

The Influence of DNA Wrapping on SWNT Optical Absorption in Perpendicular Polarization

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ABSTRACT

Numerous electronics applications have been proposed for discrete single-walled carbon nanotubes (SWNTs) due to their exceptional electronic properties, which vary with diameter and chirality of the tube. Any solution processing to sort as-grown SWNTs by type requires a robust dispersion method that must overcome nanotube insolubility and strong van der Waals attraction between tubes. Functionalization of SWNTs with helically wrapped single-stranded DNA yields stable hybrid structures that disperse in aqueous solution.[1], [2] Since these hybrids are intended for use in optical and electronic devices, we investigate whether the optical properties of DNA-wrapped SWNTs are different than those of bare nanotubes. We find changes in the optical absorption spectra in perpendicular polarization, including circular dichroism of achiral nanotubes. These effects may serve as characterization tools to identify the presence of a DNA wrap.

Keywords: carbon nanotube, optical absorption, DNA, circular dichroism

1 INTRODUCTION

Single-walled carbon nanotubes are being studied as potential components in of the next generation of transistors, field emitters, photodetectors, and biological sensors [3], to name a few potential applications, but to realize these devices, methods must be developed to gain control over the material. Currently all nanotube fabrication processes produce tubes of various structures and, hence, various electronic properties. If we wish to take advantage of the unique properties of a specific SWNT structure, starting with currently available material, SWNTs must first be dispersed in solution. Single-stranded DNA can form a stable hybrid with a SWNT, allowing dispersion. Ion exchange chromatography has been used with success to help sort DNA-SWNT hybrids by structure and electronic properties [1], [2], and methods are being developed for controlled placement of the hybrids. Since a DNA-SWNT hybrid is not readily dismantled, and indeed the DNA wrap may prove useful for some applications, it is important to determine whether the DNA changes optical or electronic

properties of SWNTs.

For the case of optical absorption of light parallel to the SWNT axis, the direct optical bandgap of a semiconducting SWNT decreases only slightly due to DNA wrapping. This result of our earlier work [4] is in agreement with experiments using parallel polarization.[5] For the present work, we consider optical absorption with perpendicular (or circular) polarization. Although perpendicular absorption is weaker than parallel absorption, it has been successfully measured for surfactant dispersed SWNTs.[6]–[8] We find changes in absorption spectra upon hybridization with DNA, including new transitions prohibited for pristine nanotubes in the same polarization. In addition, we find circular dichroism for non-chiral SWNTs. These optical effects may be used to verify the presence of DNA-wrapping. Understanding these effects could also aid in the characterization and identification of nanotubes by type.

2 RESULTS

The ionized DNA backbone has a net negative charge, and this charged helical wrap breaks the symmetry of a bare SWNT. The potential of the DNA is too strong for a perturbative approach, so we numerically solve the joint Schrödinger-Poisson equations beyond the perturbation approximation to determine the changes in optical absorption resulting from hybridization.

As observed previously, absorption of light with *parallel* polarization should not change significantly upon DNA hybridization.[4] In contrast, Figure 1 shows that for a semiconducting zigzag (5,0) DNA-SWNT hybrid, the optical absorption coefficients for light polarized *perpendicularly to the SWNT axis* (dashed orange curve) drastically differ from the bare tube absorption in the same polarization (solid black curve). The first absorption peak in cross-polarization for the bare SWNT corresponds to E_{12} and E_{21} transitions. This peak is also present for the DNA-SWNT hybrid, although it is shifted to higher frequency. In addition, a peak at lower frequency near that of the bare E_{11} transitions appears as a consequence of the lifting of selection rules. The upper insets show absorption-luminescence maps for the bare (left) and DNA-wrapped (right) (5,0) nanotube. Additional transitions can clearly be seen for the hy-

