Advanced Energy Research Section

Rong Xiang, Foreign Visiting Researcher
(Professor in Zhejiang University,
866 Yuhang Road, Xihu District, Hangzhou, Zhejiang
Province, China)

1. Summary

The author spent three months (July. 1, 2023-Sept. 31, 2023) as a guest professor at the Uji campus of Kyoto University, hosted by the Y.Miyauchi group.

Here the author reports an investigation on (6,5) single-walled carbon nanotubes dispersion and optical characterization.

2. Introduction

Single-walled carbon nanotubes (SWCNT) possess a wide array of remarkable mechanical, chemical, and electronic properties, rendering them as ideal candidates for diverse applications, including composites, energy storage, biological and chemical sensors, flexible electronics, and transparent electrodes. In particular, the high charge-carrier mobility of semiconducting (sc-) SWCNT together with the ability for solution processing hold a great promise for high-performance low-cost transistor applications. [1] Many of these properties depend sensitively on SWCNT structure, which is characterized by the chiral index (n,m) that denotes the length and orientation of the circumferential vector in the hexagonal carbon lattice. Electronic properties are notably influenced, with subtle structural variations causing tubes to transition from metallic to semiconducting with diverse band gaps. Therefore, to fully exploit their technological potential, it is essential to have monodisperse single-chirality SWCNT with a single (n,m) index. [2]

Post-growth sorting of SWCNTs is essential due to the fact that their growth typically results in mixtures of various semiconducting and metallic nanotube species. Among the various sorting techniques available, such as gel chromatography, density gradient ultracentrifugation (DGU), and aqueous two-phase separation, selectively wrapping SWCNTs with conjugated polymers is a method that yields highly pure semiconducting and even monochiral dispersions with relatively low effort. [1] For instance, the polyfluorene copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,60-{2,20-bipyridine})](PFO-BPy) yields almost monochiral (6,5) SWCNT dispersions. Therefore, PFO-BPy is widely used for the dispersion of single chirality SWCNT with small diameter. In general, polymer-sorted SWCNTs exhibit very low residual metallic content and little inter-tube interactions, which results in high purity dispersion. Here, we realized high purity (6,5) SWCNT dispersion by using PFO-BPy and characterized its optical properties.

3. Experimental observations

(1) (6,5) SWCNT dispersion

All (6,5) SWCNT dispersions were prepared from the same CoMoCAT® raw material (Sigma Aldrich 773735). For polymer-wrapping with tip sonication, 17.6mg PFO-BPy (American Dye Source, Lot#23G004A1) were dissolved in 30ml toluene before adding 7.6mg CoMoCAT raw material. After adding CoMoCAT and raw material, a respectively 10-minute bath sonication is required to mix the solution evenly. Subsequently, tip sonication was carried out using a BRANSON SONITIER 250 ultrasonic crusher at 40% power and 30% duty cycle for 3 hours. The solution was stirred evenly every hour, and the temperature was maintained at 20°C using a cooling bath. The dispersion step was followed by centrifugation at 19000 g (Eppendorf himac CS 100FNX) for 30 min with an intermediate supernatant extraction. Due to the high-purity (6,5) SWCNT, we can observe that the final purified solution exhibits a strong purple color in figure 1. [3] By adjusting parameters such as the power and time of tip sonication, the concentration of the solution can be adjusted, while also influencing the quality and purity of the separated carbon nanotubes.

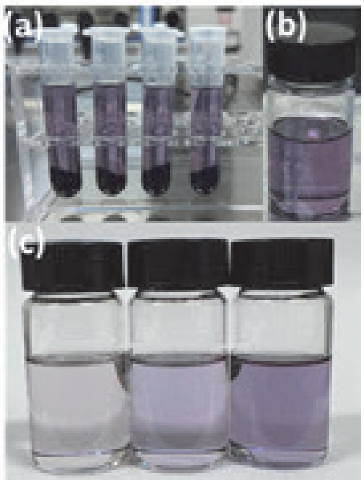

Fig. 1 (a) Solution after centrifugation (the supernatant consists of 65 tubes and the black sediment is impurities). (b) Extracted supernatant（c）Different concentrations of (6,5) solutions obtained by changing the tip sonication time

(2) Optical characterization

From absorption spectrum, each type of single-chirality species can be clearly identified. Figure 2 illustrates the absorption spectrum of the CoMoCAT

SWCNT dissolved in toluene by PFO-BPy, a typical solvent demonstrating selective extraction of semiconducting SWCNT. At 996nm, a prominent peak is evident, indicating absorption by the (6,5) SWCNT. Notably, the background absorption in the NIR region is minimal, a typical trait of PFO-dissolved SWCNT toluene solutions. This stands in stark contrast to numerous other dispersants such as surfactants, aromatic compounds, and polymers, which often exhibit significant background absorption in the NIR region. Furthermore, there is almost negligible absorption observed within the 400-550nm range, characteristic of metallic SWCNTs. This underscores a distinct advantage of PFO dispersants over many other SWCNT dispersants

