

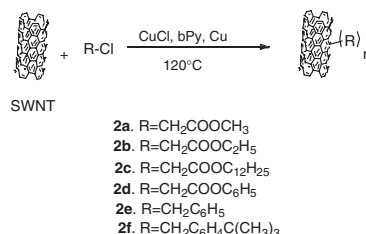
## Covalent Attachment of Organic Groups onto Single-walled Carbon Nanotubes via Copper(I)-promoted Radical Addition

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Functionalization of single-walled carbon nanotubes (SWNTs) via atom-transfer radical addition in the presence of copper(I/II) redox systems allows for covalent attachment of a variety of different groups such as carboxylate and aryl. Modified SWNTs were characterized by ATR-IR, TG-MS, as well as Raman spectra, clearly indicating the formation of covalent bonding between organic groups and nanotubes.



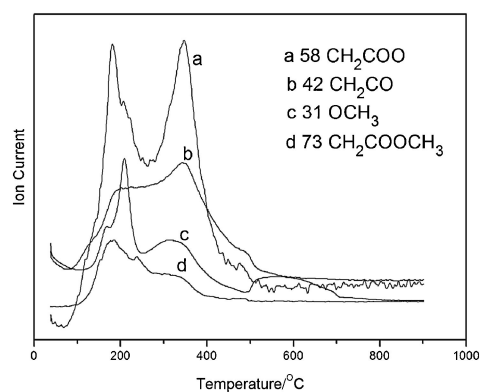
**Scheme 1.** Functionalization of SWNTs via ATRA.

Single-walled carbon nanotubes (SWNTs) have been drawing much attention for their unique physical properties and potential applications.<sup>1</sup> Organic-molecule modification of SWNTs is often necessary to take full advantage of their notable properties.<sup>2</sup> Functionalization reactions can be divided into two categories: 1) Treating SWNTs with strong oxidizing agents to generate carboxylic groups that can be further derivatized by amidation or esterification,<sup>3</sup> 2) highly reactive intermediates, such as radicals, carbenes, and nitrenes, attacking the SWNT sidewall,<sup>4</sup> in which addition of organic radicals have attracted more interest due to less stringent reaction conditions being required. Examples described include diazonium salts, photolysis of carbon-iodine bonds and thermal decomposition of peroxides or azo compound.<sup>5</sup>

Copper(I)-promoted atom-transfer radical addition (ATRA) has widespread applications in organic synthesis.<sup>6</sup> A halogen atom transfers from an alkyl halide (R-X) to the Cu(I) complex generating the corresponding Cu(II) complex and an organic radical (R•) which can undergo further addition, coupling, or cyclization reaction. The halogen-atom transfer reaction is a reversible process, and high conversion of the alkyl halide could occur if the addition of copper(0) powder reduces the excess copper(II) to copper(I).<sup>7</sup> Li et al.<sup>8</sup> reported the synthesis of C<sub>60</sub>-end-bonded polymer using addition reaction of polymer radical. Recently, Lin et al.<sup>9</sup> and Paik et al.<sup>10</sup> reported the functionalization of multiwalled carbon nanotubes via a similar process. Here, we describe the addition of a variety of organic radicals generated from copper(I)-promoted ATRA to SWNTs to enhance the solubility of the nanotubes.

It should be noted that our method is distinctly different from the previously reported-nanotubes-modification approach of atom-transfer radical polymerization (ATRP).<sup>11</sup> The later belongs to the “grafting from” technique: covalently modified carbon nanotubes served as macroinitiators initiating radical polymerization of vinyl monomer which was promoted by Cu(I) complex, to generate the tethered polymer chains. There was a large amount of highly reactive vinyl monomer in the reaction system, so initiated radicals would not add to nanotubes but to vinyl monomer there.

SWNTs produced by CVD were purified according to published literature.<sup>2,3</sup> The modification reaction is presented in Scheme 1. To a suspension of the purified SWNTs in dry *ortho*-

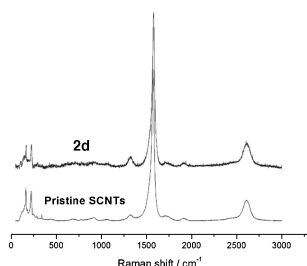


**Figure 1.** Ion current versus temperature plots from thermal degradation TG-MS studies of obtained product **2a**.

dichlorobenzene (*o*-DCB) were added R-X, CuCl, ligand bipyridine (bPy), and Cu powder. The mixture was stirred at 120 °C for 3 days under N<sub>2</sub>, and then stirred at 25 °C for 2 h under air. The modified SWNTs were separated by filtration through a PTFE membrane (0.22 μm), and cleaned with HCl, H<sub>2</sub>O, *o*-DCB, and CHCl<sub>3</sub>. The XPS analysis shows the presence of all anticipated elements associated with the product. For example, sample of **2c** contains mainly carbon and oxygen (Figure S1).<sup>13</sup>

