Development of Facile Synthetic Methods of Carbon Nanotubes Using a Domestic Microwave Oven

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We succeeded in the development of two facile synthetic methods of carbon nanotubes (CNTs) by using a domestic microwave oven and a commercially available small microwave furnace from Art Box™. Our handmade apparatus was cheap and the synthesis of the CNTs took only 5 min. Interestingly, we could selectively synthesize the magnetic nickel-containing CNTs and non-magnetic nickel-free CNTs by our two developed methods.

Many synthetic methods of carbon nanotubes (CNTs) have been reported to date.[1] The representative methods include the electrical arc discharge method,[2–5] laser ablation method,[6] and chemical vapor deposition method.[7,8] These conventional synthetic methods require expensive equipment, high voltage, and high vacuum. Such energy-consuming methods have a significant on the environment. Therefore, a novel less-energy-consuming method is desired.

Recently, it was reported that carbon nanotubes and nanocapsules were prepared from nickel stearate using an electrical furnace.[9] This method signficantly stimulated our interests in synthesizing CNTs from organic transition metal complexes using a domestic microwave oven. The CNT formation was proposed to directly originate from the crystalline state of nickel stearate, as illustrated in Figure 1a.[9] However, we speculated that this proposal might be not correct, but that the formation of the CNTs might originate from the discotic columnar liquid crystalline structure of nickel stearate. It is well known that the discotic columnar liquid crystalline structure of the analogous copper stearate has been thoroughly established (Figure 1c).[10] Therefore, we carried out microscopic observations, differential scanning calorimetry (DSC) measurements and temperature-dependent X-ray diffraction structural analysis to establish the columnar mesomorphism of nickel stearate (See Supporting Information). Table in Supporting Information summarizes the phase transition behavior. As can be seen from this table, nickel stearate shows a lamello-columnar ($\mathrm{Col_L}$) mesophase in 99.2–129.2 °C and a rectangular columnar ($\mathrm{Col_r}(C2/m)$) mesophase in 129.2–160.5 °C. These columnar mesophase structures were established from the temperature-dependent X-ray diffraction structural analyses (See Figure in Supporting Information). Thus, it was revealed

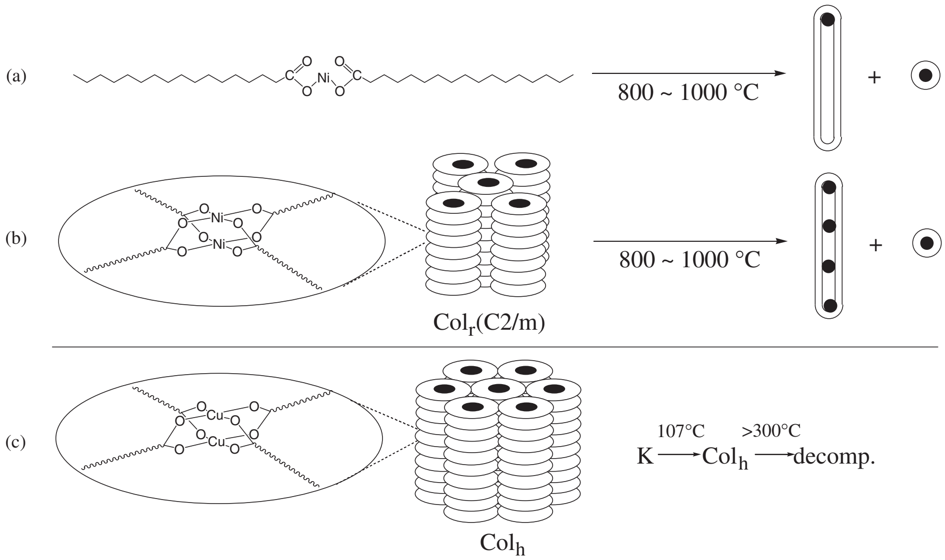

Figure 1. Proposed conversion mechanism of long chain-substituted organic transition metal complexes into CNTs containing a transition metal: (a) direct conversion mechanism from the crystalline state of nickel stearate into CNTs;[9] (b) our proposed conversion mechanism from the discotic columnar liquid crystalline structure of nickel stearate into CNTs; and (c) a well-established discotic columnar liquid crystalline structure of analogous copper stearate.[10]

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that nickel stearate shows two mesophases having a columnar structure according to our expectation. As illustrated in Figure 1b, the columnar mesophase structure of nickel stearate well resembles the nickel-containing CNT structure. If the columns of nickel stearate would be calcinated without oxygen, the peripheral organic parts might carbonize and convert into CNTs using the central nickel metals as a catalyst, thus maintaining the columnar structure. Therefore, we speculated that discotic columnar liquid crystalline compounds containing a transition metal[11] might be converted into CNTs.

