

Polymer Structure and Solvent Effects on the Selective Dispersion of Single-Walled Carbon Nanotubes

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Abstract:

Several light-emitted polymers with aromatic backbone structures have been used as dispersing agents to disperse SWCNTs in organic solvents. Dispersion results varied while different combination of polymers and solvents were chosen. While one solvent gives relatively high solubility of nanotubes, that leads to poor selectivity of dispersed SWCNT species; if polymer structures show more limitation on the conformation change, it results in great selectivity. Optical absorbance, photoluminescence-excitation maps and electron microscopy images have been used to characterized these solutions.

Introduction:

A SWCNT can be considered as a graphene sheet rolled into a cylindrical shape and either capped with semi-sphere structure of fullerene molecule or not. The wrapping of the graphene sheet leads to many distinct possible structures, defined by the chiral indices (n, m) , with a third of the species being metallic and the remainder being semiconducting. Fig. 1(a) is a segment of graphene sheet map showing (n, m) nanotubes in which those metallic tubes are marked with red and the others behave semiconducting. Fig. 1(b) and (c) show schematic examples of density of states (DOS) of metallic and semiconducting carbon nanotubes, respectively.

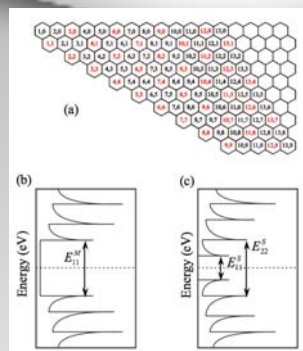


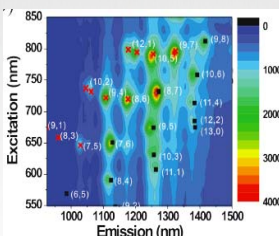
Figure 1: (a) a segment of graphene sheet shows the construction of nanotubes with (n, m) indices. When the number of $n-m$ is a multiple of 3, this makes the nanotube behave metallic properties. These metallic tubes are marked with red, and the others, which behave semiconducting, are marked as black. (b) and (c) represent the DOS for metallic and semiconducting nanotubes, respectively. The characteristic of quantized energy levels are due to the extremely small sizes of nanotubes.

Due to the unique electrical structures of SWCNTs, it is possible to analyze the distribution of nanotube species by photoluminescence (PL) spectroscopy. SWCNTs are excited through their E_{22} electronic transitions and resonantly emit light with energy matching their E_{11} electronic transitions, as shown in Fig. 1(c).

However, it is known that nanotubes are grown as bundles in which the presence of metallic SWCNTs provides efficient non-radiative decay pathways for photo-excited carriers in semiconducting nanotubes.

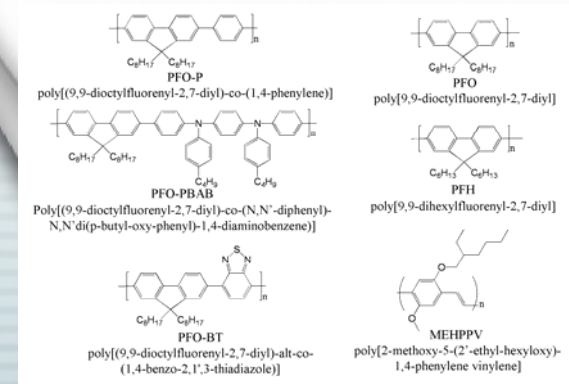
The dispersion of SWCNTs in solutions is useful for their analysis, purification and modification. Fig. 2 shows a photoluminescence excitation (PLE) map of dispersion of HiPCO produced SWCNTs using ionic surfactant, sodium dodecylbenzene sulfonate (SDBS), in aqueous solution.

Figure 2: a PLE map where color scale represents the intensity of emission from SWCNTs. The peaks correspond to the resonantly enhanced emission from nanotubes' E_{11} energy levels when the excitation matches their E_{22} electronic levels. The points indicate theoretical positions for the energy gaps of the corresponding (n, m) indexed nanotube species. The red crosses correspond to the family of tube species for which $q = -1$ and the black squares to the family where $q = +1$.



