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Photodegrading hexaazapentacene dispersant for surface-clean semiconducting single-walled carbon nanotubes

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ABSTRACT

To remove dispersant molecules on the surface of single-walled carbon nanotubes (SWCNTs) is one of main challenges for its practical application in electronics. In this paper, we demonstrated a photodegradable process as a promising method to remove off the dispersants from the surface of semiconducting SWCNTs (s-SWCNTs). A N-heterocyclic aromatic compound, 1,2,5,6-Tetra(5-octylthiophene-2-yl)-Hexaazapentacene (noted as 4HP-C8), was synthesized and used to enrich s-SWCNTs with high yield and purity. Importantly, 4HP-C8 was found to be sensitive to UV irradiation and therefore could be photodegraded into fragments, which provided a facile approach to harvest "dispersant-free" s-SWCNTs. The degradation process and reaction kinetics of 4HP-C8 were also carefully investigated.

1. Introduction

Since the outstanding optical and electrical properties, single-walled carbon nanotube (SWCNT) have been regarded as one of the most promising materials for nanoscience and nanotechnology [1–5]. However, as-produced SWCNTs contain different chiralities nanotubes, exhibiting different properties [6,7], which is a bottleneck for practical application. Various approaches have been directed toward separation of SWCNTs with specific structures, such as density gradient centrifugation [8,9], ion exchange chromatography [10], gel chromatography [11–14], electrophoresis [15–17], aqueous-two-phase (ATP) system [18–21], conjugated polymers wrapping [22–24] and small molecules extraction [25–28]. One main drawback of these approaches in both aqueous or organic solution is that the dispersant around the SWCNTs are difficult to be removed because of their strong supramolecular interaction, which greatly decreased the performance of SWCNTs in electronic applications due to increase either the Schottky barrier of inter-nanotube or the contact resistance between SWCNTs and the electrode [29].

In order to get the "dispersant-free" s-SWCNTs, a lot of efforts have been made over the past decade. In the aqueous system, it is understandable that the surfactants on the surface of the SWCNTs are in a dynamic equilibrium with those in the bulk solution [30]. Most of the dispersants can be removed by filtration or dialysis [31,32], but these methods will lead to the aggregation of the tubes [33]. In recent years, many attempts have been made to obtain "dispersant-free" s-SWCNTs in organic system [34–36]. Liang and coworkers synthesized a series of redox and pH responsive polymers which could release from the surface of the SWCNTs via conformational change in a controlled manner [36–38]. Bao and coworkers presented a Velcro-like H-bonded supramolecular polymer, which could release upon triggered polymer disassembly by addition of strong protonic acid to the dispersion of the enriched s-SWCNTs [39]. However, to develop a facile and low defect technique to obtain the "dispersant-free" s-SWCNTs is still a challenging work.

In this context, we developed a facile method to obtain the "dispersant-free" and high purity s-SWCNTs at the same time. Herein, we synthesized a N-heterocyclic aromatic compound, 1,2,5,6-Tetra(5-octylthiophene-2-yl)-Hexaazapentacene (4HP-C8) which exhibited high efficiency for enriching high purity of s-SWCNTs. The molecules on the surface of s-SWCNTs could be decomposed under the UV photoradiation in the solution. The Gas

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Chromatography-Mass Spectrometer (GC–MS) proved the small molecule had been degraded into soluble fragments. The photodegradation process can be estimated as a fast third-order reaction resulting from the carefully kinetic analysis of the UV–Vis absorption spectra. The surface-clean s-SWCNTs can be collected, redispersed in solvent and coated into thin film easily. The statistical results of Atomic Force Microscope (AFM) confirmed that rare dispersant can be found on the surface of SWCNTs.

2. Experimental

2.1. Materials

Synthetic procedures for 4HP-C8 are given in the Supporting Information Scheme 1 and the structural properties and thermal performance of 4HP-C8 were shown in Figure S1–S3. Raw SWCNTs were purchased from Carbon Solutions Inc. (batch of #AP-A 204).

2.2. Instrumentations

Optical absorption spectra were recorded on a UV–Vis–NIR spectrophotometer (Lambda 750) and a UV–Vis spectrophotometer (Jasco V-660). Raman spectra were measured by a LabRAM HR Raman spectrometer from HORIBA Jobin Yvon. Atomic force microscope images were recorded on a Veeco Dimension 3100 AFM. The light source used in the photodegradation-experiment was an instrument with a high pressure mercury lamp (wavelength 365 nm, power 500 W) and a filter. All of the ultrasonic process was completed with a sonicator (SONICS VCX500) and the gas chromatograph-mass spectrometry was measured by a gas chromatography and mass spectrometer (Agilent 6890N/5973N). The nuclear magnetic resonance was recorded on a VNMRS 400 MHz spectrometer (Varian. Inc., Palo Alto. CA), CF_3COOD was used as the solvent. The rotary evaporator (IKA RV10 Basic) also has been employed in the experiment.

