

# A Simple Way to Chemically React Single-Wall Carbon Nanotubes with Organic Materials Using Ultrasonication

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## ABSTRACT

Ultrasonication of single-wall carbon nanotubes (SWNTs) in a monochlorobenzene (MCB) solution of poly(methyl methacrylate) (PMMA) enabled us to react SWNTs with MCB or PMMA chemically. After the SWNTs reacted with these organic materials, they turned into ragged SWNTs (r-SWNTs) with many defects in the sidewall when burned in oxygen. We think that the sonochemical reaction of SWNTs and organic materials is a simple method to functionalize SWNTs.

Single-wall carbon nanotubes (SWNTs)<sup>1</sup> have been investigated in many fields, including physical chemistry, material science, solid-state physics, and electronic engineering. However, the chemical modification of SWNTs at the molecular level has been little studied to date. This is largely because it is difficult to obtain pure SWNTs, and SWNTs do not dissolve in solvents. Several studies of chemical modifications of SWNTs have been reported. For example, Chen et al. reported on the derivatization of SWNTs dissolved in organic solutions with thionylchloride and octadecylamine, and on the functionalization of the nanotube wall by reacting the soluble SWNTs with dichlorocarbene.<sup>2</sup> Wong et al. reported modification of multiwall carbon nanotubes (MWNTs) via amide bond formation between carboxy functional groups bonded to the open ends of MWNTs and amines.<sup>3</sup> They found that the modified MWNTs were chemically sensitive as atomic force microscopy (AFM) tips. Mickelson et al. reported the chemical modification of SWNT sidewalls by fluorination, which was performed by heating purified SWNTs in fluorine.<sup>4</sup>

We have reported that ultrasonication of SWNTs in a monochlorobenzene (MCB) solution of poly(methyl methacrylate) (PMMA) followed by filtration is an effective way to purify SWNTs.<sup>5</sup> The polymer-assisted purification method enabled us to remove impurities from as-grown SWNTs effectively and to cut and shorten SWNTs. We have also found that SWNTs containing many holes are formed when

shortened SWNTs are heated in oxygen gas. We named these compounds ragged SWNTs (r-SWNTs) and reported on their thermal instability. Unlike normal SWNTs, they degrade at about 1000 °C.<sup>6</sup>

While investigating the purification of SWNTs by polymer-assisted ultrasonication, we found that SWNTs reacted chemically with the organic liquid during ultrasonic irradiation. In this letter, we confirm that a simple sonochemical reaction of SWNTs with MCB and PMMA occurs.

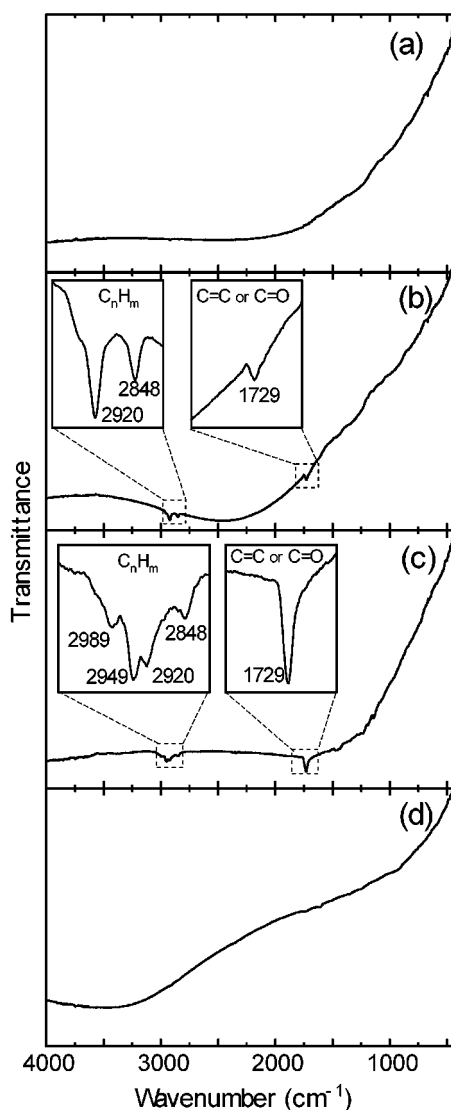
As-grown SWNTs were prepared using a previously described procedure.<sup>7</sup> Two mixtures of SWNTs and organic liquids were prepared in this study. One was a mixture of as-grown SWNTs (10 mg) and a 2% MCB solution (30 mL) of PMMA (SWNTs/PMMA/MCB); the other was a solution of SWNTs (10 mg) and MCB (30 mL) (SWNTs/MCB). These mixtures were dispersed and sonicated using an ultrasonic processor (Dr. Hielscher UP400s) with a microtip sonotrode 3 mm in diameter. The ultrasonic processor was operated continuously at 300 W/cm<sup>2</sup> for 5 h. The sonicated SWNTs were thoroughly suspended in the solvent and formed a pulpy colloidal suspension. The suspension was filtered through 20- and 5- $\mu$ m pores to remove impurities, such as amorphous carbon and metal particles.

