

# Formation Route of Carbon Nanotubes in a Gel Matrix

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Using FTIR, XRD, XPS, SEM, TEM, and TGA methods, we describe a novel solid-state route for carbon nanotube formation. Carbon nanotubes have been synthesized at 300 °C for the first time in a gel matrix prepared by the sol–gel method. Acetylacetone (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>) was used as a solid-state carbon source and was preintroduced into a gel matrix of Co-doped Al<sub>2</sub>O<sub>3</sub> via metal-chelating. Upon heating, acetylacetonate groups (C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) anchored in the matrix were converted into carbon nanotubes while nanometer size Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> were formed. As the synthetic growth is confined within the gel space, the present method can be further developed to make 1D, 2D, and 3D carbon nanotubes by controlling the shape and dimension of a gel matrix.

## Introduction

At present, synthesis of carbon nanotubes (CNTs) is normally conducted on a vapor-to-solid interface at ca. 500–3500 °C via various vapor phase methods, such as arc discharge, laser ablation, catalytic pyrolysis, and chemical vapor deposition.<sup>1–8</sup> To explore other alternatives, solid-state synthesis needs to be considered because solid-state reactions can take place simultaneously across an entire bulk phase rather than only on a vapor–solid interface. In this regard, condensed-phase CNTs preparation had been conducted with electrolysis method by passing an electric current between carbon electrodes in molten lithium chloride.<sup>9</sup> Recently, channel materials (such as channels of alumina and of AlPO<sub>4</sub>-5 zeolite)<sup>10</sup> have been utilized as solid-state templates to grow CNTs inside the channels.

Strictly speaking, these growths should be classified again as the vapor-phase type or interfacial growths, as the source carbon (hydrocarbons or other carbon-containing compounds) is still from the vapor phase and a substrate (channel solid) is required. To search for solid-state methods (i.e., based on solid reactions rather than on solid templates), recently, we had used layered compounds of organic-anion pillared clays as precursors for solid-state preparation of CNTs.<sup>11</sup> It should be mentioned that the recent advance in sol–gel science has allowed one to tailor-make a gel matrix with great flexibility in terms of compositional, structural, and textural properties at low temperatures. The sol–gel-derived solid matrixes, which can be deliberately anchored with both organic compounds and metal additives, could be possibly utilized as a solid carbon source. It should be noted that the sol–gel-derived gel matrixes are solid solutions (i.e., amorphous mixtures), unlike the organic-anion pillared clays that are well-defined chemical compounds in the crystalline phase.<sup>11</sup>

In this paper, we describe an initial exploratory work on our synthetic concept for carbon nanotubes in a tailor-made gel matrix. Acetylacetone (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, or acacH) was used as a solid-state carbon source and was preintroduced into a gel matrix of Co-doped Al<sub>2</sub>O<sub>3</sub> via metal-chelating. At only 300 °C, acetylacetonate groups (C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>, or acac) anchored in the matrix were converted into carbon nanotubes while nanometer size Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> were formed. As the synthetic growth is confined within the gel space, the present method may be further developed in future to prepare 1D, 2D, and 3D carbon nanotubes with better controls of shape and dimension.

## Experimental Section

Figure 1 gives a schematic flowchart of the preparation method used in this work. The acetylacetone-containing xe-