2.3. Sample preparation

2.3.1. The preparation of SWCNTs dispersion

1.5 mg SWCNTs and 6 mg 4HP-C8 were added in 6 mL toluene solvent. Then the solution was sonicated with a tip horn sonicator for 1 h at 7 W total power and then was centrifuged at 20,000*g* for 0.5 h to remove remaining bundles and insoluble impurities. The upper 90% of the supernatant was collected for the follow-up works.

2.3.2. The preparation of the samples for Raman spectra characterization

The silicon wafers were used as the substrates. The commercially purchased silicon wafers were washed before using. It was necessary to ultrasonic-clean about 5 min followed by acetone, ethanol, deionized water as the media successively. Then the wafers were on standby after heating to 120 centigrade for 20 min, following dropped the SWCNTs dispersion on silicon wafers and washed them with toluene. After that, the wafers were baked at 120 centigrade for 20 min after air-drying.

2.3.3. The preparation of the samples for AFM characterization

The silicon wafers were used as the substrate similarly. Different from preparation of the Raman samples, the dispersion were diluted several times according to the absorption for obtaining relatively sparse SWCNT films. The samples before photolysis were made by drop casting. The preparation of "dispersant-free" SWCNTs film by photolysis method was as follows: first, the wafer in the diluted SWCNTs dispersion was kept vertically; then the ultraviolet light radiated it for 30 min, making most of the suspended s-SWCNTs in semi-stable state. Finally, the wafer was standing for 1 h. The samples were baked at 120 centigrade after air-drying.

2.3.4. The preparation of the sample for the gas chromatography-mass spectra characterization

0.1 mg/mL 4HP-C8 powders were added in 40 mL toluene solution. The solution was placed under the ultraviolet light until the color change completely. Then the rotary evaporator was used to condense the solution to 2 mL after photolysis.

3. Results and discussion

Compared to the conjugated polymers, conjugated small molecules may provide some unique properties for sorting the s-SWCNTs. Fig. 1 shows the diagram of the sample preparation process. After a simple process of ultrasonic dispersing and centrifugation, high-purity s-SWCNTs dispersion was obtained. After the s-SWCNT dispersion was radiated under the UV light for several minutes, the isolated s-SWCNTs, as flocculating sediments could be observed in the solution. Then most of the organic products could be removed by 0.1 μm filtration membrane, and the "sediments" left on the membrane. Finally, the monodispersed s-SWCNTs can be re-dispersed by sonicating in chloroform.

Fig. 2a shows the absorption spectra of the Arc-SWCNTs dispersed by 4HP-C8, where obvious sharp peaks can be seen in the S22 (800–1200 nm) region indicating that the Arc-SWCNTs were well monodispersed. In the M11 (600–800 nm) region, the dispersion by 4HP-C8 exhibits a more smooth and depressed tendency, indicating that the m-SWCNTs are highly depleted after the sorting procedure. The red region can be attributed to the absorption of 4HP-C8. Compared with this region before photodegradation, the region of s-SWCNTs re-dispersed in chloroform has obvious lower intensity of absorption, that means the dispersants have be effectively removed by the photolysis. Raman characterization with the excitation energy of 1.96 eV (633 nm) which can probe both m-SWCNTs and s-SWCNTs, was used to further measure the purity of 4HP-C8 dispersed Arc-SWCNTs solution. As shown in the Fig. S4, the Raman peak ω_{RBM} at 158.4 cm^{-1} represents the s-SWCNT with diameter D_t of 1.58 nm estimated by $\omega_{RBM} = 234/D_t + 10$, which can be identified as (15, 8) tubes [40]. There is no peak at 169 cm^{-1} compared with the pristine, which indicates that the bulk of the dispersion was the large-diameter s-SWCNTs. The G^- features which represent the tangential modes of SWCNTs were also used to verify the purity of s-SWCNTs [40,41]. As shown in Fig. 2b, the G^- mode of Arc-SWCNTs powders are broad, which corresponds to the Breit-Wigne-Fano profile because of phonon-plasmon coupling only in metallic nanotubes [42]. Compared with the original SWCNTs, the BWF peak of SWCNTs disappeared after dispersing by 4HP-C8, that means the 4HP-C8 enriched s-SWCNTs with high purity. In addition, it is observed that the 4HP-C8@s-SWCNTs have several peaks at 1350-1550 cm^{-1} which can be attributed to the Raman resonant of the small molecules.

4HP-C8 has a ribbon-like conjugated skeleton, and the chemical bonds in the middle of the skeleton bear enormous tension. It is inferred that the structure will be unstable under high energy radiation. As shown in Fig. 3, when the 4HP-C8 toluene solution was placed under UV light for several minutes, the color changed from purple red to claybank. In order to explore the photolysis process in details, the tracked absorption spectra were measured together with different irradiated times. As the irradiated time increases, the intensity of the absorption peaks at 330 nm and 536 nm which correspond to the n-π^* transition and the π-π^* transition