In this study, we used a domestic microwave oven and a commercially available small microwave furnace from Art Box™[12] instead of an energy-consuming electric furnace. As shown in Figure 2, the Art Box was set in the domestic microwave oven and inert nitrogen gas was pumped through the Art Box. The inside of the Art Box is coated with silicon carbide and can be heated by microwave irradiation. The temperature can be controlled by an attached thermocouple by the a microwave radiation time and power controller.[13] An example of a small muffle furnace (Yamato FP300), which has a cavity almost the same size as a domestic microwave oven, is also used. The electric power consumption (P) of this muffle furnace is $P = 100\,\mathrm{V} \times 26\,\mathrm{A} = 2600\,\mathrm{W}$. On the other hand, that of the Zojirushi microwave oven (ES-HA196) used in this study was 1160 W and the maximum microwave output was 600 W. The time to reach 800 °C is more than 60 min. for the muffle furnace, whereas it is only 5 min. for the Art Box in the microwave oven. From the viewpoint of energy consumption, this microwave heating is a considerably less energy-consuming method in comparison to the conventional furnace heating.

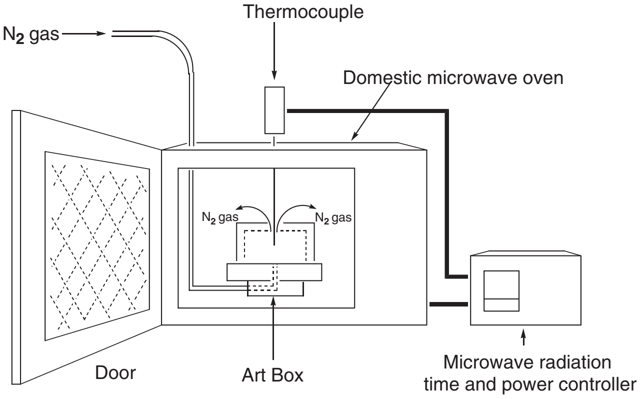


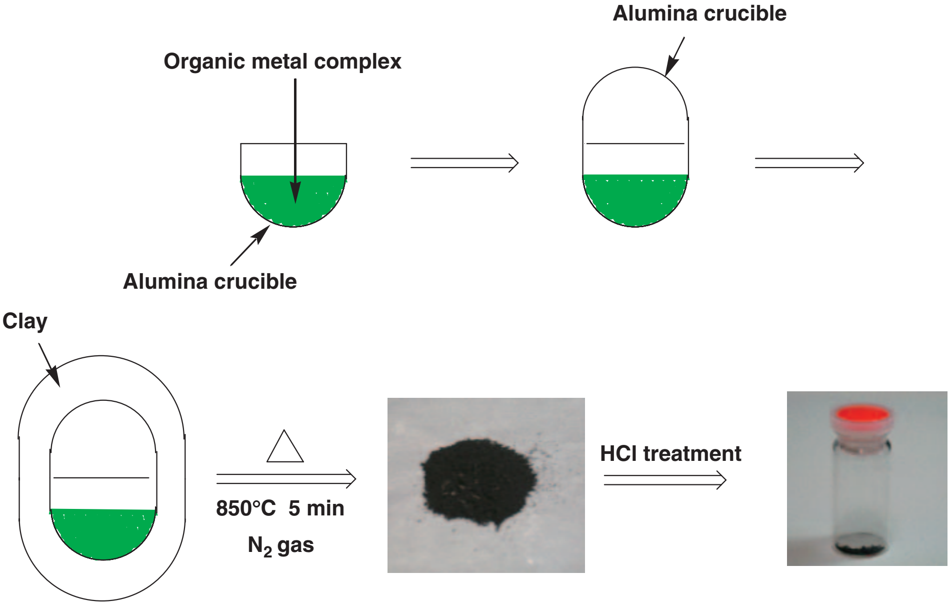
Figure 2. Our handmade apparatus using a domestic microwave oven and an Art Box™.

Until now, there have been several reports on the synthesis of CNTs using microwave radiation.[14–17] Some methods adopted microwave plasma chemical deposition using flammable methane gas or acetylene gas.[14,15] They required expensive gas controllers to precisely regulate the flows of the flammable gases. Kuo and his co-workers used a susceptor to absorb the microwaves and self-generate the heat for growth of the CNTs from flowing methanol on a Si substrate.[16] For this method, no external heating is required, but the choice of susceptors is very critical. Kharissova developed a highly efficient one-step technique to synthesize long and aligned CNTs with or without Fe filling by microwave irradiation heating from a ferrocene.[17] In this study, we developed novel methods without using a flammable gas or an expensive gas controller.

