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## Review—Progress toward Applications of Carbon Nanotube Photoluminescence

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In the fifteen years following the discovery of single-walled carbon nanotube (SWCNT) photoluminescence, investigators have made significant progress in their understanding of the phenomenon and toward the development of applications. The intrinsic potential of semiconducting carbon nanotubes – a family of bright, photostable near infrared (NIR) fluorophores (900–2100 nm) with tunable properties, has motivated their use as optical probes and sensors. In this perspective, we highlight the advances made in the synthesis, processing, modification, separation, and metrology of carbon nanotubes in the context of applications of their photoluminescence.

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Single-walled carbon nanotubes are hollow cylinders of graphene, with diameters of approximately 1 nm and lengths that typically range from  $\sim 10$  nm to  $10 \mu\text{m}$ .<sup>1</sup> The hexagonal graphene lattice, composed entirely of  $\text{sp}^2$ -bonded carbon, can be rolled at varying angles to create seamless cylinders representing different nanotube structures.<sup>2</sup> Each distinct nanotube structure, or helicity, is uniquely identifiable by a pair of (n,m) integers, known as its chiral indices. Additionally, nanotubes exist as enantiomers, with (n,m) and (m,n) corresponding to the same chirality but different handedness.<sup>3</sup>

The electronic bandgap between valence and conducting bands in the density of states determines whether a SWCNT is metallic (0 meV bandgap), semi-metallic (<100 meV bandgap) or semiconducting (> 500 meV).<sup>3</sup> One-third of nanotube chiralities are metallic.<sup>1,4</sup> As quasi-one dimensional nanomaterials, semiconducting SWCNTs contain sharp peaks known as van Hove singularities in their density of states, which determine the optical properties of the SWCNTs. For semiconducting nanotubes, photoexcitation at distinct absorption transitions ( $E_{ii}$ ,  $i = 1$  to 4) can result in intrinsic bandgap photoluminescence which occurs only at the lowest energy transition ( $E_{11}$ ) at the band edge, in the near-infrared (NIR) spectral region.

Since the original observation of near-infrared emission from carbon nanotubes,<sup>5</sup> investigations of nanotube photoluminescence have spanned several areas: 1) understanding and enhancing carbon nanotube photoluminescence, 2) the development of experimental tools to optically characterize the NIR emission of carbon nanotubes at the ensemble and single-molecule level, and 3) the application of the imaging and sensing capabilities of nanotubes in increasingly complex environments (Figure 1). Regarding their synthesis, a number of techniques have been developed to increase the yield and purity of single-walled carbon nanotubes.<sup>6</sup> Relatively pristine, defect-free nanotubes, required to observe photoluminescence, were synthesized via several methods, including the high-pressure carbon monoxide (HiPco) process.<sup>7</sup> Most methods generate a mixture of nanotube chiralities that must be separated to obtain a structurally pure sample, although methods, such as the CoMoCAT (using a cobalt molybdenum catalyst) process, have been developed to narrow the distribution of chiralities synthesized.<sup>8</sup> An alternative ‘bottom up’ approach proposes a small molecule structural template for synthesizing nanotubes of a particular chirality.<sup>9</sup> Recently, single chirality growth with over 90% specificity,<sup>10</sup> and elongation of single chirality nanotube precursors to

several hundred nanometers in length<sup>11</sup> was accomplished. As work on increasing the yield and scalability of these synthesis processes continues, pre-dispersed carbon nanotubes of a specific chirality may be available for a variety of research applications.

Semiconducting carbon nanotubes quench upon contact with metallic nanotubes,<sup>5</sup> necessitating methods to individually disperse SWCNT mixtures in solutions or composites. However, the hydrophobic graphitic surface of as-produced carbon nanotubes renders them insoluble in water, while strong inter-tube van der Waals interactions cause the formation of bundles/aggregates.<sup>12</sup> Investigations into the individual dispersal of SWCNTs to result in luminescent suspensions found that certain dispersants facilitate aqueous suspension, including charged and non-ionic surfactants.<sup>13</sup> To allow for stable suspensions upon removal of unbound dispersants, molecules with greater binding affinity were needed. Studies found dispersants, including biomolecules such as lipids, DNA and proteins, which could stably suspend SWCNTs. Modular materials, such as polyethylene glycol-lipid conjugates,<sup>14</sup> derivatizable polymer libraries,<sup>15,16</sup> and single-stranded DNA,<sup>17</sup> have been used to construct numerous SWCNT complexes for imaging and sensor applications.

