

Esterification of Chemical Functional Single-Wall Carbon Nanotubes

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Abstract

Two kinds of chemical functional single-wall carbon nanotubes (SWNTs) are covalently coupled into special V-type superstructure by the esterification in pyridine medium. Both SWNTs bundles and individual SWNTs can be bound effectively through the deacidification path. The esterification between different kinds of modified SWNTs takes place on their ends and the crystallinity of SWNTs are well remained during the course. Interestingly, the inclinations between coupled SWNTs are very closely to the ester bond angle ($109^{\circ}18'$). Furthermore, the formation mechanism about the peculiar structure has been proposed in the paper. The results suggest that selected connection bonds will determine the different angles of coupled SWNTs.

Introduction

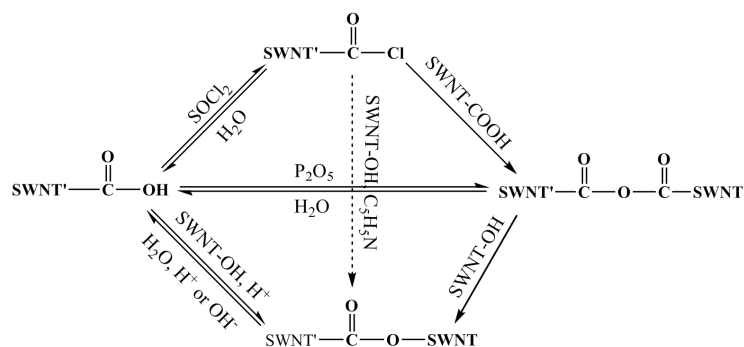
The commercially available SWNTs are generally grown with long string shape, which have shown promise for wide applications such as high performance composites, energy storage media, nano-scale electronic devices and biochemical sensors etc.^[1] Despite their importance, however, intellectualized placement, orientation, and shape control of nanotubes should be very meaningful in both scientific and practical. Sano et al developed nanotube chemistry to assemble SWNTs into ring and star-shaped superstructures.^[2,3] Moreover, Wang et al used nanopatterned affinity templates to form desired architectures by strongly attractions between SWNTs and carboxylic groups.^[4] Cohen and Mahadevan employed the mesoscopic continuum theory to quantitatively investigate those filamentous structures.^[5] These researches are commonly focused on the nanotubes with identical chemical properties, however, the supramolecular interactions between different kinds of modified SWNTs are not mentioned so far.

Actually, it has been a long-standing big challenge to efficiently integrate SWNTs into multifunctional structures or devices.^[6] Due to the irregular and angular surface designs of most electronic circuit, the processes to assemble SWNTs in these nanoelectronic devices should be facile coupling/discoupling, high site-selectivity and smart angle-designability. In related chemical processes, SWNTs are often considered as polyfunctional macromolecules, and particular chemical reactions are confirmed to take place at their ends and sidewalls with different efficiencies.^[7] Therefore, the covalent CNTs chemistry is expected to meet the assembling requirements for its favorable stability, accessibility and selectivity during competitive hybridization.^[8] Herein, we report the special V-type linkages between two kinds of modified nanotubes.

Experimental Section

In a typical experiment, the ammonia-purified SWNTs (SWNT-NH₃)^[9] were first chemically oxidized for obtaining carboxylated SWNTs (SWNT-COOH), and then converted to the acyl chloride intermediate (SWNT-COCl) by treated with thionyl chloride (SOCl₂) at 80 °C for 12 h. Second, 5.0 mg of SWNT-COCl directly reacted with equivalent hydroxyl SWNTs (SWNT-OH)^[10] in pyridine solvent at -18 °C, with sustained magnetic stirring for 12 h. Finally, the homogeneous SWNTs solution was filtered, water washed and vacuum dried to obtain the linked SWNTs (ST-O-ST). The directly coupling of SWNTs has been based on the esterification of respective functionalize tubes (see

scheme 1). It should be mentioned that low molar concentration of functional groups on the nanotube tips restrict the efficiencies of coupling reactions. Preliminary experiments suggest that only special process (see the dashed arrow in scheme 1) can generate detectable reaction yields and thus the other approaches are really inefficient.