Katoh et al. reported that benzene derivatives, such as fluorobenzene, chlorobenzene, and bromobenzene, are polymerized during irradiation by ultrasound.<sup>8</sup> In our study, the filtrate was therefore rinsed three times to remove any polymerized chlorobenzene and decomposed PMMA species. After rinsing to remove any residual MCB solvent and carbonaceous impurities, the rinsed filtrate was burned in dry oxygen gas at 400 °C for 30 min. The structural change

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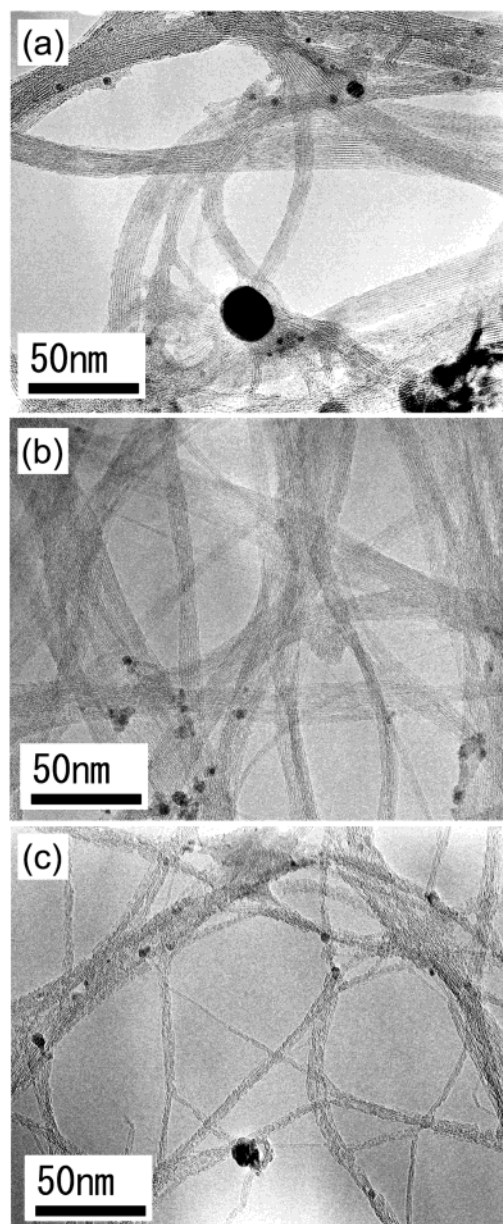
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**Figure 1.** FT-IR spectra of (a) as-grown SWNTs, (b) an ultrasonicated SWNT/ MCB mixture, (c) an ultrasonicated SWNT/ PMMA/ MCB mixture, and (d) an ultrasonicated toluene/ SWNT mixture.

resulting from sonication and burning was characterized by electron microscopy (SEM, TEM) and spectroscopy (UV, FT-IR, Raman).

Figures 1a,b,c, and d show solid-state diffuse reflectance FT-IR spectra ( $450\text{--}4000\text{ cm}^{-1}$ ) of as-grown SWNTs and sonicated mixtures of toluene/ SWNT, SWNT/ MCB, and SWNT/ PMMA/ MCB, respectively. The FT-IR spectra indicate that SWNTs reacted chemically with MCB and PMMA after ultrasonication. No peak was observed in the FT-IR spectrum of as-grown SWNTs (Figure 1a). For the SWNT/ MCB mixture (Figure 1b, three peaks were observed. The peak at  $1729\text{ cm}^{-1}$  corresponds to a C=C double bond or the C=O bond in carbonyl groups. The oxygen atoms may originate from oxygen dissolved in the solvent. The other two peaks, at  $2848$  and  $2920\text{ cm}^{-1}$ , correspond to the stretching mode of C-H bond vibration in saturated hydrocarbons. The absorption peak corresponding to benzene rings was not observed, indicating that the benzene ring in the MCB molecule decomposed into reactive fragment species