Experimental:

Several conjugated polymers are used as surfactants to disperse HiPCO produced SWCNTs in three organic solvents: toluene, tetrahydrofuran (THF) and chloroform. The molecular structures of polymers are depicted in Fig. 3 below.



Conclusion:

SWCNTs have been successfully dispersed using several light-emitted aromatic polymers in organic solvents. It is found that the dispersion results are strongly dependent on the polymer structures and solvents. Solvents not only change the total solubility of SWCNTs, but also alter the conformation of solubilized polymers thus changing the selective dispersion of nanotubes. In toluene, PFO shows great preference of chiral angle in favor of armchair structure; PFO-BT not just shows diameter preference but even has extreme species preference of $(10,5)$ species. Though chloroform give the highest solubility of SWCNTs with all polymers, the dispersed nanotubes mostly remain bundled giving no photoluminescence response. The work done in this study opens the potential of bulk purification of SWCNTs.

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References:

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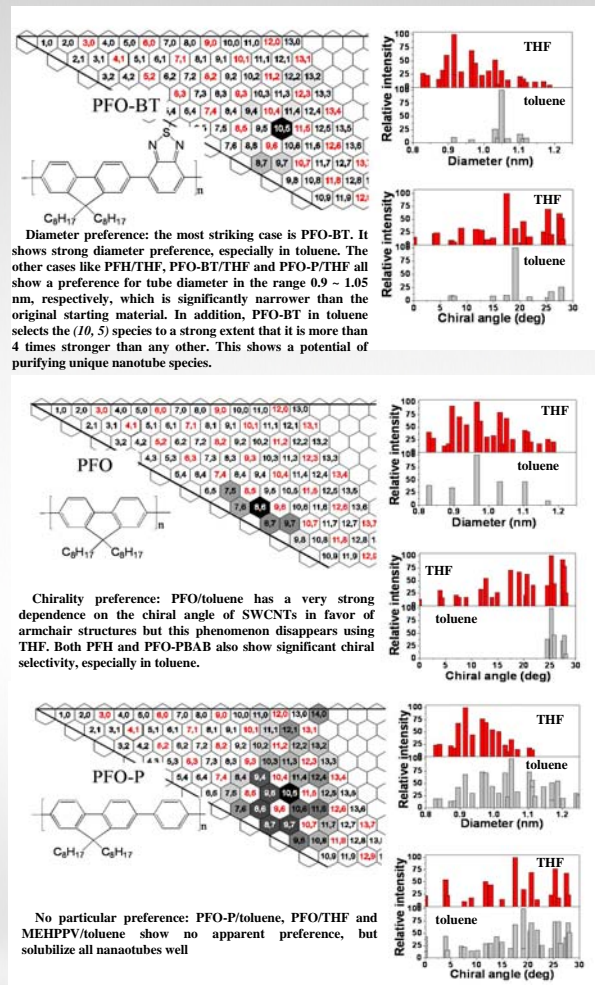
Results:

To better compare the PLE results of different polymer/solvent combinations quantitatively, we calculate the intensity of each peak and for each PLE map, the fitted intensity is normalized by the species which shows the highest intensity and represented as a percentage. The table below shows the calculation results.