Scheme 1. Schematic presentation for the possible strategies used to obtain the end-to-end coupled SWNTs (SWNT and SWNT' represent the different functionalize nanotubes, respectively. The red arrow indicates the major reaction path in our experiment).

Results and discussion

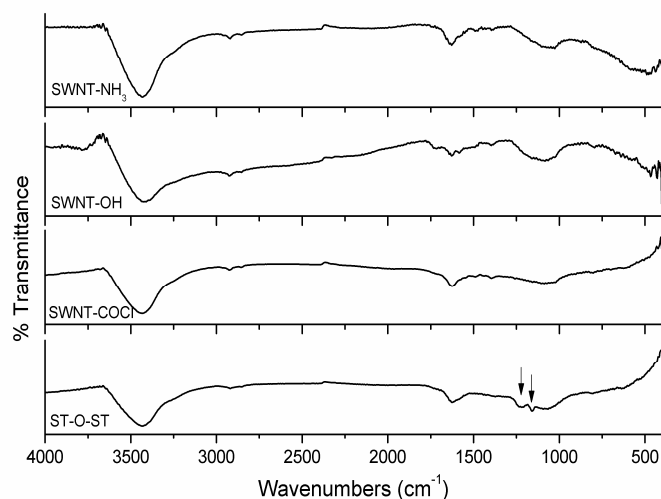


Fig. 1. FT-IR spectra of SWNT-NH₃, SWNT-OH, SWNT-COCl and ST-O-ST samples.

In this paper, FT-IR spectra are used to investigate the functional groups of different SWNTs samples before and after the chemical process respectively (Fig. 1). In the chemical process, reactants (SWNT-OH and SWNT-COCl) and resultants (ST-O-ST) exhibit different chemical properties, which can be detected by the FT-IR absorption bands. In the high frequency region, a broad band around 3400 cm⁻¹ represents the O-H stretches from alcoholic or phenolic groups, which is expanded and downshifted in SWNT-OH. It indicates that the SWNT-OH sample possesses more hydroxyl groups than the others. In the low frequency region, a band at 1050 cm⁻¹ is related to C-O stretches of the SWNT-O-C and C-OH units, which can be observed clearly except the SWNT-COCl, indicating that the hydroxyl groups are absence in SWNT-COCl sample. It suggests that the carboxylic groups of the SWNT-COOH can completely react with SOCl₂ and generate the SWNT-COCl sample effectively. In addition, the 1630 cm⁻¹ band (lower in SWNT-OH) is assigned to C=O stretching of quinone groups added preferentially to the ends of tubes. Strong conjugation effects of C=O bond and SWNTs in ST-O-ST sample induce the upward shifting of the band, which is attributed to the formation of ester bonds attached to the aromatic rings of the carbon nanotubes.^[11] Comparing with the FT-IR curves of different samples, it can be seen that the ST-O-ST curve has new sharp bands at 1220 and 1160 cm⁻¹ (see the two arrows in Fig.1), which represent the symmetry and dissymmetry

stretching vibration of ester bonds (-C-O-C-). Based on the above analysis, we can confirm that quantities of covalent ester bonds are formed in the chemical reaction between the SWNT-OH and SWNT-COCl.

TEM images shown in Fig. 2 reveal the typical microstructures of different V-type linkages. Fig. 2a shows the coupling of two SWNTs bundles and Fig. 2c is a magnification of the connected section. Multiple end-connections of SWNTs bundles can be observed distinctly and the sharp corner appears special obtuse angle. The coupling of individual SWNTs can be viewed in Fig. 2b and the single-linkage between two parallel SWNTs bundles is shown in Fig. 1d. The well-pronounced connection angles of α and β are measured as 109° (Fig. 2e, f), which are markedly similar to the included angle of aromatic ester bonds. Associating with the above FT-IR analysis, it suggests that the esterification between two kinds of SWNTs reactants induces their self-assembling and forms the specific spatial conformation simultaneously. Although as-grown SWNTs often present various kinked structures in TEM observations, the special included angle of coupled SWNTs should not be ascribed to happenchance. In addition, some separate SWNTs can be seen in the images. It indicates that the efficiency of coupling reaction need to be further improved. Basically, the reaction yield will be limited by the quantities of reactants, including the concentration of SWNTs and the quantities of functional groups on them.