In this paper, we wish to report the development of two facile synthetic methods of carbon nanotubes using a domestic microwave oven. This enabled us to selectively synthesize the magnetic nickel-containing CNTs and non-magnetic nickel-free CNTs.

Results and Discussion

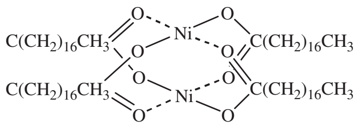
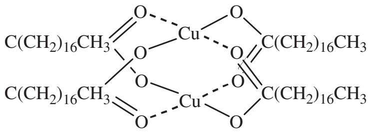
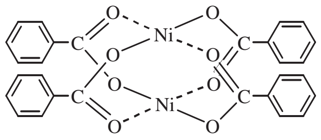
Metal Complex Method. We first developed a novel CNT synthetic procedure using the metal complex method. As illustrated in Scheme 1, an organic transition metal complex was poured into an alumina crucible which was capped by another alumina crucible. The combined crucibles were



Scheme 1. Novel CNT synthetic procedure developed by us: the metal complex method.

enclosed in clay to avoid burning it out in air. The reaction conditions for the synthesis of the CNTs using our microwave oven setup were as follows. The inside of the Art Box was purged with inert nitrogen gas for ten minutes before starting the microwave irradiation. The temperature of the Art Box inside was programmed to heat to 850 °C in 5 min, this temperature was then maintained for 5 min, and then it was cooled down to rt in 5 min. The crude products were treated with a hydrochloric acid aqueous solution to remove any remaining uncoated metal particles.

Table 1. Yields of Carbon Products by the Metal Complex Method[a)]

Metal complex	Yield/% After heating	Yield/% After the treatment with conc. HCl
 Nickel stearate	17.8	1.02
 Copper stearate	10.9	0
 Nickel benzoate *n*-hydrate	10.8	0.85

a) These yields were calculated as follows: Yield (%) = (weight of the product/weight of the starting metal complex) × 100.

Table 1 lists the yields of the carbon products by the metal complex method. When the metal complex was nickel stearate, the crude yield was 17.8% after heating, while the purified yield was 1.02% after treatment with the concentrated hydrochloric acid aqueous solution. In contrast to nickel stearate, copper stearate produced lustrous reddish brown metal after heating and nothing after the HCl treatment. In this case, the product may be only copper metal and totally washed away after the HCl treatment. It is attributable to the catalytic ability. Nickel has the catalytic ability to produce carbon nanotubes, whereas copper has no catalytic ability.[1] Therefore, copper stearate did not produce any carbon products. To obtain further evidence, we chose another nickel complex, nickel benzoate *n*-hydrate, as the starting material. Based on our expectation, it also gave carbon products even after the HCl treatment.

Figure 3 shows TEM images of the product from the nickel stearate. As can be seen in photographs (a)–(d), carbon nanotubes and carbon nanocapsules containing nickel metals were clearly formed. As can be seen in photographs (e)–(h), the nanotubes and nonocapsules are multi-walled. Figure 4 is TEM images of the products from the nickel benzoate *n*-hydrate. As can be seen in these photographs, nickel benzoate also gave multi-walled carbon nanotubes and nanocapsules containing nickel metal.

To certify the formation of the carbon nanotubes, we also measured the laser Raman spectra of the products from nickel stearate and the products from nickel benzoate. As can be seen

