

Functionalization of Shortened SWCNTs Using Esterification

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Carbon nanotubes (CNTs) have been one of the intensively-studied topics in the fields of nanoscience and nanotechnology due to their unique electronic, mechanical, and chemical properties.^{1,2} Shortened single-walled carbon nanotubes (s-SWCNTs) with length of 100-300 nm are promising nanomaterials in the applications of nanoscale electronic devices,³ field-emission displays,⁴ chemical sensors,⁵ and nanobiosensors.⁶ s-SWCNTs can be soluble in common organic solvents by covalent functionalization of CNTs. Several reactions have been developed for chemical modification and functionalization of CNTs including non-covalent (ionic) interaction,⁷ amidation,⁸ and esterification.⁹ Among the reported reactions, the ester bond formed by esterification of CNT-acid chloride and alcohols can be cleaved easily through acid- or base-catalyzed hydrolysis. This method was used for the purification of carbon nanotubes, where CNTs are solubilized by esterification and the soluble CNTs are purified by the cleavage.^{10,11}

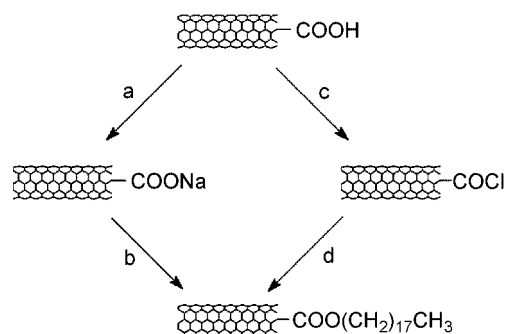
In this paper, we report a new esterification scheme for functionalizing s-SWCNTs: an ester bond formation between carboxylate and alkyl bromide (Scheme 1). Compared with the reported method where the formation of acid chloride is required, the new scheme needs a simple deprotonation of CNT-COOH. The chemical shortening of full-length SWCNTs was carried out by oxidation in the mixture of concentrated H₂SO₄ and HNO₃ (3 : 1) under

sonication for 24 h at temperatures between 35 and 40 °C. The resulting SWCNTs were polished in a mixture of concentrated H₂SO₄ and 30% aqueous H₂O₂ (4 : 1) under heating for 2 hrs at 70 °C to produce s-SWCNTs. Concentrated HCl was then added,¹⁰ which resulted in the terminal carboxyl functionalities as indicated by IR measurement ($\nu_{\text{C=O}} = 1709 \text{ cm}^{-1}$, Figure 1a). The length of the s-SWCNTs was in the range of 300 nm-2 μm .

We synthesized the covalently functionalized s-SWCNTs by esterification of SWCNTs-COONa and 1-bromooctadecane. To produce soluble SWCNTs, the s-SWCNTs were converted into the corresponding s-SWCNTs-COONa by treatment with NaOH in the presence of distilled water. s-SWCNTs (10 mg) were added to a solution of NaOH (0.4 g) in distilled water (2 mL) with vigorous stirring and kept at room temperature for 1 h. A mixture of s-SWCNT-COONa and 1 g of 1-bromooctadecane (melting point: 28 °C) was kept at 120 °C for 5 days. After cooling to room temperature, the resulting mixture was sonicated in 200 mL of ethanol for 10 min. The products were collected with PTFE membrane filter (0.45 μm pore size). Residual 1-bromooctadecane was removed by washing with ethanol four times. The resulting product was dried at room temperature under vacuum, and sonicated in 500 mL of THF for about 10 min. After the impurities were removed by filter paper (8 μm pore size), a black-colored solution was concentrated under reduced pressure. The yield of ester-bonded s-SWCNTs was usually over 54% (0.54 mg) based on the s-SWCNTs. The functionalized s-SWCNTs were also produced by esterification through acyl chloride.¹²

Figure 1a shows the FT-IR spectrum taken after the acid mixture treatment. The characteristic vibrational modes of carbonyl group (1709 cm^{-1}) and hydroxyl group (3420 cm^{-1}) were observed. Figure 1c shows the carboxylate peak and the aliphatic chain (C-H stretch) peaks at 1731 cm^{-1} , and 2919 and 2850 cm^{-1} , respectively. Figures 1d and e show IR spectra of 1-octadecanol and the functionalized s-SWCNTs, respectively: the carboxylate peak (1730 cm^{-1}) and the aliphatic chain peaks (2922 and 2853 cm^{-1}). The ¹H NMR spectrum of the functionalized s-SWCNTs showed the presence of the long aliphatic chains on the s-SWCNTs: δ 0.83 (t, 3H, $J = 6.7 \text{ Hz}$), 1.21-1.32 (bs, 30H), 1.60 (bs, 2H), 4.09 (bs, 2H).

The SEM images of the starting SWCNTs and the functionalized s-SWCNTs are shown in Figure 2. In Figure



Scheme 1. A schematic illustration of preparation of functionalized SWCNTs through two different esterification methods: (a) NaOH, H₂O, RT, 1 h, (b) 1-bromooctadecane, 120 °C, 5 days, (c) SOCl₂, DMF, reflux, 24 h, and (d) 1-octadecanol, Et₃N, 100 °C, 8 days.