ATR-IR spectroscopy indicates the presence of organic moieties. For instance, the spectrum of **2c** contains peaks of the characteristic carbonyl stretching mode at 1745 cm<sup>-1</sup> and strong alkyl stretches (C-H) at 2927 and 2845 cm<sup>-1</sup> (Figure S2).<sup>13</sup>

Further evidence for covalent functionalization of organic groups to SWNTs has been provided by Thermogravimetry-mass spectrometry (TG-MS) analysis. For example, the TG-MS data of **2a** (Figure 1) shows the evolution curves for the parent ion with CH<sub>2</sub>COOCH<sub>3</sub> (*m/z* 73), and for the fragment ions with CH<sub>2</sub>COO (*m/z* 58), CH<sub>2</sub>CO (*m/z* 42), and OCH<sub>3</sub> (*m/z* 31). All peaks appear at the same temperature, which indicates that all fragment ions originate from the detaching CH<sub>2</sub>COOCH<sub>3</sub> radical. The peaks begin at about 155 °C, which is comparable to



**Figure 2.** Raman spectra of pristine SWNTs and **2d** (Spectra have been normalized at the 1572 nm (G-band)).

**Table 1.** Raman  $I_D/I_G$  of pristine SWNTs (**1a**) and **2a–2f**

	Sample						
	<b>1a</b>	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>2e</b>	<b>2f</b>
$I_D/I_G$ (%)	3.5	4.4	5.2	6.0	6.7	6.5	5.3

that for alkylated SWNTs (about 160 °C) and 2-carboxyethylated SWNTs (170 °C).<sup>12</sup> TGA provides a measure of the degree of functionalization. The weight losses measured by TGA are: 14% (**2a**), 16% (**2b**), 24% (**2c**), and 21% (**2d**) (Figure S3).<sup>13</sup> The degree of functionalization was estimated to be ca. 2–4%.

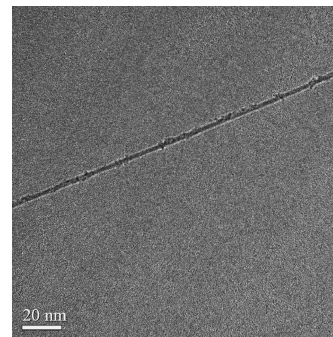
Direct evidence for the sidewall covalent functionalization of SWNTs is obtained from Raman spectroscopy. The pristine SWNTs provided typical Raman spectra of carbon nanotubes (Figure 2): the weak D band at 1318  $\text{cm}^{-1}$ , strong G band at 1573  $\text{cm}^{-1}$ , and the radical-breathing mode at 150–350  $\text{cm}^{-1}$ , respectively. Table 1 shows the Raman  $I_D/I_G$  of the pristine SWNTs and product **2a–2f**. The relative intensity of the D band appeared to be significantly enhanced after modification, and this is characteristic of all the products obtained (Figure S4).<sup>13</sup> The existence of RBM regions at 150–350  $\text{cm}^{-1}$  in the functionalized tubes suggests that the tubular structure of SWNTs is preserved essentially after functionalized via copper(I)-promoted ATRA as the bands are still clearly visible. The absorption spectrum of **2c** (Figure S5)<sup>13</sup> show the distinctive van Hove singularities, indicating the preservation of the structural and electronic integrity of SWNTs after modification.

The obtained products exhibit remarkable improved solubility in organic solvents. For example, **2c** is soluble in DCB (0.8  $\text{mg mL}^{-1}$ ),  $\text{CHCl}_3$  (0.6  $\text{mg mL}^{-1}$ ), DMF (0.4  $\text{mg mL}^{-1}$ ), and tetrachloroethane (0.7  $\text{mg mL}^{-1}$ ).

Individual modified SWNTs were observed via AFM (Figure S6)<sup>13</sup> and TEM (Figure 3). Their diameter of 1–3 nm, confirmed by height data of AFM and diameter measurement of TEM, corresponds to that of the SWNTs produced by CVD. Small bundles were observed as well.

In summary, we have developed a novel approach to Covalent Attachment of Organic Groups onto SWNTs by atom-transfer radical addition in the presence of copper(I/II) redox systems.

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**Figure 3.** TEM of **2c**.

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