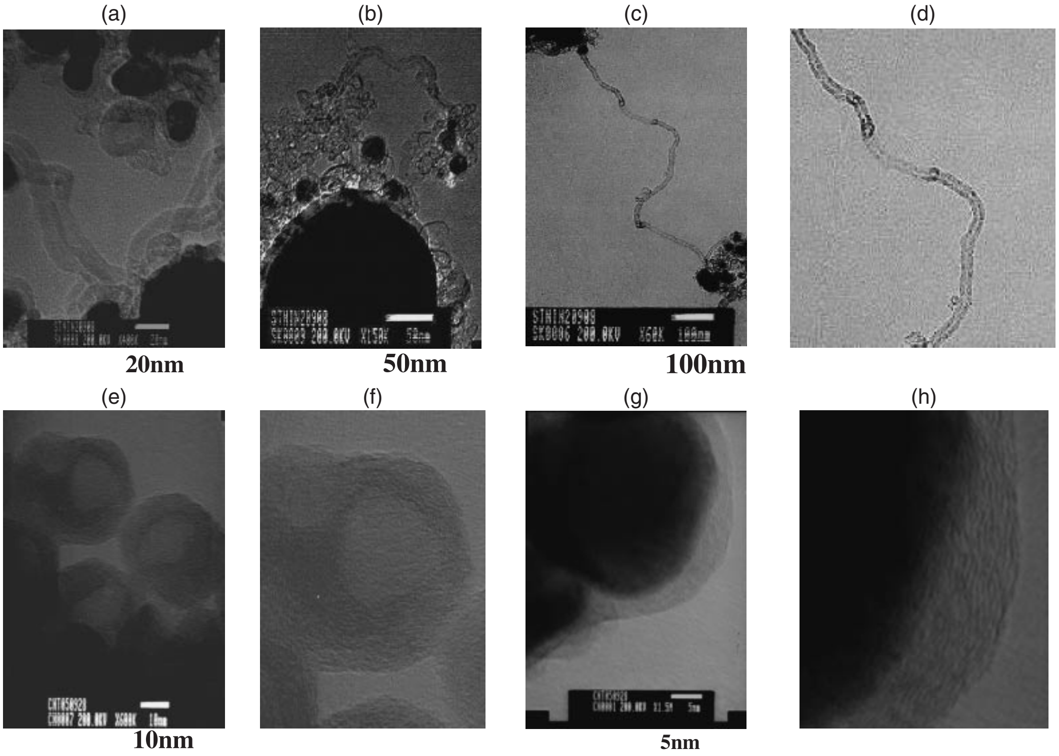


Figure 3. TEM images of the products from nickel stearate.

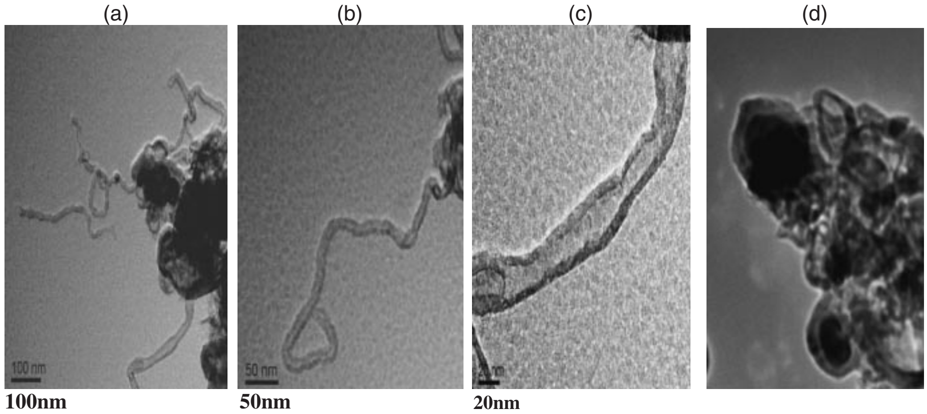


Figure 4. TEM images of the products from nickel benzoate *n*-hydrate.

from these two spectra in Figure 5, both the G and D bands could be observed. The G band is attributable to the formation of the graphene structure, and the D band originates from the defects in the graphene structure.[1] Judging from the height ratio of the D band to G band, nickel benzoate produced better quality CNTs than the nickel stearate.

Mixture Method. We postulated that even if we used a mixture of metal nickel and stearic acid, instead of the corresponding organic metal complex, nickel stearate, we could prepare carbon nanotubes. Therefore, we first mixed nickel particles and stearic acid, and put them in the bottom of the crucible, as illustrated in Figure 6a. Using this setup, we expected that the resulting carbon would be deposited onto the nickel particles. However, the resulting amorphous carbon was deposited onto the ceiling of the crucible. Therefore, nickel metal should be coated on the ceiling of the cap crucible and stearic acid should be placed in the cup crucible, as illustrated in Figure 6b. Using this setup, the resulting carbon would be deposited onto the nickel particles, and carbon nanotubes would be formed on the surface of the nickel particles.

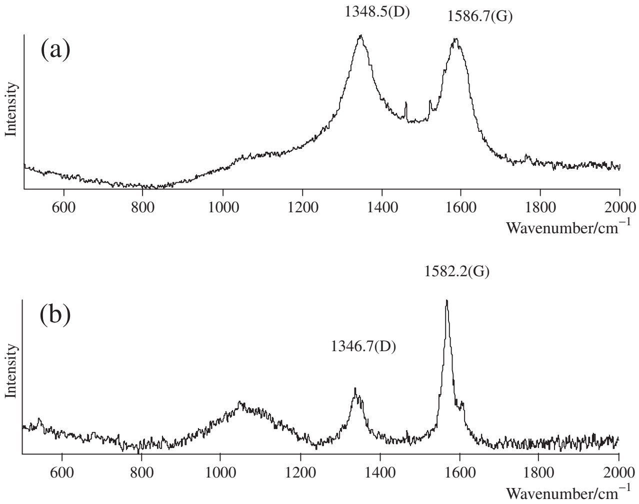


Figure 5. Laser Raman spectra: (a) the products from nickel stearate and (b) the products from nickel benzoate. The wavelength of the laser is 514 nm.

