Temperature- and Magnetic Field-Dependent Photoluminescence from Solvent-Free Nanotube-Aerogel Ensembles

Parra-Vasquez, A.N.G. (C-PCS-LANL); Rice, W.D. (NHMFL-LANL); Crooker, S.A. (NHMFL-LANL); Montano, G. (CINT-LANL); Doorn, S.K. (CINT-LANL); Duque, J.G. (C-PCS-LANL)

Introduction: The unique and remarkably diverse electronic and optical properties of single-walled carbon nanotubes (SWCNTs) have shown promise for a variety of technologically relevant applications.[1] One major roadblock to straightforward optoelectronic adaptation is the inability to maintain the unique optical and electrical properties of SWCNTs when their solution concentrations are substantially increased, a situation which enhances van der Waals-assisted aggregation. When SWCNTs have been individualized with either certain polymers or surfactants, semiconducting nanotubes show clear excitonic photoluminescence (PL) from the lowest, parity-allowed singlet level.[2] However, the molecules that wrap, and thus individualize SWCNTs, also introduce a dielectric environment that alters the electronic structure of the nanotube.[3] Furthermore, retained water and certain wrapping molecules can cause significant stress on SWCNTs at low temperatures, a behavior known to also modify the electronic and optical properties.[4]

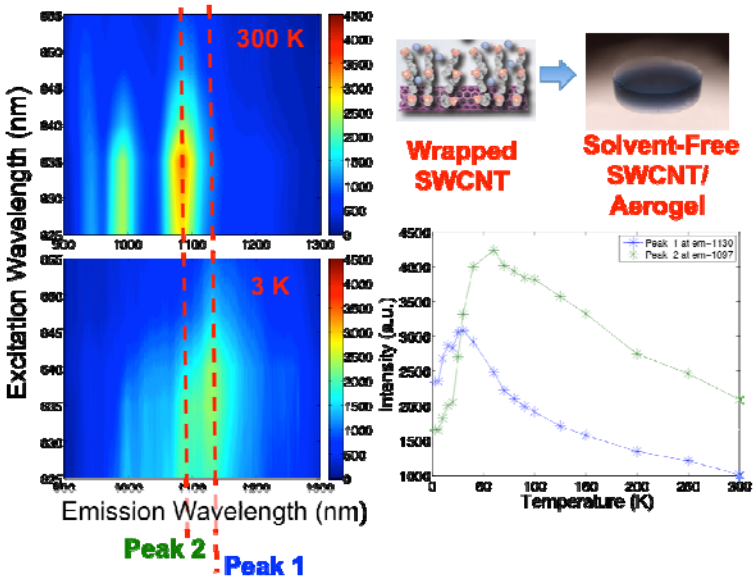

Figure 1: Cartoon of wrapped SWCNTs that are then transferred into a silicon-based aerogel to maintain isolation while removing the solvent. Such an aerogel (prepared with DOC wrapped SWCNTs) allows for photoluminescence emission at 300 and 3 K. A careful comparison at these two temperature extremes reveals a slight shift in emission and a change in emission intensity. The temperature dependence of two different nanotube peaks shows different, but similar, temperature dependence.

Experiment: To avoid these non-intrinsic environmental effects, we suspended SWCNTs in a silicon-based aerogel (Fig. 1), a process which not only maintains nanotube individualization and thus PL, but which should also substantially reduce, if not eliminate, solvent-nanotube interactions. To test the remnant SWCNT-surfactant-aerogel environmental interactions, we optically created excitons with visible light (625-655 nm) and detected their emission in the near-infrared regime (900-1300 nm) for several temperatures between 3 and 300 K. Figure 1 shows photoluminescence excitation at 300 and 3 K. These maps reveal the presence of two different peaks emitting between 1050 and 1150 nm. As temperature decreases, we clearly observe a redshift in the emission of the (8,4) chirality SWCNT peak (1097 nm). In addition, the magnitude of the excitonic PL first increases with lower temperature until around 50 K (4.3 meV or ~1 THz) before sharply decreasing in intensity as temperature continues to decrease (Fig. 1). This temperature-dependent decrease stems from excitons relaxing to their lowest energy state, a parity-forbidden 'dark' level. However, environmental interactions lead to mixing between the parity-allowed and parity-forbidden exciton singlet states, both changing the shape of the temperature-dependent PL curve and preventing the PL from being completely quenched at the lowest temperatures. By comparing the temperature- and magnetic field- dependent PL for four different SWCNT-surfactant-aerogel configurations, we quantified the degree of environmental interaction between the nanotubes and their surfactant-aerogel hosts. This comparison will allow for a better understanding of SWCNTs in solvent-free aerogels, but also new chemical optimization routes for producing ensembles of nanotubes that behave as truly-isolated SWCNTs.

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[1] Jorio, Dresselhaus, and Dresselhaus. *Carbon Nanotubes: Advanced Topics in Synthesis, Structure, Properties and Applications*. **2007**. [2] O'Connell *et al*. *Science* **2002**, *297*, 593-596. [3] Duque *et al*. *ACS Nano* **2011**, 5, 6686-6694. [4] Arnold *et al*. *Nano Letters* **2004**, 4, 2349-2354.