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Functionalization of Single-Walled Carbon Nanotubes (SWNTs) with Stimuli-Responsive Dispersants

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Carbon nanotubes (CNTs) have promised great opportunities for the development of next-generation materials science and technology, given their extraordinary mechanical and electronic properties. Ever since their first discovery in the early 1990s [1], carbon nanotubes have not only attracted enormous academic curiosity, but also fueled up extensive and continued pursuit of technological applications in numerous fields, such as field effect transistors, light emitting devices, photovoltaic materials, chemical sensors, actuators, and catalysis [2-4]. Carbon nanotubes belong to a unique family of carbon allotrope with a tubular shape, a diameter of 1-2 nm, and a length on the micron scale. Depending on the structure of layers, carbon nanotubes can be single-walled and multiple-walled. Conceptually, a single-walled carbon nanotube can be perceived as being formed by wrapping a single layer of graphene sheet into a cylindrical structure. According to the different angles in which the graphene sheet is wrapped, the resulting tubes can be characterized as different types, such as "zigzag", "armchair", and "chiral", defined by a chiral vector (C_h) and two indices (n,m) [5]. Typically, if m = 0, the SWNTs are called "zigzag" nanotubes, if n = m, they are "armchair", and if otherwise, the SWNTs are categorized as "chiral". Apart from chirality, SWNTs can also be simply divided into two electronic types, namely metallic and semiconducting, based on their electronic properties. Nanotubes with chiral indices n-m = 3x (x is an integer) are usually metallic, while others are semiconducting.

The small diameters and high aspect ratios of SWNTs make them useful in the fabrication of various nanoscale devices; however, the direct use of pristine SWNTs in device applications is facing two significant hurdles. First, SWNTs show a strong tendency to aggregation and exist as heavily entangled bundles in the solid state, making them virtually insoluble in any solvents and considerably limiting the processability of pristine SWNTs. Second, most of commercially available as produced SWNTs are mixtures of numerous chiral species, while separation and sorting out a particular type(s) of SWNTs turn out to be a very challenging task to undertake. Indeed, how to produce structurally homogeneous SWNTs has become an ultimate goal in the present carbon nanotube research. This issue has been tackled by two different approaches according to present literature reports. The first one focuses on developing direct methods for controlled and selective synthesis of SWNTs. For instance, controlled growth of SWNTs with specific chirality can be achieved using finely tuned metallic nanoparticles as catalysts [6]. Bottom-up template synthesis presents another fundamentally appealing way, in which synthetically prepared hoop-shaped macrocycles are used as the starting materials for controlled growth of SWNTs with discrete chirality [7]. Without doubt these methods have led to significant breakthroughs in terms of acquiring structurally pure SWNTs, they are facing challenges of scaling up and limited range of tube chirality. Presently, the most commonly used methods for purification of SWNTs still rely on selective functionalization of as produced SWNT mixtures. In principle, different types of SWNTs should give distinct chemical reactivity and non-covalent interactions with a wide range of chemical species. On the basis of this assumption, various covalent and noncovalent methods have been devised to purify or separate SWNTs. For example, aryl diazonium salts can be used to selectively functionalize the metallic fraction of HiPCO SWNTs, affording efficient chemical separation of metallic and semiconducting nanotubes [8]. On the other hand, a large array of functional molecules, macromolecules, and biomolecules has been found to interact with SWNTs significantly via noncovalent forces (e.g. π stacking, van der Waals) to debundle and disperse SWNTs into various solvents. Efficient dispersion hence allows for separation of SWNTs by various means. For instance, short-stranded DNA (ss-DNA) can be wrapped around SWNTs to form stable suspension, which upon ion-exchange chromatographic separation results in separation of specific SWNTs [9]. Density gradient centrifugation of suspension of SWNTs in the presence of surfactants has also been found effective at sorting out different fractions of chiral nanotube species [10]. Recently, size-exclusion of SWNT suspension has been successfully applied to acquire nearly monochiral fractions of SWNTs [11].

With the continuous development of functionalization methods leading to structurally pure SWNTs, the bottle neck hindering device applications of SWNTs is gradually widening. However, another issue emerges to be addressed in this context; that is, how to reversibly functionalize and defunctionalize SWNTs. Covalent functionalization is known to disrupt the structural integrity of SWNTs by converting the sp^2 hybridized carbons of SWNTs into sp^3 centers at the linkage positions. Because of this disadvantage, the covalent approach has found limited applications in device fabrications. Noncovalent functionalization of SWNTs due to it nondestructive nature is more desirable for the cases where the structural and electronic properties of pristine SWNTs need to be preserved. Nevertheless, in many noncovalent methods the dispersants for SWNTs such as polymers and macromolecules tend to form very strong or irreversible interactions with the surface of SWNTs, which in turn makes subsequent defunctionalization very difficult. When functionalized SWNTs are applied to electronic and optoelectronic devices, the presence of even a residual amount of dispersants may exert very significant influences on the device performance. This problem thus calls for the development of new SWNT dispersants capable of interacting and decomplexing with SWNTs in a reversible and controllable manner. In this context, some attention has been recently placed on the functionalization of SWNTs with stimuli-responsive molecules and macromolecules. So far, the external stimuli reported in the literature include solvent polarity, temperature, pH, CO_2, redox, and photo-irradiation. Smalley et al. reported that a water-soluble polymer, polystyrene sulfonate (PSS), could disperse SWNTs in aqueous solution and the resulting supramolecular complexes could be reversibly dissociated by simply changing the solvent system to reduce hydrophobicity [12,13]. Moore and Zang investigated the use of oligo(m-phenylene ethynylene)s (m-OPEs) to reversibly wrap and unwrap around SWNTs under the control of solvent polarity [14]. Most recently,