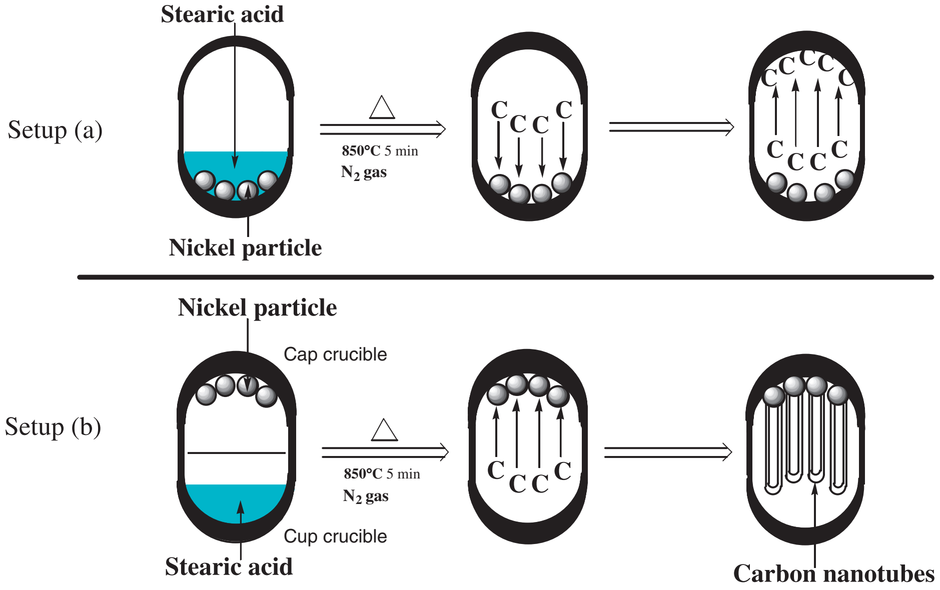
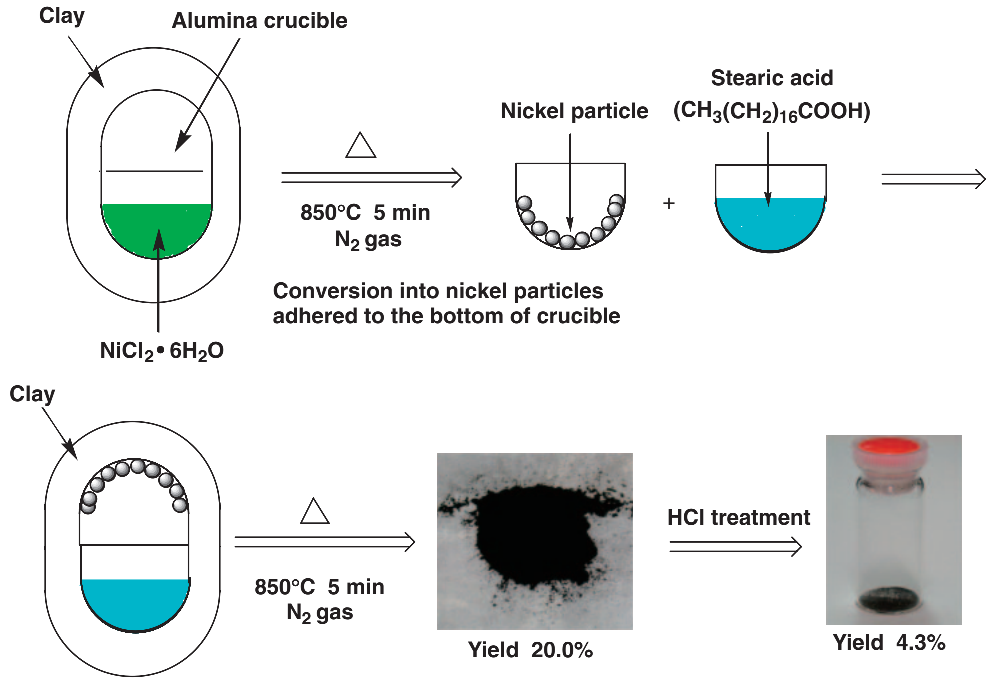


Figure 6. Illustration of setup (a) and setup (b) for the mixture method. By using setup (b), CNTs could be prepared from a mixture of nickel metal and stearic acid instead of nickel stearate.