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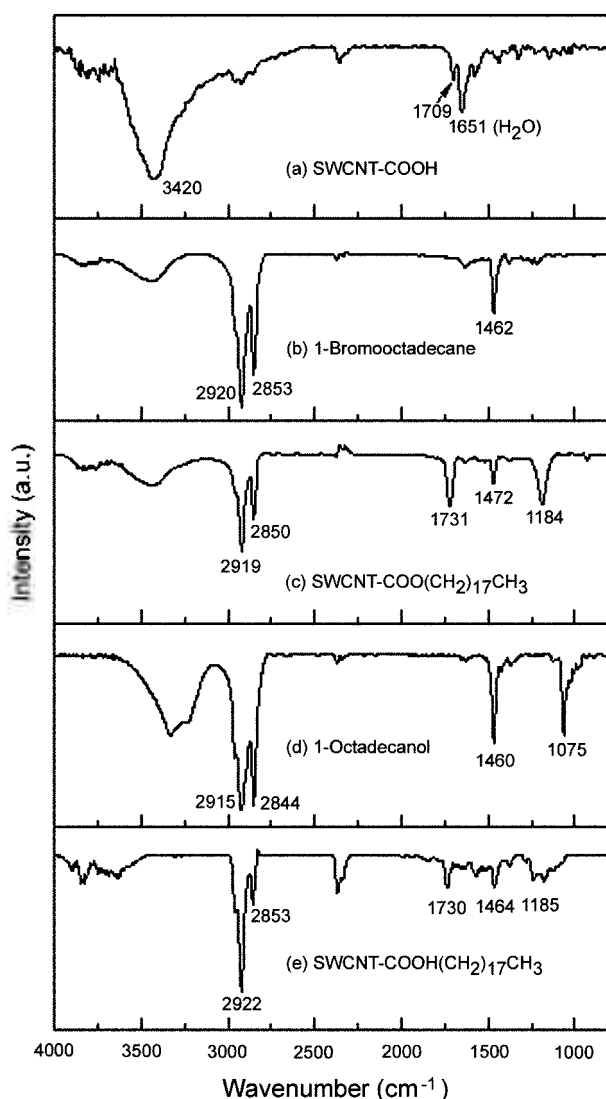


Figure 1. FT-IR spectra of (a) the oxidized SWCNTs, (b) 1-bromooctadecane, (c) the functionalized SWCNTs using SWCNT-sodium carboxylates, (d) 1-octadecanol, and (e) the functionalized SWCNTs using acyl chloride.

2a, one can find the SWCNT bundles are entangled with each other. Compared with the raw tubes (Figure 2a), the functionalized s-SWCNTs (Figure 2b) could be readily dispersed onto a solid surface. This result shows that the SWCNTs were converted from an entangled bucky paper into the dispersible s-SWCNTs, which were functionalized with 1-bromooctadecane. Since the esterification reaction could occur only on the carboxyl site of the s-SWCNTs, the chemical treatment on the s-SWCNTs for the esterification should not change much of their crystalline properties. The resulting functionalized s-SWCNTs were soluble (> 0.4 mg/mL) in organic solvents such as chloroform, dichloromethane, toluene, THF, and DMF.

In summary, we reported a new esterification method for modifying s-SWCNTs: carboxylate-alkyl bromide coupling.

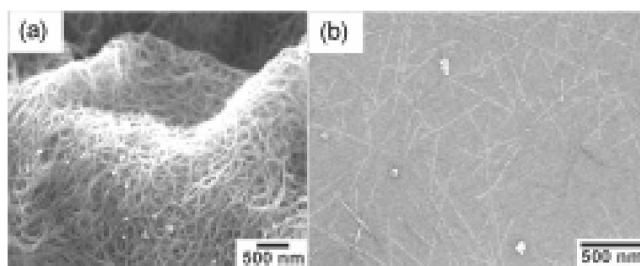


Figure 2. FE-SEM images of the carbon nanotubes (a) before and (b) after the esterification.

Although the coupling reaction of acid chloride with amines and alcohols was successfully applied to the functionalization of CNTs, the relative instability of acid chloride would result in a poor coupling yield and need a careful manipulation of the reactions. The new esterification scheme would give an opportunity to derivatize CNTs with a higher precision and a complementary way leading to orthogonal functionalization of CNTs.

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References and Notes

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12. To functionalize s-SWCNTs with ester groups via the acid chloride method, 10 mg of the oxidized material suspended in 1 mL of anhydrous DMF was added to 20 mL of thionyl chloride (SOCl_2 , Fluka) and heated under reflux for 24 h.¹⁰ The resulting mixture was rinsed with anhydrous THF. 1 g of 1-octadecanol and 0.2 mL of triethylamine (Et_3N , Aldrich) were then subsequently added. The reaction mixture was kept at 100 °C for 8 days. The processed s-SWCNTs were collected and washed with ethanol several times. After paper filtering (8 μm pore size), a black-colored solution was concentrated under reduced pressure. The resulting black solid was dried at room temperature under vacuum. The yield of ester-bonded s-SWCNTs reached about 40%.