DOE Final Technical Report

Recipient: University of Rochester

Project Title: Directing Photogenerated Charges Along Individual Carbon Nanotubes

Principal Investigator: Todd D. Krauss

Award Number : DE-FG02-06ER15821

Date of the report: 9 November 2020

Period covered by the report: 03/01/2018 – 02/28/2020

Research Accomplishments:

1) Single molecule microscopy was used to image photoluminescence (PL) brightening of individual sodium-dodecyl-sulfate (SDS)-wrapped single-walled carbon nanotubes (SWCNTs) upon addition of dithiothreitol (DTT). PL enhancement varied for each nanotube (NT), with some brightening by 16% and others by a factor of about 7. Interestingly, NTs that displayed lower initial QY values showed the largest increases in PL enhancement. SDS-SWCNTs longer than the diffraction limit were studied in order to spatially resolve the PL brightening phenomenon. Quite unexpectedly, a uniform, single-step PL brightening along the NT was consistently observed, suggesting that the PL enhancement is the result of a non-localized process (**Figure 1**). The even PL brightening seen over SWCNTs that are microns long implies that single point defect sites, which are known to have a large responsibility for exciton nonradiative decay, play no significant role in the brightening process. Interestingly, affixing the SWCNT strongly to the substrate surface mitigated the PL brightening response, consistent with a hypothesis that surfactant reorganization upon addition of DTT is responsible for exciton PL brightening.

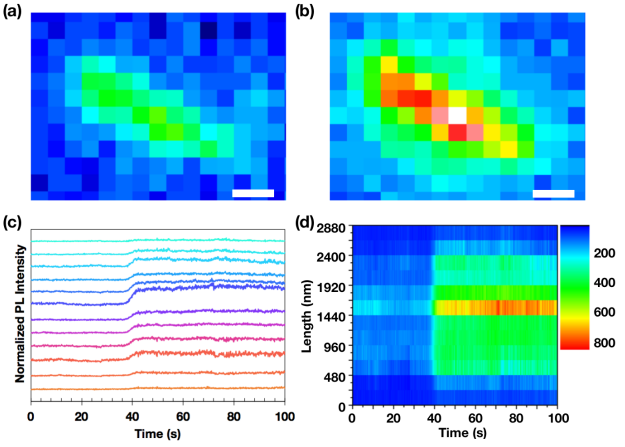

Fig. 1: PL image of a ~3 μm SWCNT before (a) and after (b) the addition of DTT under 532 nm excitation. The scale bars represent 500 nm. (c) Individual time traces of the PL intensity from each segment along the nanotube axis, extracted from a video recording the brightness process at a frame rate of 1/100 ms^{-1}. DTT solution was added to the SWCNT sample at ~ 28 s. (d) Two-dimensional PL intensity map as a function of nanotube length and experimental time, constructed from the time traces in (c).

2) A long-standing and significant challenge in the field of single-walled carbon nanotube (SWCNT) optics is to determine the influence of optically forbidden electronic states on the photophysical properties of the nanotube. Recently, two degenerate singlet-spin, odd-parity excitonic states with finite center-of-mass momenta have been characterized, termed *K*-momentum dark excitons (**Figure 2**). These excitons are optically forbidden because they have one charge carrier located at the *K* point and the other at the *K'* point and thus, due to momentum conservation, these excitons cannot arise from direct optical transitions. Recently we used variable temperature PLE spectroscopy to show that S_{11} excitons of sufficient thermal energy efficiently and elastically scatter one charge carrier to an equivalent *K*-point creating the KDE exciton. Our data strongly suggested that it was SWCNT defects that scattered the exciton (quasi elastically) into the KDE state.

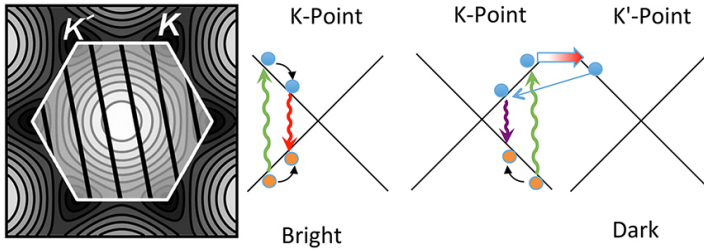

Fig. 2. (left) Brillouin Zone of SWCNTs and graphene. **(right)** Bright and dark *K*-momentum excitons and their photophysics. *K*-momentum excitons show PL (purple arrow) with the involvement of phonons (blue arrow) and defects (thick arrow).