(n, m)	q	diameter (nm)	chiral angle (deg)	SDBS	toluene										THF				
					PFO-P	PFO-PBAB	PFO-MEHPPV	PFO-PFH	PFO-BT	PFO-P	PFO-PBAB	PFO-MEHPPV	PFO-PFH	PFO-BT					
(7, 5)	-1	0.829	24.50	28.42	18.81	31.22	38.99	33.31	24.34	23.19	55.00	40.43	16.37	43.05	26.46				
(7, 6)	1	0.895	27.46	70.19	41.67	100	34.60	86.44	37.01	68.06	100	52.22	61.17	81.93	60.92				
(8, 9)	1	0.840	19.11	35.08	18.46	24.49				24.53		28.72		34.52	22.65				
(8, 9)	-1	0.966	25.28	85.95	73.43	98.68	100	100	75.28	5.8	76.45	88.33	100	100	79.81				
(8, 7)	-1	1.032	27.00	87.85	71.53	86.00	46.43	76.16	100	26.25	23.28	85.83	79.66	79.77	54.50	51.74			
(9, 4)	-1	0.916	17.48	68.14	67.99	25.71		86.81	28.11	10.47	100	54.17	71.03	48.58	63.31	100			
(9, 5)	-1	0.976	20.63	49.74	71.35	47.95		59.69	34.39		69.49	48.33	42.91	37.66	49.45	46.05			
(9, 7)	-1	1.103	25.87	100	73.68	62.10	47.02	57.59	97.99	16.67	17.75	33.33	44.19	71.81	81.21	21.14			
(9, 8)	-1	1.170	28.05	43.76	51.60	37.37	8.62				25.03	25.98	51.11		11.21				
(10, 2)	-1	0.884	8.95	16.08	36.96						17.31		17.09		14.53	32.91			
(10, 1)	1	0.936	12.73	26.92	29.61	8.29		19.69	16.94		43.89	30.67	55.04	11.70	45.14	29.47			
(10, 5)	-1	1.050	19.11	86.66	100	27.85		68.48		100	34.52	17.5	47.35	50.88	45.41	32.02			
(10, 6)	-1	1.111	21.79	44.31	56.43	22.83		30.03		7.5	13.92	24.98	41.37	33.10	22.71	16.48			
(10, 8)	-1	1.240	26.33	14.63	30.20						21.94		12.82		15.77				
(10, 9)	-1	0.873	0.00	15.98	13.72						19.15		16.15		26.31	11.21			
(11, 1)	1	0.916	4.31	12.32	16.05	3.90					22.30		16.15		26.31	11.21			
(11, 3)	-1	1.014	11.74	58.39	29.51			42.79	37.64		50.85	33.33	34.74	20.35	31.07				
(11, 4)	1	1.085	14.92	27.43	32.44	14.63		16.47		8.63	14.54	20.16	28.41	18.41	18.17	13.98			
(11, 6)	-1	1.186	20.36	30.94	55.05	11.32					14.54	20.16	28.41	18.41	18.17	13.98			
(11, 7)	-1	0.995	3.96	31.86	43.83			36.16	36.64		54.77	30.68	23.51	22.07	22.69	4.71			
(12, 2)	-1	1.041	7.59	13.47	22.09	9.17		13.99		9.07	10.26		17.09	28.42		6.69			
(12, 4)	-1	1.145	13.90	48.97	43.05	9.76					14.54	20.16	28.41	18.41	18.17	13.98			
(12, 5)	1	1.201	16.63	19.41							14.54	20.16	28.41	18.41	18.17	13.98			
(11, 2)	-1	1.120	7.05	41.03	23.73	11.76				9.21			21.37	37.31		9.42			
(13, 3)	1	1.169	10.16		15.98														

The data are presented graphically in schematic representations called graphene sheet maps and histograms of the PL intensity as a function of diameter and chiral angle. A example is shown in Fig. 4. SDBS is thought to be of non-selectivity of dispersing SWCNTs so the illustrations suggest HiPCO produced nanotubes have a wide distribution of diameters, from 0.8 -1.25 nm and of chiral angles from 0 to 30°.

Interesting results are found that polymer structures and solvents both have great influence on the nanotube dispersions. Due to the limitation of space, we simply classify the results for different combination of polymer/solvent into three groups.



Diameter preference: the most striking case is PFO-BT. It shows strong diameter preference, especially in toluene. The other cases like PFH/THF, PFO-BT/THF and PFO-P/THF all show a preference for tube diameter in the range 0.9 - 1.05 nm, respectively, which is significantly narrower than the original starting material. In addition, PFO-BT in toluene selects the $(10, 5)$ species to a strong extent that it is more than 4 times stronger than any other. This shows a potential of purifying unique nanotube species.

Chirality preference: PFO/toluene has a very strong dependence on the chiral angle of SWCNTs in favor of armchair structures but this phenomenon disappears using THF. Both PFH and PFO-PBAB also show significant chiral selectivity, especially in toluene.

No particular preference: PFO-P/toluene, PFO/THF and MEHPPV/toluene show no apparent preference, but solubilize all nanotubes well