Scheme 2. Novel CNT synthetic procedure developed by us: the mixture method.

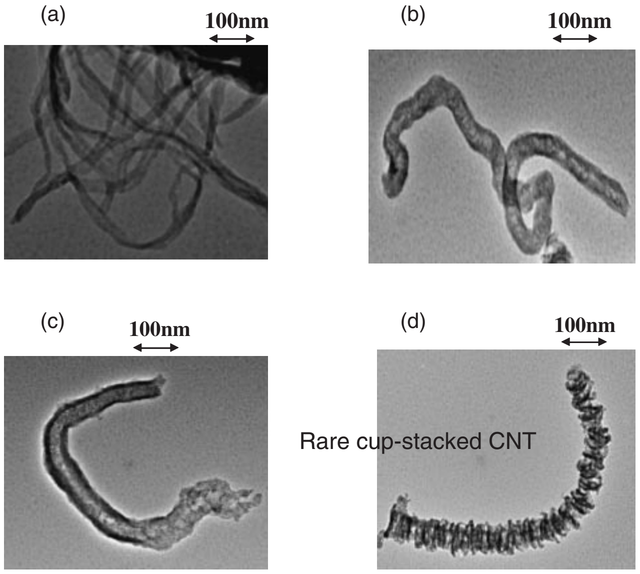


Figure 7. TEM images of the products from stearic acid in the nickel-coated crucible.

Therefore, another novel CNT synthetic mixture method was developed. As illustrated in Scheme 2, nickel dichloride hexahydrate was heated by microwaves at 850 °C for 5 min under nitrogen gas to convert it into nickel particles that adhered to the bottom of the crucible. This crucible was used a cap cover another crucible containing stearic acid. The combined crucibles were heated by microwaves at 850 °C for 5 min under nitrogen gas. The resulting black powder was purified by HCl treatment to remove the resulting unreacted nickel. The purified products were obtained in 4.3% yield.

As can be seen from TEM images (a)–(c) in Figure 7, many curled carbon nanotubes were formed. We also noticed that these nanotubes did not contain nickel metal. TEM image (d) shows a very rare cup-stacked carbon nanotube. As shown in Figure 8, the laser Raman spectrum of the product certified the formation of the defective carbon nanotubes. In comparison with the Raman spectrum of the product made by the mixture method from stearic acid and metal nickel in Figure 8 and the Raman spectrum of the product made by the metal complex method from nickel stearate in Figure 5, both D bands are almost equal in size. Hence, the quality of the CNTs may be equally low for both methods. On the other hand, the CNTs synthesized by the metal complex method from nickel benzoate gave a relatively small D band, which shows a higher quality than those of the products from stearic acid/metal nickel and the products from nickel stearate. Therefore, the influence of the starting material on the CNT quality may be more crucial than the influence of the method on the quality.

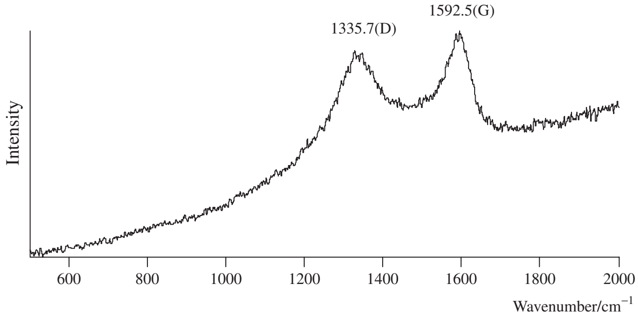


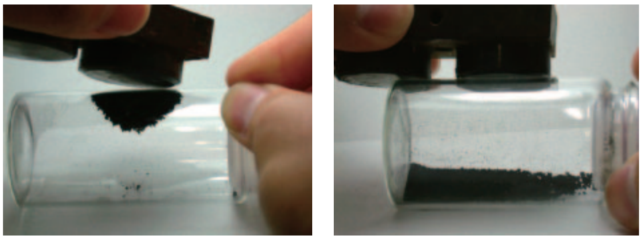
Figure 8. Laser Raman spectrum of the product from stearic acid and metal nickel confirmed the formation of defective CNTs. The wavelength of the laser is 514 nm.

