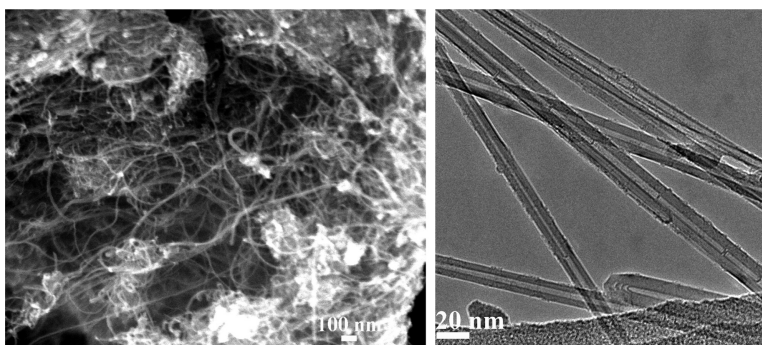


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## Synthesis of Multiwalled Carbon Nanotubes through a Modified Wolff–Kishner Reduction Process

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Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima,<sup>1</sup> there has been great interest in developing new methods for the synthesis of CNTs due to their potential applications in various technologies.<sup>2–4</sup> Methods developed so far include arc discharge,<sup>5</sup> laser vaporization,<sup>6,7</sup> pyrolysis,<sup>8,9</sup> chemical vapor deposition,<sup>10</sup> high-temperature hydrothermal<sup>11,12</sup> and low- and high-temperature solvothermal.<sup>13,14</sup> Here we report the synthesis of multiwalled CNTs (MWCNTs) by reducing ethyl alcohol with NaBH<sub>4</sub> in a high concentration, strong basic solution without intentionally adding the conventional catalysts of Fe/Co/Ni, following a modified Wolff–Kishner reduction process. This technique opens a new route for the synthesis of CNTs.

The Wolff–Kishner reduction normally refers to a base-catalyzed process that leads ultimately to the production of alkane from the corresponding aldehydes or ketones,<sup>15–17</sup> which involves first converting aldehydes or ketones to the corresponding hydrazone and then decomposition of this intermediate in the presence of strong basic conditions to yield the reduced alkyl derivative (the corresponding alkane) and nitrogen.<sup>15,16</sup> In this report, we utilize a similar process to directly synthesize MWCNTs through the reduction of ethyl alcohol with NaBH<sub>4</sub> under a strong basic solvent with high NaOH concentration.

In a typical synthesis, 80 mL of ethyl alcohol (90%), 4.2 g of NaBH<sub>4</sub> (99.99%), and 15 mL of 10 M NaOH (97%) solution were added to a 250 mL flask. The mixtures were stirred with a magnetic stirrer for 30 min and then transferred to a Parr reactor (model 4750, Parr Company, Moline, IL) with a capacity of 125 mL. The Parr reactor was sealed and then kept at 180 °C for 20 h in a furnace and then cooled to room temperature. The products were washed with alcohol and distilled water several times and then dried in a vacuum oven at 60 °C for 10 h.

Panels a and b of Figure 1 show the low- and medium-magnification field emission scanning electron microscopy (FE-SEM) images of the MWCNTs, respectively, demonstrating the diameters of 10–40 nm and lengths of up to several tens of micrometers.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were used to further characterize the microstructure of the as-synthesized MWCNTs. Panels a–d of Figure 2 show the typical TEM and HRTEM images of the as-prepared MWCNTs. The nanotubes exhibit a straight morphology, as shown in a and c of Figure 2. In general, the nanotubes have an outer diameter in the range of 10–40 nm and a length of up to 25 μm. The inner diameters are 3–6 nm. It is clearly seen that some nanotubes have a bamboo-like structure, as shown in b and d of Figure 2. The high-magnification microstructure studies of the tips show that almost all nanotubes have closed ends with different shapes. Figure 2c reveals that some CNTs have a conical tip structure. The HRTEM studies indicate that these conical tips are end-closed and have bamboo-shaped structure (Figure 2d).

