultrafast transient absorption spectroscopy to the semiconducting (6,5) SWNT (Fig. 1a) and show that charge-carriers can be identified by their effect on excitonic resonances, in particular the large Stark shift that they induce on high-energy, easily polarizable excitons (S_{22} and S_{33}). Having identified the Stark shift as a good spectroscopic fingerprint for charge-carriers, we are able to study their dynamics in a nearly ideal 1D system. We find that a fraction of the absorbed photons generates geminate charge-carrier pairs within our temporal resolution (≈ 50 fs), which then recombine on the picosecond timescale following the characteristic kinetic law of random walk in 1D.

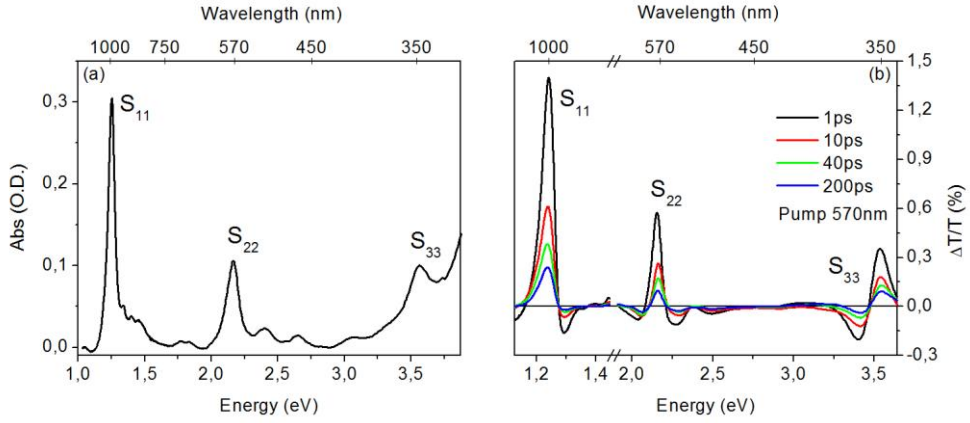

Fig. 1. (a) Ground state absorption spectrum of the (6,5) semiconducting carbon nanotubes used for the experiments. The sharp peaks are due to excitonic transitions, in particular S_{11} at approximately 1 μm, S_{22} at 570 nm and S_{33} at 350 nm. (b) ΔT/T spectra for the (6,5) CNT sample at different pump-probe delays for 570 nm excitation wavelength.

Our analysis starts from the observation that the first derivative of the ground state absorption spectrum, i.e. a photoinduced red shift of the excitonic transition, can reproduce many of the features observed in the differential transmission (ΔT/T) spectra of semiconducting SWNTs (Fig 1b). This effect can be ascribed to different physical mechanisms, such as bi-excitons or trions formation, thermal effects or Stark effect. Here we unambiguously demonstrate that this derivative shape is indeed due to strong local electric field induced by photogenerated charge-carriers, which shifts the electronic transitions by Stark effect [4]. In particular, we show that the energy shift is stronger for excitons with lower binding energy, as for S_{33} with respect to S_{11}, as expected for the Stark effect (Fig. 1b). This suggests that the higher energy S_{33} exciton is ideally suited for directly probing charge-carriers in SWNTs and can be exploited to further analyze the charge photogeneration process and to study charge-carrier dynamics in one dimension. Our data show that the free charge- carriers are generated within 50 fs. The temporal evolution of the S_{33} pump-probe dynamics is very accurately reproduced by a power law $\sim t^{-0.5}$ (Fig. 2b). A monomolecular power law decay is the predicted dynamics for *geminate* recombination of free particles after random walk in an infinite one-dimensional chain. A more detailed modelling of the geminate recombination process indicates that the initial distance between the geminate e-h pair is of the same order of magnitude of the exciton correlation length, thus suggesting that charge-carriers arise from instantaneous linear exciton dissociation.

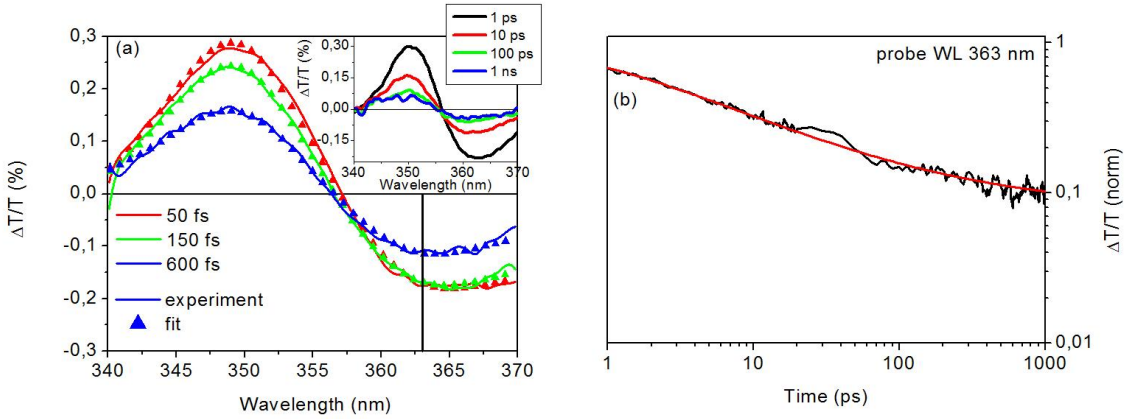

Fig. 2. (a) ΔT/T spectra at different pump-probe delays for the S_{33} exciton, following excitation at S_{11}, together with a fitting model based on the energy shift contribution from Stark effect. (b) Dynamics at 363 nm for excitation at S_{11} and fitting with a $\sim t^{-0.5}$ power law.

Our results shed new light onto the charge photogeneration mechanism in SWNTs, suggesting that the nascent exciton dissociates spontaneously, perhaps in presence of extrinsic screening of the Coulomb attraction, possibly due to water or other ambient contamination [5].

References

[1] T. Ando, "Excitons in Carbon Nanotubes", J. Phys. Soc. Jpn. **66**, 1066-1073 (1997).

[2] F. Wang, G. Duckovic, L. E. Brus and T. F. Heinz, "The optical resonances in carbon nanotubes arise from excitons", Science **308**, 838-840 (2005).

[3] L. Luer, S. Hoseinkhani, D. Polli, J. Cochet, T. Hertel and G. Lanzani, "Size and mobility of excitons in (6,5) carbon nanotubes", Nature Phys. **5**, 54-58 (2009).

[4] G. Soavi, F. Scotognella, D. Brida, T. Hefner, F. Spath, M. R. Antognazza, T. Hertel, G. Lanzani and G. Cerullo, "Ultrafast charge photogeneration in semiconducting carbon nanotubes", J. Phys. Chem. C. **117**, 10849-10855 (2013).

[5] P. G. Collins, K. Bradley, M. Ishigami and A. Zettl, "Extreme oxygen sensitivity of electronic properties of carbon nanotubes", Science **287**, 1801-1804 (2000)