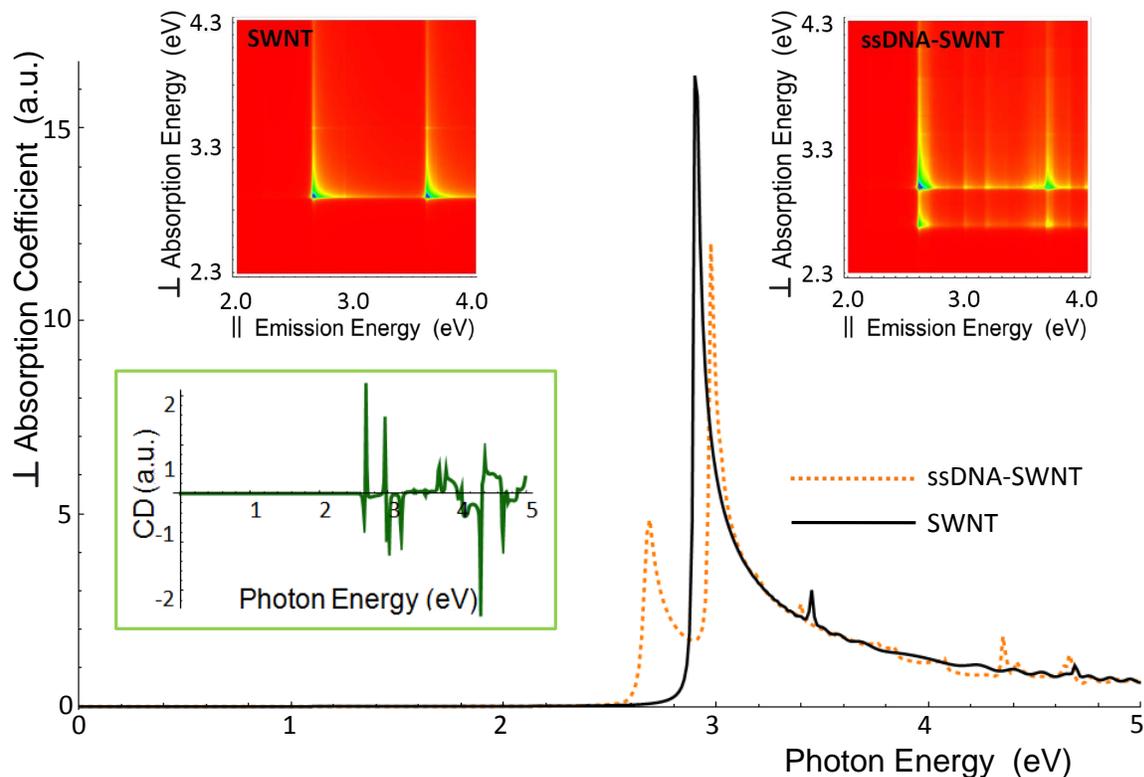


Figure 1: Calculated absorption spectrum in perpendicular polarization for a (5,0) SWNT with (dashed orange) and without (solid black) a DNA wrap. The upper left inset shows an absorption-luminescence map for the bare (5,0) SWNT, while the upper right inset shows the same for the DNA-wrapped SWNT. The lower left inset shows circular dichroism for the DNA-wrapped (5,0) SWNT.

brid.

For cross-polarized transitions, the selection rule for angular momentum is $\Delta m = \pm 1$ for the bare tube. However, angular momentum is not a good quantum number for the subbands of the wrapped SWNT, due to the helical polarization of the electron (and hole) wave functions by the Coulomb potential of the DNA, as shown in Figure 2. This symmetry breaking results in allowed perpendicularly polarized optical transitions at lower frequency near that of the $\sim E_{11}$, which is prohibited for the bare tube. The corresponding physical explanation is that the polarization of the electron (hole) due to the transverse electric field of the DNA creates a permanent dipole across the nanotube, which can then be excited by the perpendicularly polarized incident light.

3 CALCULATION METHODS

A semi-empirical orthogonal tight-binding approach was used to calculate optical absorption of several of DNA-SWNT complexes. This simple numerical approach

is chosen to capture the essential physics of the problem with low computational cost. The DNA backbone is modeled as a regular, infinite helix of point charges representing the phosphate groups wrapped around the tube (as seen in Figure 2). The angle of wrap, its position with respect to the underlying graphene lattice of the nanotube, the distance between the tube and the wrap, and linear charge density are parameters that can be obtained from molecular dynamics simulations or adjusted to the experimental data. For a broad range of these parameters, we observe similar symmetry breaking effects.

In order to break the perpendicular selection rules for angular momentum, one must mix subbands with $\Delta m = \pm 1$. The most effective wrap is along the zigzag direction of the SWNT lattice (at an angle of 60° to the circumference). Such a wrap effectively mixes the lowest conduction and valence bands of different angular momentum as a result of the phase matching [15] of the perturbation.