Since photon emission from the KDE state is formally forbidden, we *hypothesized* that the lifetime of the KDE state should be substantially longer than the PL lifetime of S_{11}, the latter of which is extremely short, on the order of tens of ps. Recently acquired time resolved PL data has confirmed our initial ideas, and also provided some unexpected findings. For example, for (6,5) SWCNTs we have found that the average PL lifetime of the KDE state is over three times longer than the lifetime of the S_{11} state as measured from filtering the PL spectrum to include only PL from the KDE state (**Figure 3**). Interestingly, the PL dynamics from the KDE state is clearly bi-exponential at 300 K, with a fast component (35 ps) that is similar to the lifetime of the S_{11} and also a longer component (200 ps) that is

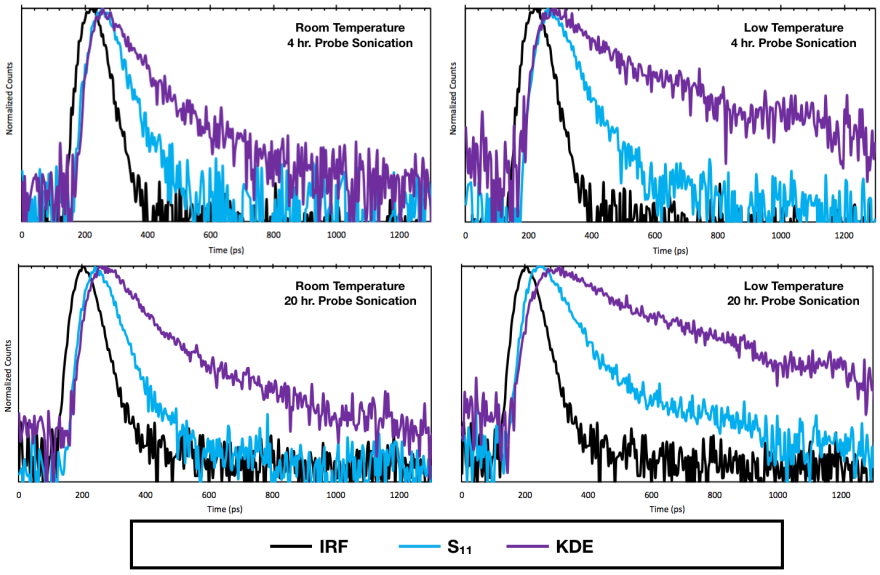

Fig. 3. PL lifetime measurements for (6,5) SWCNTs under various conditions. The PL lifetime of the KDE state is several-fold longer than the E_{11} state under every condition. At low temperatures, the lifetimes of both the E_{11} and KDE states increase, while increased sonication increases the KDE lifetime.

significantly enhanced in the KDE compared to the S_{11} PL. However, upon cooling the sample to 77 K, we found that the KDE PL decay dynamics remarkably switched to being a mono-exponential, losing the short time component completely. Since due to a long pass filter there is no possibility of contamination from other (*n,m*) chiral species, the short time component to the KDE and its disappearance at 77 K is not explained by the current model of KDE photophysics. Further, sonicating the SWCNT sample longer should increase the number of defects, which decreases PL quantum efficiency by increasing the nonradiative rate. Unexpectedly, we found that increasing sonication time increases the KDE PL lifetime by over 50%! Using a novel and simple rate-equation model for the excited state dynamics, we can explain all of our findings as arising from the complex interplay between the S_{11} and KDE states and an optically forbidden dark exciton state with zero center of mass momentum and even parity that is located a few meV below the bright S_{11} state.

3) EFM is a variation of AFM that allows for a quantitative determination of localized charges, dipole moments, and dielectric constants at the nanometer scale. A schematic of the experimental geometry for EFM is shown in **Figure 4.** By modeling the cantilever-substrate force as a capacitive interaction, local variations in dielectric constant (which affect the tip-substrate capacitance) can be determined quantitatively. By modeling the surface charge-cantilever force through a Coulombic interaction, quantitative determinations of surface charge magnitude and location are possible. EFM, even at 300K, has extremely low background noise; typically charge signals with magnitudes of less than 0.1 *e* can be resolved.

