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REVIEW

Conjugated polymer sorting of semiconducting carbon nanotubes and their electronic applications

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Summary In the past decade, single-walled carbon nanotubes (SWNTs) have aroused great interest for electronic applications due to their extraordinary charge carrier mobility, mechanical flexibility, and solution processability. However, one of the key issues preventing the wide application of SWNTs in electronics is the need to separate semiconducting SWNTs from metallic SWNTs. Sorting semiconducting SWNTs using conjugated polymers is becoming a very promising SWNT sorting method due to its high-selectivity, high-yield and simplicity of execution. In this review, we summarized the parameters that can be used to tune the selectivity and sorting yield of semiconducting SWNTs, including polymer structure, solvent, polymer-to-SWNT ratio, sonication temperature and polymer molecular weight. We also reviewed the electronic applications enabled by these polymer-sorted semiconducting SWNTs inks such as transistors, logic gates, photodetectors, solar cells and 3D electronics.

Introduction to carbon nanotubes

Carbon nanotubes were first discovered in 1991 [1] and the first carbon nanotube transistors were not fabricated until 1998 [2,3]. Since then, intense research activities into carbon-nanotube-based electronics have been conducted [4—7]. Single-walled carbon nanotubes (SWNTs) are attracted for electronic applications because of their extraordinary charge carrier mobilities [7—9], mechanical flexible/stretchability [10—15], and solution processiblity [16—19]. In particular, semiconducting SWNTs have emerged as a promising class of materials for a variety of electronic applications, such as field-effect transistors [7,20—24], optoelectronic devices [25—27], chemical and biological sensors [28—31], logic circuits [20,21,32], electronic skins [20,33], and computers [34].

The electronic properties of SWNTs are determined by their structures, which can be conceptualized as a

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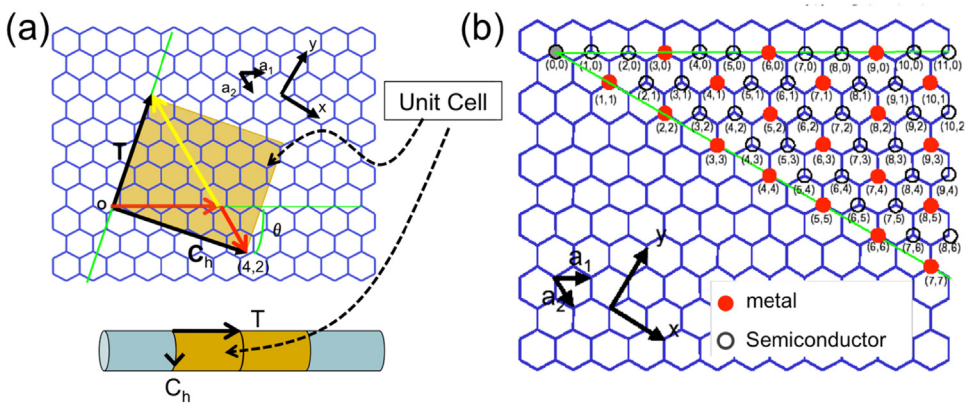

Figure 1 Graphic representation showing the structure of SWNTs. (a) Schematic illustration of the structures of a (4,2) SWNT with lattice chiral vector C_h and tube axis T. (b) Graphene sheet map showing the chirality of various metallic and semiconducting SWNTs with C_h from (0,0) to the shown SWNT chirality.

single-layer graphene sheet rolled into a cylinder along a lattice chiral vector (C_h) (Fig. 1a), described by

$$C_h = na_1 + ma_2 = (n, m)$$

where a_1 and a_2 are the unit vectors of the graphene and n and m are a pair of integers describing the chirality of the SWNT. A SWNT with a chirality of (4,2) has a chiral vector oriented in the a_1 direction for 4 unit and in the a_2 direction for 2 unit (Fig. 1a). If $m = 0$, the SWNTs are called zigzag SWNTs and if $n = m$, the SWNTs are called armchair SWNTs. For most chiralities of SWNTs (other than zigzag or armchair SWNTs), there are two optical isomers for each chirality: left-handed twist or right-handed twist. Both handed isomers have the same chiral vector (n,m) but they cannot be superimposed on each other.

The diameter (d) and chiral angle (θ) can be calculated from the indices of n and m using the following equation:

$$d = \frac{a}{\pi}\sqrt{n^2 + m^2 + nm}$$

$$\cos\theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$$

The electronic properties of SWNTs are determined by their chirality (n,m): when $n - m$ is a multiple of 3, the SWNT is metallic; when $n - m$ is not a multiple of 3, the SWNT is semiconducting (Fig. 1b). Approximately one third of SWNTs are metallic, and the remainder are semiconducting. For semiconducting SWNTs, the band gap is inversely proportional to their diameters, in accordance with a simple tight binding model [7]:

$$E_g = \gamma\left(\frac{2R_{C-C}}{d_{CNT}}\right)$$

where γ is the hopping matrix element (~3 eV), R_{C-C} is the C—C bond length, and d_{CNT} is the SWNT diameter.

Different synthesis methods can produce SWNTs with different diameters. SWNT synthesis methods for mass production include the arc discharge method [1], laser ablation [35], and chemical vapor deposition (CVD) [36—38]. The diameters of the SWNTs produced by these methods are summarized in Table 1. Unfortunately, these scalable methods

Table 1 Summary of synthesis methods, including their descriptions and the diameter ranges of the SWNTs they produce commercially.

Synthesis method		Description of the method	Diameter (nm)
Arc discharge [1]		Application of a voltage between two graphite electrodes to produce an arc; SWNTs are deposited on the electrodes	1.2—1.7
Laser ablation [35]		Application of laser pulses to graphite heated in a tube furnace to produce SWNTs	1.0—1.4
Chemical vapor deposition (CVD)[36]	High-pressure CO (HiPco)[37]	Decomposition of high-pressure CO at high temperatures to nucleate SWNTs.	0.8—1.1
	CO disproportionation on Co-Mo catalysts [38] (CoMoCAT)	Decomposition of CO gas at high temperatures with Co and Mo as catalysts to produce SWNTs	0.7—0.9