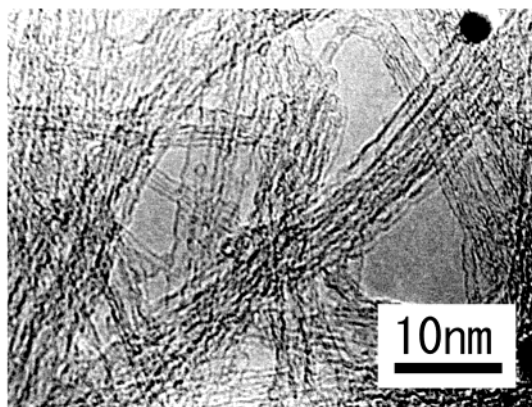


**Figure 2.** TEM images of (a) as-grown SWNTs, (b) r-SWNTs obtained after ultrasonication in MCB followed by burning, and (c) r-SWNTs obtained after ultrasonication in a PMMA/ MCB mixture followed by burning.

during ultrasonication. At the same time, ultrasound cut SWNTs,<sup>5,9</sup> producing defects in the sidewalls.<sup>10</sup> The reactive species produced by decomposition of MCB reacted easily with SWNTs, because of the reactive sites formed on the sidewalls and at the open ends.

For the SWNT/ PMMA/ MCB mixture, two additional peaks were observed, at  $2949$  and  $2989\text{ cm}^{-1}$  (Figure 1c). This suggests that two different species produced by the decomposition of PMMA reacted with the reactive sites induced on SWNTs by ultrasound.

When toluene was used as a solvent instead of MCB, no absorption peak was observed in the FT-IR spectrum (Figure 1d), because toluene is less reactive than MCB.<sup>8</sup> Thus, this suggests that reactive MCB plays an important role in the ultrasonic synthesis with SWNTs.



**Figure 3.** A high-magnification TEM image of r-SWNTs with many defects in the SWNT sidewall.

After burning the sonicated samples, the FT-IR peaks disappear. This may be due to the removal of the SWNT-bonded functional groups originating from MCB or PMMA. The disappearance of the functional groups is obvious in the TEM images. Figure 2 shows TEM images of as-grown SWNTs (Figure 2a), and sonicated SWNT/MCB and SWNT/PMMA/MCB mixtures that were subsequently oxidized (Figures 2b and c, respectively). The as-grown SWNTs contained many impurities, such as metal particles and amorphous carbons (Figure 2a). After the treatment, it is clear that most impurities were removed, as we reported previously<sup>5</sup> (Figures 2b,c). The bundles obtained using PMMA/MCB (Figure 2c) are thinner than those obtained using only MCB (Figure 2b). This suggests that adhesion of PMMA around thin SWNT bundles prevents them from reforming thick bundles.<sup>11</sup>

A high-magnification TEM image corresponding to Figure 2c shows that many defects formed in the sidewall (Figure 3). These SWNTs look like leaves that have been eaten by worms and are full of holes (r-SWNTs).<sup>6</sup> The defects should correspond to the reaction sites formed on the SWNT sidewalls after the removal of functional groups. The number of defects was roughly estimated from the TEM image (Figure 3), and ranged from 1 to 3 sites per 1 nm length.

Ultrasound forms hot spots in the mixture of SWNTs and organic liquids, where the temperature and pressure can instantaneously exceed 100 MPa and 5000 K,<sup>12</sup> respectively. Organic molecules, such as MCB and PMMA, are decomposed at the hot spots, and reactive species are formed. At the same time, the sidewalls of the SWNTs are damaged, and carbon-dangling bonds form as a result of the high temperature and pressure. We think that reactive organic species react chemically with the dangling bonds of the SWNTs. The species that bond to the SWNT sidewalls are easily removed by burning in oxygen gas, forming holes on the sidewalls.

By precise control of the irradiation power and duration during ultrasonication, it should be possible to control the synthesis of SWNTs and organic molecules. Our simple ultrasonication technique should enable us to functionalize SWNTs in various ways, with different combinations of organic solvents and soluble materials, such as polymers.

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