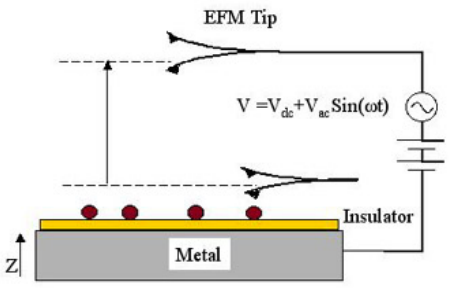

Fig. 4. Schematic of the typical experimental setup for EFM. A DC (V_{dc}) and AC (V_{ac}) voltage is applied to a metal AFM tip and Coulombic forces on the tip from surface charges are detected.

We have discovered surprisingly large electrostatic charge variations along relatively long NTs spun coat on a Si^{++} substrate coated with a few nm thick SiO_2 layer (**Figure 5)**. While the topographic and dielectric images show a homogeneous NT along its entire 2 μm length, (**Figures 5a,c**), the EFM charge image reveals significant heterogeneity in static charge along the NT (**Figure 5b**). For ease of visualization, in **Figure 5d** we include a "charge profile" image, where the charge signal of the NT at the spatial resolution limit of 20 nm was plotted and color coded. Indeed, for dozens of NTs solubilized in aqueous suspension using standard ionic surfactants (e.g. sodium deoxycholate) we found charge variations all along the NT with magnitudes on the order of 1 *e* to a few *e*, with both positive and negative signs. In terms of their origin, the charges seem to be correlated with the presence of surfactant coating the NT. Indeed, EFM images of surfactant aggregates away from NTs show both positive and negative charges of similar magnitude to what we observe on the NT. Our EFM data is consistent with reports showing that ionic surfactants can form structureless clumps or aggregates on the NT surface, and that ionic surfactants can cause NTs to carry a significant static charge. Further, if the surfactant is rinsed off the NT, the EFM charge image of the uncoated NTs becomes significantly more homogeneous, with NTs imaging approximately neutral. However, as also seen in the charge profile in **Figure 5**, even bare NT sections (blue star) away from regions covered in surfactant (*e.g.* green star) exhibit a

charge signal. This is strong evidence that the NT is locally responding to compensate for the surfactant charge. Using the capacitance of the AFM tip-substrate to convert charge to potential, one notices that the surface potential change we measure is similar to potentials reported from EFM images of NTs with localized sp^3 defects arising from covalent functionalization of the SWCNT sidewall. Altogether, our EFM data provides a compelling possible explanation for the source of potential energy minima along the NT that localize excitons at low temperature.

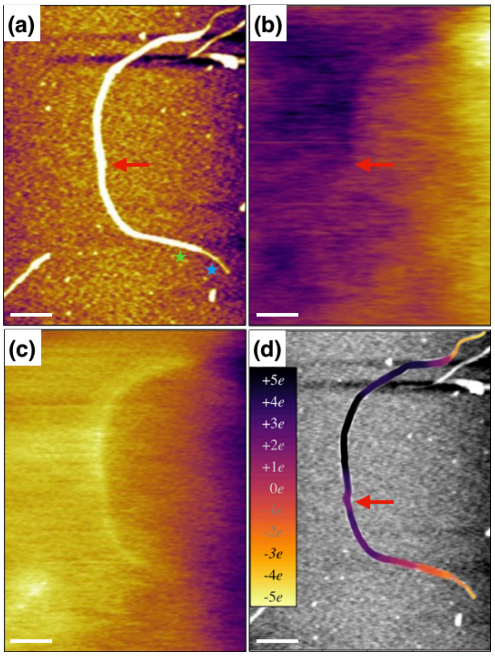

Fig. 5. EFM images of (a) topography, (b) charge, (c) dielectric constant, and (d) charge profile for a single NT. Dark (bright) contrast in (b) is positive (negative) charge. Red arrow points to a defect (kink) which indicates a discontinuity in the charge signal. The NT diameter is 2 nm at the green star (surfactant coated) and 0.8 nm (bare NT diameter) at the blue star. Scale bars are 200 nm.

Publications:

One manuscript submitted and two manuscripts in preparation.

Students involved in this project:

Graduate Students: Trevor Tumeil (100%), Erin Christensen (66%)

Unexpended funds: None.