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Mulla and Zhao disclosed a new type of dithiafulvene-endcapped conjugated oligomers, which could effectively disperse SWNTs in chloroform and release pristine SWNTs upon addition of hexanes [14]. Chen and co-workers used temperature and pH-sensitive polymers, such as poly(N-isopropylacrylamide) (PNIPAAm) and poly-L-lysine (PLL), to achieve reversible dispersion and release of SWNTs in water [15]. A CO_2 responsive polymer carrying pyrene and amidinium moieties was synthesized by the Zhang group, and this polymer was found to give controllable dispersion and aggregation of SWNTs [16]. The Zhao group recently developed a class redox-active tetrathiafulvalene vinylogue based conjugated polymers, which could effective disperse SWNTs in organic solutions and drop off pristine SWNTs upon addition of oxidants or acids [17]. The Zhang group recently developed a poly(ethylene glycol)-terminated malachite green derivatives (PEG-MG) which could noncovalently interact with SWNTs to form soluble complexes in water [18]. Upon UV-Vis irradiation, the malachite green group underwent a photoinduced C-C bond cleavage process to form a cationic trityl product that led to decomplexation of the SWNT-PEG assemblies. Adronov and co-workers recently prepared a photoisomerizable azobenzene-containing conjugated polymer to achieve selective interactions with SWNTs under photochemical control [19].

A major advantage of using stimuli-responsive dispersants for SWNTs is that the functionalization/defunctionalization sequence can be repetitively executed. As such, if the dispersant shows selectivity for certain types of SWNTs, even though in a moderate-to-low degree, efficient purification of SWNTs may still be attainable by a recyclable manner analogous to recrystallization. Of the above mentioned methods, solvent control appears to be a very promising one for scaled up and cost-effective production in comparison to other chemical and photochemical approaches, given the cleanness and minimal chemical disruption involved. In addition, fundamental investigations of properties of stimuli-responsive materials need to be continued in order to facilitate rational design of SWNT dispersants with better performances. It is therefore envisaged that research along this direction should yield more fruitful results and eventually open a new avenue for pure SWNT based technologies.

References

1. Iijima S (1991) Helical microtubules of graphitic carbon. Nature 354: 56-58.
2. De Volder MF, Tawfick SH, Baughman RH, Hart AJ (2013) Carbon nanotubes: present and future commercial applications. Science 339: 535-539.
3. Park S, Vosguerichian M, Bao Z (2013) A review of fabrication and applications of carbon nanotube film-based flexible electronics. Nanoscale 5: 1727-1752.
4. Goldoni A, Petaccia L, Lizzit S, Larciprete R (2010) Sensing gases with carbon nanotubes: a review of the actual situation. J Phys Condens Matter 22: 013001.
5. Dresselhaus MS, Dresselhaus G, Eklund, PC (1996) Science of fullerenes and carbon nanotubes. Academic Press, Elsevier Science, USA.
6. He M, Jiang H, Liu B, Fedotov PV, Chernov AI, et al. (2013) Chiral-selective growth of single-walled carbon nanotubes on lattice-mismatched epitaxial cobalt nanoparticles. Sci Rep 3: 1460.
7. Jasti R, Bertozzi CR (2010) Progress and challenges for the bottom-up synthesis of carbon nanotubes with discrete chirality. Chem Phys Lett 494: 1-7.
8. Strano MS, Dyke CA, Usrey ML, Barone PW, Allen MJ, et al. (2003) Electronic structure control of single-walled carbon nanotube functionalization. Science 301: 1519-1522.
9. Tu X, Manohar S, Jagota A, Zheng M (2009) DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes. Nature 460: 250-253.
10. Arnold MS, Green AA, Hulvat JF, Stupp SI, Hersam MC (2006) Sorting carbon nanotubes by electronic structure using density differentiation. Nat Nanotechnol 1: 60-65.
11. Flavel BS, Kappes MM, Krupke R, Hennrich F (2013) Separation of single-walled carbon nanotubes by 1-dodecanol-mediated size-exclusion chromatography. ACS Nano 7: 3557-3564.
12. O'Connell MJ, Boul P, Ericson LM, Huffman C, Wang Y, et al. (2001) Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. Chemical Physics Letters 342: 265-271.
13. Zhang Z, Che Y, Smaldone RA, Xu M, Bunes BR, et al. (2010) Reversible dispersion and release of carbon nanotubes using foldable oligomers. J Am Chem Soc 132: 14113-14117.
14. Mulla K, Zhao Y (2013) When dithiafulvenyl functionalized pi-conjugated oligomers meet fullerenes and single-walled carbon nanotubes. J Mater Chem C.
15. Wang D, Chen L (2007) Temperature and pH-responsive single-walled carbon nanotube dispersions. Nano Lett 7: 1480-1484.
16. Chen S, Jiang Y, Wang Z, Zhang X, Dai L, et al. (2008) Light-controlled single-walled carbon nanotube dispersions in aqueous solution. Langmuir 24: 9233-9236.
17. Liang S, Chen G, Peddle J, Zhao Y (2012) Reversible dispersion and releasing of single-walled carbon nanotubes by a stimuli-responsive TTFV-phenylacetylene polymer. Chem Commun (Camb) 48: 3100-3102.
18. Yu G, Xue M, Zhang Z, Li J, Han C, et al. (2012) A water-soluble pillar[6]arene: synthesis, host-guest chemistry, and its application in dispersion of multiwalled carbon nanotubes in water. J Am Chem Soc 134: 13248-13251.
19. Imin P, Imit M, Adronov A (2012) Supramolecular functionalization of single-walled carbon nanotubes (SWNTs) with a photoisomerizable conjugated polymer. Macromolecules 45: 5045-5050.