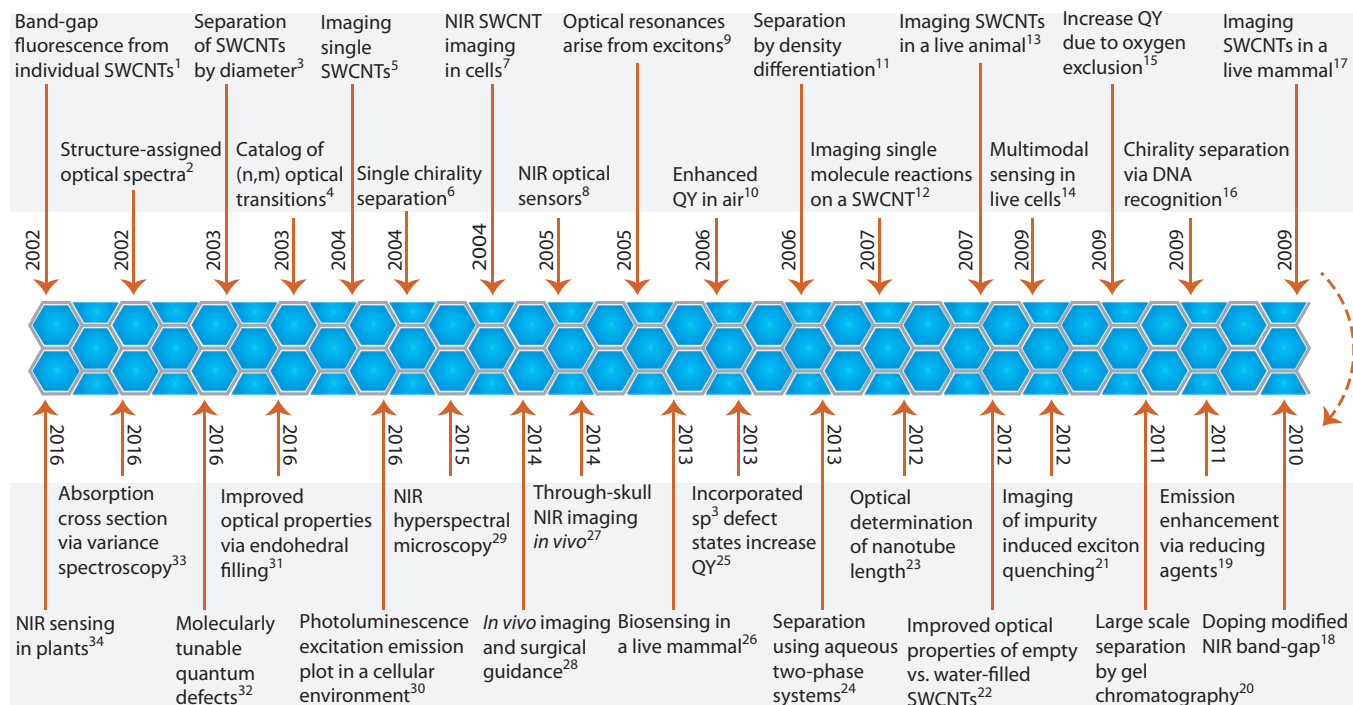
The optical properties of carbon nanotubes depend on their (n,m) chirality (species). Spectrofluorimetric measurements on individual SWCNT suspensions initially identified over 33 semiconducting nanotube chiralities,<sup>18</sup> and an empirical model followed which predicted optical transitions for over 100 different chiralities.<sup>19</sup> For electronic applications in particular, separating metallic and semiconducting nanotubes is critical,<sup>20</sup> and biological imaging studies would benefit from highly purified photoluminescent samples with well-defined optical absorption and emission bands.<sup>21</sup> Early successes, including the separation of metallic and semiconducting nanotubes,<sup>22</sup> and concomitant length and diameter separation,<sup>23</sup> suggested that the sorting problem would be fundamentally solvable. Promising solutions for obtaining a high yield of dispersed chirality-sorted nanotube samples include separation by density gradient ultracentrifugation,<sup>24</sup> DNA recognition of specific chiralities,<sup>25</sup> gel chromatography,<sup>26</sup> and aqueous two phase systems,<sup>23</sup> in addition to intrinsically selective dispersions.<sup>27</sup> Nanotube samples enriched in a few specific chiralities, along with highly pure metallic and semiconducting preparations, are now commercially available.

Photoluminescence from semiconducting nanotubes is due to the generation and recombination of excitons.<sup>28</sup> During their short excited-state lifetime,<sup>29</sup> mobile excitons sample thousands of atomic sites to efficiently sense their local environment.<sup>30</sup> Defects in the  $\text{sp}^2$  carbon surface and certain small molecule adsorbents can provide

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**Figure 1.** A timeline of advancements in the measurement, processing, separation, modification, and application of photoluminescent single-walled carbon nanotubes. References are listed in the Supplementary Information.

a non-radiative relaxation pathway which directly causes exciton quenching.<sup>31</sup> The initial estimates of nanotube quantum yield (QY) in solution were relatively low ( $<0.1\%$ ) and heterogeneous.<sup>32</sup> However, subsequent single molecule studies<sup>33</sup> showed that nanotube emission is significantly brighter in air.<sup>34</sup> The addition of reducing agents to nanotubes in solution,<sup>35</sup> removal of water from the internal volume of a nanotube,<sup>36</sup> reduction of oxygen in contact with the nanotube surface,<sup>37</sup> and controlled endohedral filling of the nanotube<sup>38</sup> have significantly increased the experimentally observed nanotube quantum yield.