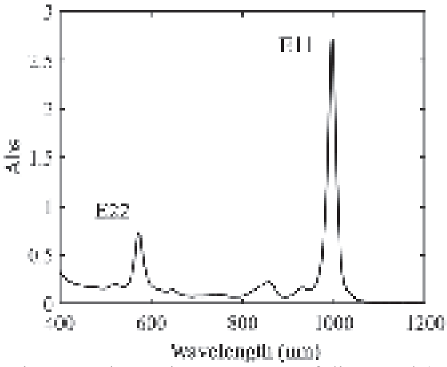

Fig. 2 Vis-NIR Absorption spectrum of dispersed (6,5) SWCNT solution

Photoluminescence (PL) spectroscopy serves as a potent tool for determining the chirality indices(n,m) of SWCNT. To identify all nanotube species within the dispersion, photoluminescence-excitation(PLE) maps are measured as shown in Fig. 3. As shown in Figure 3, we can only see the (6,5) SWCNT peak emission (996 nm) and peak excitation (575 nm) which indicates that the purity of (6,5) SWCNT in the solution is very high.

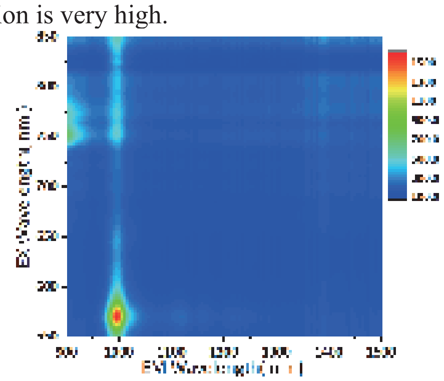

Fig. 3 PLE maps of dispersed (6,5) SWCNT solution

To further determine whether the extracted SWCNT contain other semiconducting- and/or metallic-SWCNT, the Raman spectra (532nm excitation) of the extracted tubes were measured (Figure 4). The SWCNT dispersions were drop-cast on Glass slide. The radial breathing mode (RBM) in the regions of 240-350 cm^{-1} and 150-240 cm^{-1} is attributed to the semiconducting and metallic SWCNT respectively. As depicted in the figure, for the PFO-BPy extracted SWCNT, we observe distinct peaks in the region of 240-350 cm^{-1} and almost no peaks in the 150-240 cm^{-1} region which indicates that the extracted SWCNTs are predominantly semiconducting SWCNTs, aligning well with previous reports utilizing PFOs and their derivatives. However, through normalized Raman spectroscopy, we can observe that the solution dispersed through tip sonication has a particularly high D peak, and the corresponding high GD ratio indicates that the quality of carbon nanotubes is not very high. How to improve both purity and quality is a topic that needs further research in future studies.

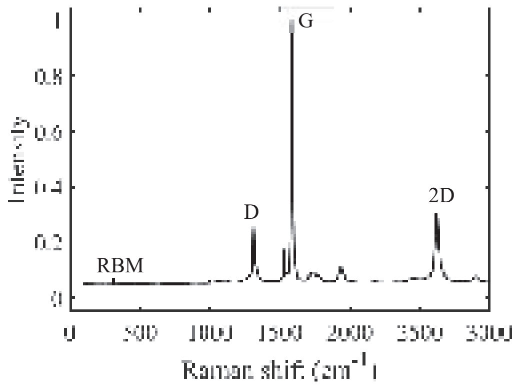

Fig. 4 Raman spectrum of dispersed (6,5) SWCNT solution

(3) (6,5) SWCNT film deposition

With high purity (6,5) SWCNT solution, we can obtain a film through filtration. Here, we use vacuum filtration to form a SWCNT film. Two viable filter papers are considered: the AAO inorganic filter paper (Whatman AnodiscTM25) and the VCWP filter paper (Merck, VCWP02500). Vacuum filtration is advantageous for achieving a uniform and complete film. Once the film is obtained, it becomes necessary to separate the film from the filter paper. The removal of VCWP filter paper is relatively simple, requiring only acetone to completely dissolve the filter paper, but the resulting film tends to be relatively impure. On the other hand, removing the AAO filter paper is relatively difficult, requiring long-term soaking to form a submonolayer[4] that facilitates the separation of the film and filter paper. However, this method results in a cleaner film.

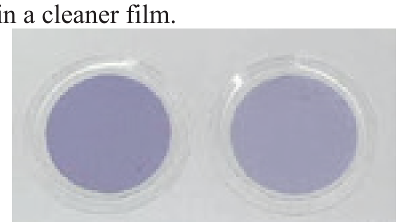

Fig. 5 (6,5) SWCNT film with different thickness

[1] Graf A. et al Carbon, 2016, 105: 593-599.
[2] Sanchez-Valencia J R.et al Nature,
[3] 2014, 512(7512): 61-64.
[4] Ozawa H. et al Chemistry Letters, 2011, 40(3): 239-241.
[5] Zhang C. et al ACS nano, 2022, 16(11): 18630-18636.