The photographs in Figure 9 show the magnetic properties of the products. As can be seen from photo (a), the products prepared by the metal complex method were attracted to a magnet. On the other hand, as can be seen from photo (b), the products prepared by the mixture method were not attracted to the magnet. Thus, magnetic nickel-containing CNTs and non-magnetic nickel-free CNTs could be selectively prepared.

Figure 10 shows our proposed reaction mechanism for these two novel methods. For (a), the metal complex method, the starting material forms a columnar structure containing one-dimensional nickel stacking surrounded by alkyl chains. Therefore, the resulting CNTs contain metals in the center. For (b), the mixture method, the resulting carbon is deposited onto the surface of the nickel particles, and carbon nanotubes grow from these surface. The stopper-like nickel particles can be easily removed by the HCl treatment.

Conclusion

We could synthesize carbon nanotubes in only 5 min of heating using a domestic microwave oven and a commercially available small microwave furnace from Art Box™. Our apparatus is very cheap in comparison with conventional equipment. By using our developed metal complex method and mixture method, the magnetic nickel-containing CNTs and non-magnetic nickel-free CNTs can be selectively prepared.



(a) The metal complex method (b) The mixture method

Figure 9. Magnetic properties of the products: (a) the products by the metal complex method and (b) the products by the mixture method. Thus, the magnetic nickel-containing CNTs and the non-magnetic nickel-free CNTs could be selectively prepared.

Experimental

A Handmade Apparatus for Synthesis of CNTs. A domestic microwave oven, Zojirushi ES-HA196 (600 W), was modified by us in order to attach a thermocouple to control the temperature of the Art Box™. When the thermocouple sheath was attached to the cabinet ceiling metal plate, lightning did not occur.[13] The temperature in Art Box was monitored by the thermocouple and safely controlled by the radiation time and power controller, CHINO MODEL KP. The Art Box is a commercially available small furnace for the glass art hobby.[12] The inside can be heated to 900 °C for several minutes by microwave irradiation in a domestic microwave oven. An inert nitrogen gas flows into the Art Box through a silicon tube.

Chemicals. Nickel stearate, nickel benzoate *n*-hydrate, and copper stearate were purchased from Strem Chemicals, Soekawa Chemicals, and Wako Chemicals, respectively. They were used without further purification.

Synthesis of CNTs by Metal Complex Method. Scheme 1 illustrates the synthetic procedure for the CNTs using the metal complex method. As the starting materials, nickel stearate, copper stearate, and nickel benzoate *n*-hydrate were employed. In the alumina crucible, one of the starting transition metal complexes (1.00 g) was placed. The crucible was capped with another empty crucible and these two combined crucibles were covered with clay. After drying the clay, it was calcinated in the Art Box by microwave irradiation under a nitrogen atmosphere at 850 °C for 5 min. After cooling to room temperature, the black products were collected from the bottom crucible. The crude black products were placed in a test tube. To the test tube, about 8 mL of concentrated hydrochloric acid solution was added in order to remove the remaining nickel metal particles. The test tube was immersed in the water bath of Sharp UT-105S ultrasonic cleaner and treated by ultrasonic vibration for one hour. After an overnight stand, the black powders precipitated in the test tube bottom. The supernatant solution was then pipetted off. The precipitate was washed

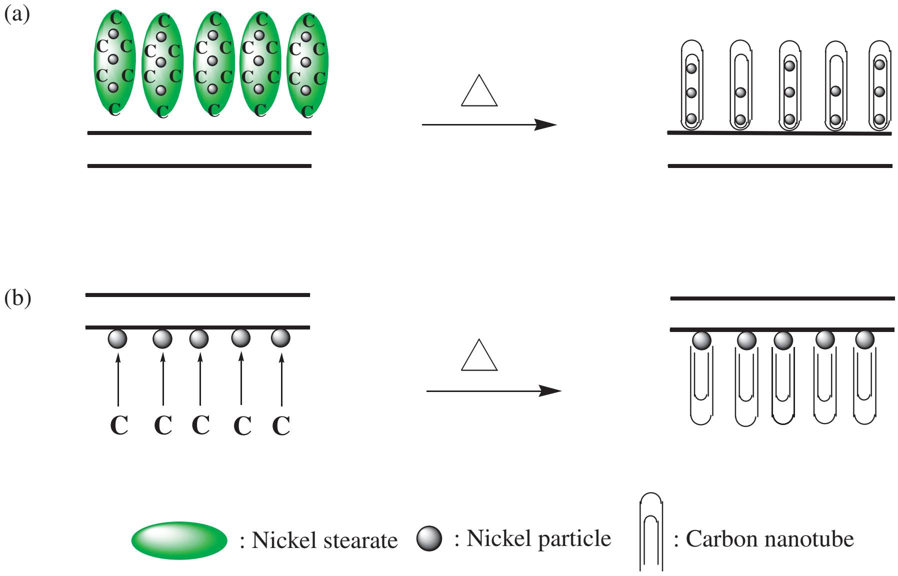


Figure 10. Our proposed mechanism of carbon products: (a) the metal complex method and (b) the mixture method.

several times by adding about 8 mL of water and pipetting off the supernatant solution until the wash water become neutral. After drying the residue, a pure black powder was obtained. Table 1 lists the yields of the carbon products by this metal complex method. Each of the percent yields was calculated as the weight of the product divided by weight of the starting metal complex.