Chemical modifications of the nanotube surface can controllably modulate their optical properties. Covalent doping of the nanotube surface with a low concentration of oxygen atoms resulted in emission at longer wavelengths by up to hundreds of nanometers.<sup>39</sup> An immediate benefit of such a red-shift is the ability to excite the nanotube at its  $E_{11}$  peak and detect emission at the shifted  $E_{11}$  peak. In live cells, the increase in detected signal and decrease in autofluorescence led to a 20-fold increase in image contrast, when compared with the pristine nanotubes.<sup>39</sup> The controlled introduction of  $sp^3$  defects into the  $sp^2$  nanotube lattice can create a new optically allowed defect state, from which nanotube emission is red-shifted and can be over 28-fold brighter.<sup>40</sup> By tailoring the surface functional group used to introduce the defect state, nanotube emission from a specific chirality is tunable over a shift of  $\sim 70$  nm.<sup>41</sup> An exciting possibility from these chemical modifications is that the ability to excite each nanotube chirality at both  $E_{22}$  and  $E_{11}$  transitions, combined with the tunability of the  $E_{11}^*$  emission, nearly triples the number of available spectrally distinct NIR imaging probes.

Spectrofluorometric techniques have been developed to characterize nanotube suspensions at both the ensemble and single-nanotube levels. The chiral distribution of photoluminescent carbon nanotubes can be determined by acquiring two-dimensional photoluminescence excitation emission plots,<sup>18</sup> which can now be acquired in a high-throughput manner.<sup>42,43</sup> Single carbon nanotube photoluminescence was first imaged using InGaAs cameras coupled with a fluorescence microscope.<sup>44</sup> Advanced techniques which combine single-particle tracking with statistical variations in a dilute sample can accurately determine the absorption cross-section<sup>45</sup> and length distribution<sup>46</sup> of

carbon nanotubes in solution, while single nanotube-counting techniques can directly determine molarity.<sup>47</sup> A recently developed spectral imaging technique, hyperspectral microscopy, can acquire the full spectra from each pixel in an entire field of view – thus allowing the spectral analysis of single nanotubes.<sup>48</sup> The increasing availability of instruments for the optical characterization and imaging of carbon nanotube emission will expand the abilities of diverse researchers to make contributions to the field.

The exceptional optical properties of nanotube photoluminescence have been employed for a number of sensing and bioimaging applications.<sup>49,50</sup> NIR emission from an individual nanotube<sup>48</sup> can be detected in cells.<sup>51</sup> Recently, single nanotube tracking was used in live cells to resolve intracellular fluctuations,<sup>52</sup> and in tissues to map the composition of extracellular space in the live brain.<sup>53</sup> As  $E_{11}$  emission lies within the near-infrared window in biological tissue,<sup>54</sup> nanotubes in whole organisms were detectable in a live invertebrate,<sup>55</sup> and then a live mammal.<sup>14</sup> Advancements in optical techniques have now led to surgical guidance<sup>56</sup> and through-skull imaging<sup>21</sup> in live mice. In parallel, the use of carbon nanotubes as optical sensors<sup>57</sup> was extended to the measurement of strain in composites,<sup>58</sup> multimodal optical sensing in live cells,<sup>59</sup> and measurements in live plants.<sup>60</sup> Excitingly, SWCNT optical sensors were also shown to function in live mice for over 400 days.<sup>61</sup>

## Conclusions and Outlook

The use of carbon nanotube photoluminescence for applications in imaging and sensing is motivated by the goal of approaching scientific and technological problems that are currently intractable or extremely difficult. Such problems may be addressed by the unique properties of nanotube photoluminescence, including high photostability, NIR emission range, narrow bandwidths, large Stokes shift, large number of optically separable emission bands, and environmental sensitivity. Applications of SWCNT optical probes will require high quantum yields, homogeneous samples of essentially one chirality, well-defined and narrow length distributions, and the ability to independently choose the dispersant/coating.

The understanding of the photophysics governing the modulation of carbon nanotube emission is critical for the rational design of sensitive and specific sensors. As detection platforms, nanotubes can function as both the recognition and signal transduction element. A general set of rules for predicting the effect of a specific non-covalent functionalization on the optical response of the sensor prototype would be valuable. Similarly, our understanding of how covalent modifications affect the optical response of the nanotube is still preliminary.

For biological applications, a key concern is the potential toxicity of single-walled carbon nanotubes. Although it is clear to many researchers that the major sources of carbon nanotube-associated toxicity i.e. metallic catalyst impurities, length, diameter, chemical functionalization, and aggregation state—are completely dependent on how the sample is processed, studies that systematically explore cellular toxicity as a function of these parameters are limited. Investigations that map the range of nanotube parameters with respect to biocompatibility will be extremely useful and could preemptively answer questions concerning toxicity in future applications.

The last 15 years of research into single-walled carbon nanotube photoluminescence have resulted in notable progress toward applications. A convergence between our conceptual understanding of nanotube photoluminescence and its modulation, the breadth of instruments for optical characterization, and the range of applications currently under development by multiple investigators, suggest greater expansion of the field and convergence with multiple disciplines.

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