The partial absorption coefficient is calculated for a

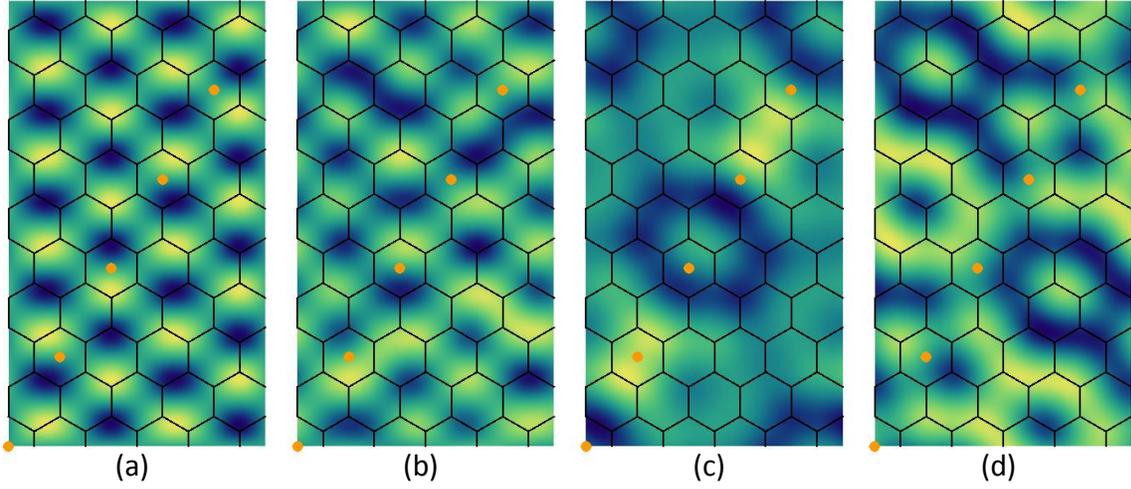


Figure 2: Wavefunctions for the unscrrolled (5,0) SWNT: (a) Unperturbed (bare) SWNT, (b) LUMO, (c) HOMO-2, and (d) HOMO-6. The projected charges of the idealized helical wrap can be seen as diagonal lines of dots.

$$\alpha_{\pm}(\hbar\omega, k) \propto \sum_i \sum_f \frac{q^2 |\langle \psi(k, m_f, \lambda_f) | \vec{p} \cdot \vec{e}_{\pm} | \psi(k, m_i, \lambda_i) \rangle|^2}{m_0 \omega} \times \frac{f(E_i(k, m_i, \lambda_i)) [1 - f(E_f(k, m_f, \lambda_f))] \Gamma}{[E_f(k, m_f, \lambda_f) - E_i(k, m_i, \lambda_i) - \hbar\omega]^2 + \Gamma^2} \quad (1)$$

bare SWNT as shown in Equation (1), where $\hbar\omega$ is the energy of the incident light, k is the electron wavevector, q is the magnitude of the electron charge, m_i and m_f refer to the initial and final angular momentum quantum numbers, λ_i and λ_f label the band (conduction or valence) of the initial and final states, m_0 is the free electron mass, $f(E)$ is the Fermi-Dirac function, and Γ is a phenomenological broadening parameter, which was set to 0.008 eV for these simulations. $|p_{\pm}| = qR |\langle \psi(k, m_i, \lambda_i) | e^{\pm i\theta} | \psi(k, m_i \pm 1, \lambda_f) \rangle|$ is the dipole matrix element for a transition from an initial state (with energy E_i) in the valence band, $|k, m_i, \lambda_i\rangle$, to a final state (of energy E_f) in the conduction band, $|k, m_f, \lambda_f\rangle$, for incident light with the circular polarization \vec{e}_{\pm} , with the selection rule for angular momentum $\Delta m = m_f - m_i = \pm 1$. One can exclude the DNA from the spectra analysis because the DNA absorption edge [9], [10] is at approximately 4.1 eV, which is well above the main IR spectral features of the SWNT itself.

The total absorption spectrum is determined by integrating the partial absorption coefficient Equation (1) over the wavevector inside the first Brillouin zone, $\alpha_{\pm}(\hbar\omega) = \int_{BZ} \alpha_{\pm}(\hbar\omega, k) dk$, and is plotted in Figure 1. Absorption of cross-polarized light drastically differs for the hybrid and the bare tube.

The circular dichroism (CD) spectrum of the DNA-SWNT hybrid is given by the difference in absorption for right and left circularly polarized light: $CD = \alpha_+ - \alpha_-$ (lower left inset of Figure 1). This CD is not the result

of any chirality of the DNA, because DNA absorption is not included in this work. Then the optical activity must be fully attributed to the nanotube itself and the "natural" helicity of the electron states. This result is further supported by the experimental data in Ref.[11]. Similar results were seen for a variety of achiral as well as chiral tubes.

4 DISCUSSION AND CONCLUSIONS

The exact geometry of the DNA wrap for an arbitrary tube is not yet known, and may not be uniform across the length of a SWNT. The effect of variation of the parameters of the wrap and/or tube diameters should be considered. Our simulations showed that CD and the cross-polarized absorption spectrum do not change significantly when a given helical wrap is displaced along the length of the tube or rotated about the axis of the tube.[14] Neither of these shifts changes the helical angle of the DNA backbone. In contrast, absorption spectra did change when the helical angle changed, due to the importance of symmetry matching between the SWNT lattice and the DNA backbone helical angle. Despite these changes, a general qualitative feature of the helical symmetry breaking remains: new van Hove singularities appear in the optical data. A random coating of DNA with no particular symmetry is expected to yield at most in a broad, featureless background.

In summary, we predict that SWNT optical absorption in perpendicular polarization can be used for optical detection of regular helical DNA wrapping. We calculated optical absorption spectra, as well as circular dichroism for DNA-wrapped single-wall nanotubes. The Coulomb potential of the ionized DNA wrap polarizes the electronic structure of the tube and results in helical symmetry breaking in an intrinsically achiral SWNT. We predict qualitative changes in the absorption of circularly or linearly polarized light with its electric field perpendicular to the nanotube axis. Namely, new transitions appear in the cross-polarized absorption of the SWNT at wavelengths substantially larger than those of all allowed perpendicular E_{12} transitions in the bare tube. We propose to use the splitting and shift of the lowest perpendicular absorption peak to experimentally identify the existence and symmetry of the wrapping.

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