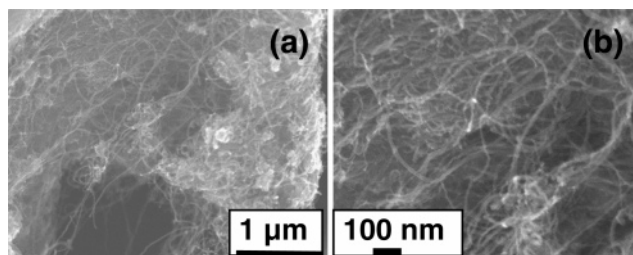


Figure 1. (a) Low- and (b) medium-magnification SEM images of the as-prepared MWCNTs.

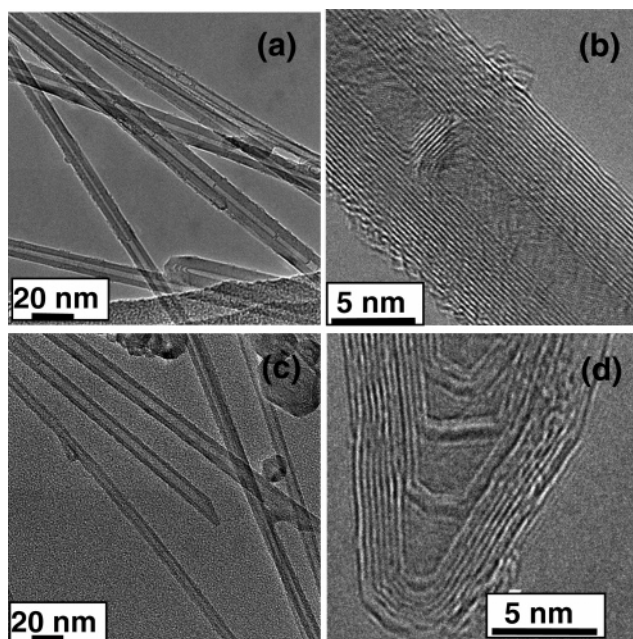
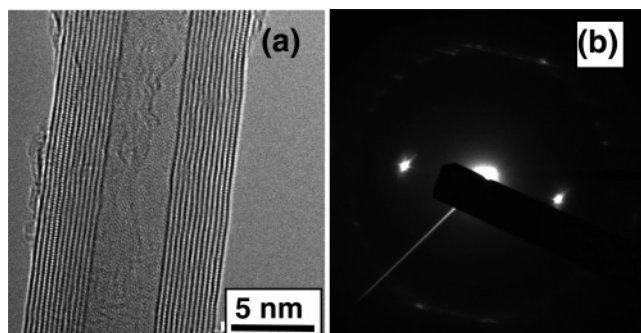


Figure 2. TEM and HRTEM images of the as-prepared carbon nanotubes. (a and b) Some carbon nanotubes have a bamboo-like structure. (c and d) Some carbon nanotubes have a conical tip structure.

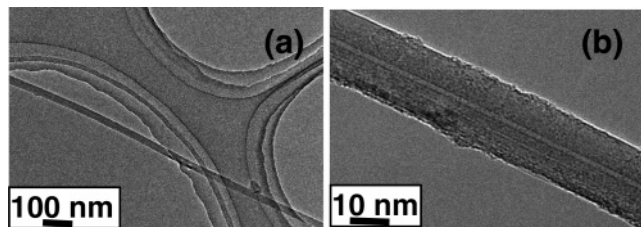
Figure 3a shows the HRTEM image of an individual MWCNT, indicating the high crystallinity of the walls. The walls are composed of graphite sheets aligned parallel to the tube axis. The inter-wall spacing is about 0.34 nm, consistent with the standard spacing. The selected area electron diffraction (SAED) pattern shown in Figure 3b also exhibits that the nanotube is well-crystallized.

During TEM examinations of the as-prepared CNTs, some CNTs with very small inner diameters were detected. In a low-magnification image, the CNT looks like a solid nanowire (Figure 4a). The high-magnification image demonstrates that the inner diameter is about 2 nm and uniform along its length axis (Figure 4b), and the outer diameter is about 20 nm.