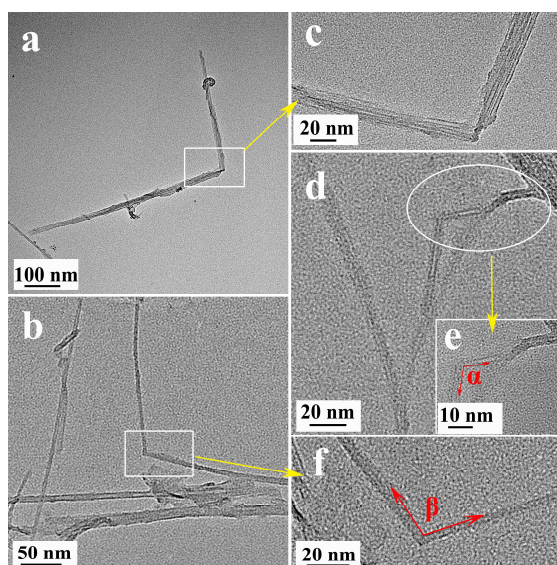
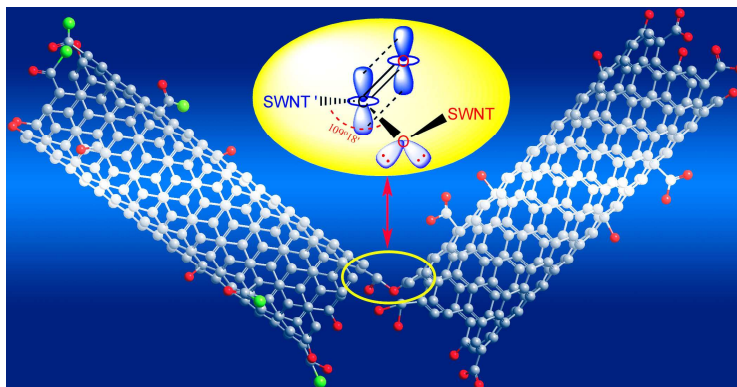


Fig. 2. TEM images of the coupled bundles of SWNTs (a), individual SWNTs (b) and the single-linkage between two parallel SWNTs bundles (d). The figure c, e and f are magnifications of corresponding sections. The angles of connection are measured as about 109° (see α and β).

To suggest an explanation of the obtained results, a simulation scheme has been proposed to illustrate the V-type coupling of SWNTs (see scheme 2). After pretreatment process, hydroxyl and acyl chloride functional groups are introduced into different SWNTs, respectively. Subsequently, under low-temperature and organic base conditions, the two groups react directly with deacidification and generate ester linkages between SWNTs. There are two suggests about the formation of V-type couplings: (1) the coupled reactions are site-selectivity and the ends of SWNTs are more available than the sidewalls. Steric hindrance effects play a central role in the end-selective interaction. Rather large steric hindrances of the active points located on sidewalls block the generation of esterification, on the other side, the ends possess more reactivity and mobility because of their higher dangle bonds densities and shorter rotative moments, which are favorable to chemical reactions and create end-to-end connections easily; (2) ester linkage between the two coupled SWNTs induces them to form delocalized π bond because of the p- π and π - π conjugation effects. The carbon atoms in -C-O-C- of ester bond are sp and sp² hybridization, respectively. Therefore, two SWNTs are restricted by the

ester bond angle ($109^{\circ}18'$) in the delocalized π orbital plane of ST-O-ST supramolecule, which can induce to the V-type directivity of coupled SWNTs during self-assembled course. The minimal diameter of SWNTs (about 1-3 nm) ensure their coupling angle very closely to the ester bond angle.



Scheme 2. Schematic of the V-type structure originated from two coupled SWNTs. The SWNT' and SWNT denote SWNT-COCl and SWNT-OH, respectively. Three kinds of color balls mean the C (grey), O (red) and Cl (green) atoms, respectively.

Summary

In summary, we have successfully developed an effective method for covalent coupling different chemical processed SWNTs to controllable V-type framework. The results suggest that selected connection bonds will determine the different angles of coupled SWNTs. The angular self-assembled coupling will lead to site-selective and orientation-designable interconnections of SWNTs, which can promote the self-adjusting “bottom-up” route to produce multifunctional CNTs structures and devices besides the micro-template fabrication techniques.

Acknowledgments

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