Synthesis of Metal-Free CNTs by Mixture Method. Scheme 2 illustrates the synthetic procedure of the metal-free CNTs by the mixture method. To an alumina crucible, nickel chloride hexahydrate (3.00 g) was added. The crucible was capped with another crucible and these two combined crucibles were covered with clay. After drying the clay, it was calcinated in the Art Box by microwave irradiation under a nitrogen atmosphere at 850 °C for 5 min. The inside wall of the bottom crucible was coated with nickel metal particles. To another new alumina crucible, 4.00 g of stearic acid was added. This crucible was capped with the nickel-coated crucible, and these two combined crucibles were covered with clay, as illustrated in Scheme 1. After drying the clay, it was calcinated in the Art Box at 850 °C under a nitrogen atmosphere by microwave irradiation for 5 min. After cooling to room temperature, 0.80 g of the black crude products were collected from the top crucible. The yield was 20.0% based on the stearic acid carbon source. The crude black products were purified by the same manner described for the previous method. After drying the residue, 0.17 g of the black powders were obtained. The yield was 4.3% based on the stearic acid carbon source.

Measurements. The purified black products were observed using a transmission electron microscope (JEOL Datum JEM-2010). The laser Raman spectra were recorded by a Kaiser Optical Systems, Inc., Raman spectrometer (Hololab 5000).

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Supporting Information

Table S1 lists phase transition temperatures and enthalpy changes of nickel stearate. Figure S1 shows small-angle X-ray diffraction patterns of two liquid crystalline phases of nickel stearate. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

References

1 Y. Saito, *Introductory Materials Science for Carbon Nanotubes*, Corona-Sha, Tokyo, **2005**.

2 S. Iijima, *Nature* **1991**, *354*, 56.

3 S. A. Majetich, J. O. Artman, M. E. McHenry, N. T. Nuhfer, S. W. Staley, *Phys. Rev. B* **1993**, *48*, 16845.

4 T. Hayashi, S. Hirono, M. Tomita, S. Umemura, *Nature* **1996**, *381*, 772.

5 P. J. F. Harris, S. C. Tsang, *Chem. Phys. Lett.* **1998**, *293*, 53.

6 A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer, R. E. Smalley, *Science* **1996**, *273*, 483.

7 M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, H. W. Kroto, *J. Phys. Chem. Solids* **1993**, *54*, 1841.

8 B. H. Liu, J. Ding, Z. Y. Zhong, Z. L. Dong, T. White, J. Y. Lin, *Chem. Phys. Lett.* **2002**, *358*, 96.

9 J. Geng, D. Jefferson, B. F. G. Johnson, *J. Mater. Chem.* **2005**, *15*, 844.

10 A. M. Godquin-Giroud, J. C. Marchon, D. Guillon, A. Skoulios, *J. Phys., Lett.* **1984**, *45*, 681.

11 J. L. Serrano, *Metallomesogens: Synthesis, Properties, and Applications*, Vch Verlagsgesellschaft Mbh, Weinheim, **1996**.

12 The small furnace for domestic microwave oven is called as Art Box or Denshi Renji Rutsubo Ro (=Microwave Oven Crucible Furnace) in Japan.

13 K. Naitoh, T. Takizawa, T. Matsuse, *Jpn. J. Appl. Phys.* **1999**, *38*, L724.

14 M. Chen, C.-M. Chen, C.-F. Chen, *Thin Solid Films* **2002**, *420–421*, 230.

15 E. H. Hong, K.-H. Lee, S. H. Oh, C.-G. Park, *Adv. Funct. Mater.* **2003**, *13*, 961.

16 T.-F. Kuo, Z.-Y. Juang, C.-H. Tsai, Y.-M. Tsau, H.-F. Cheng, I.-N. Lin, *J. Vac. Sci. Technol., B* **2001**, *19*, 1030.

17 O. V. Kharissova, *Rev. Adv. Mater. Sci.* **2004**, *7*, 50.