The efforts have been made to rationalize the formation process of CNTs. Shi and co-authors<sup>18</sup> used tetraethoxysilane (TEOS) as



**Figure 3.** (a) HRTEM image and (b) SAED pattern of an individual CNT, showing that the CNT has a high-crystalline structure.



**Figure 4.** (a) Low- and (b) high-magnification TEM images of an individual CNT, showing the very small inner diameter of about 2 nm.

carbon sources to successfully synthesize carbon nanotubes, in which the decomposition of TEOS results in  $\text{SiO}_2$  and oxygen-containing hydrocarbon, and then the oxygen-containing hydrocarbon further decomposes into carbon nanotubes. It has been reported that alcohols react directly with  $\text{NaBH}_4$  to produce  $\text{H}_2$ , alkyl borates, and alkoxy borohydrides.<sup>19</sup> For our present case, the possible reaction is that ethyl alcohol reacts with  $\text{NaBH}_4$  in high concentration, strong basic solution to produce  $\text{H}_2$ , triethyl borate  $((\text{OC}_2\text{H}_5)_3\text{B})$ , and other alkoxy borohydrides. The intermediate  $(\text{OC}_2\text{H}_5)_3\text{B}$  decomposes into  $\text{B}_2\text{O}_3$  and oxygen-containing hydrocarbon; the freshly formed oxygen-containing hydrocarbon further decomposes and forms carbon nanotubes and other chemicals. The whole formation process is similar to the Wolff–Kishner reduction process, which involves first converting aldehydes or ketones to the corresponding hydrazone and then decomposition of this intermediate in the presence of strong basic conditions to yield the reduced alkyl derivative (the corresponding alkane) and nitrogen.<sup>15,16</sup> Our experiments indicated that a  $\text{NaOH}$  aqueous solution with high concentration was essential for the formation of the CNTs. There were no CNTs formed when the reactions were conducted in aqueous solutions with low  $\text{NaOH}$  concentration. We propose that the role of high concentration  $\text{NaOH}$  is most likely as a chemical catalyst during the formation of CNTs, which catalyzes reduction of ethyl alcohol with  $\text{NaBH}_4$  under hydrothermal conditions. Several growth mechanisms have been used to explain the growth of carbon nanotubes depending on the synthesis technique.<sup>20</sup> In our current experiments, no conventional catalysts, such as  $\text{Fe}/\text{Co}/\text{Ni}$ , were used. Therefore, the growth mechanism is different from that of the equilibrium ambient-pressure catalytic synthesis. The CNTs prepared via our present technique have characteristics similar to those of the high-temperature hydrothermal method,<sup>11,12</sup> such as straight

morphology, highly graphitic layers, etc. This strongly suggests that the growth of CNTs under our experimental conditions may be similar to the pressure-induced carbon condensation growth mechanism.<sup>11,12</sup> A high density fluid phase, from which growth occurs, changes its compositions rapidly as carbon condenses, traversing a range of compositions during which different phenomena can take place. This may explain the formation of CNTs and bamboo-like CNTs in our experiments.

Our synthetic approach has several advantages compared with other available methods. First, the ethyl alcohol acts not only as carbon sources but also as the solvent, which decreases the cost of production and also allows the reaction to be performed under mild conditions. Second, it is promising for the production of high purity CNTs because no catalysts are added. Finally, the yield of as-prepared CNTs estimated by SEM and TEM observations is about 50% relative to the samples on copper grids, which is higher than those obtained with other recently reported low-temperature methods.<sup>21,22</sup>

In conclusion, using a modified Wolff–Kishner reduction process, we have successfully grown highly graphitized very straight MWCNTs without adding any conventional catalysts, such as  $\text{Fe}/\text{Ni}/\text{Co}$ , at a very low-temperature of  $180^\circ\text{C}$ . This technique opens a new route for the synthesis of CNTs and other carbon nanostructures.

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