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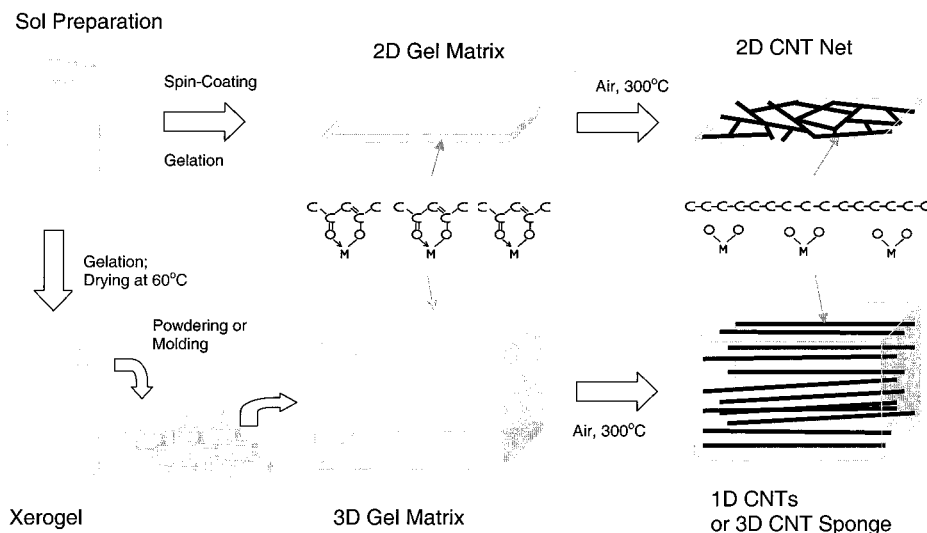
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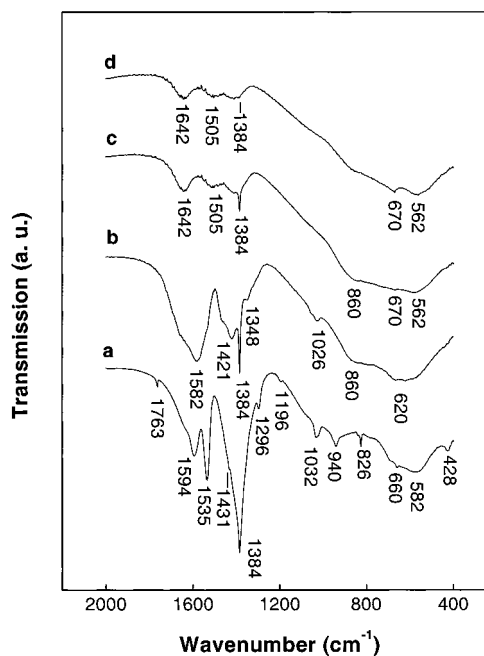


**Figure 1.** Schematic flowchart of the solid-state synthesis of carbon nanotubes (CNTs) in a gel matrix. The first oval insert indicates the acetylacetonate groups ( $C_5H_7O_2$ ) are anchored in the gel matrix, forming the metal (M)–acetylacetonate complexes (hydrogen atoms are not shown). The second oval insert shows the formation of metal oxide and CNTs after heating at 300 °C, noting that only one graphitic layer (side view) is illustrated.

rogel matrixes of Co-doped  $Al_2O_3$  were prepared by a sol–gel method similar to our previous work on the oxide systems of  $Li_2O-Nb_2O_5$  and  $CoO-CoAl_2O_4-Al_2O_3$ .<sup>12a,b</sup> The approach involved sol preparation from metal alkoxides (e.g., aluminum tri-*sec*-butoxide) and chelating agent (acacH) and introduction of secondary metals from inorganic salts (e.g.,  $Co(NO_3)_2 \cdot 6H_2O$ ).

In a typical gel-matrix synthesis, 5.1 mL of aluminum tri-*sec*-butoxide (ASB) was dissolved in 23.0 mL of 2-propanol in which 0.7 mL of acetylacetonate (acacH) was premixed under nitrogen atmosphere. The hydrolysis and the introduction of the secondary metal were then commenced simultaneously by adding a cobaltous nitrate hexahydrate solution ( $Co(NO_3)_2 \cdot 6H_2O$ ; 1.0 M, 5.2 mL) dropwise to the above acac-chelated ASB under vigorous manual stirring. The resultant viscous colloidal suspension was further stirred at room temperature for 30 min, and a full gelation occurred within 5 days. The resultant wet gel was then aged and dried at 60 °C in an oven for another 5 days. The as-prepared xerogels were ground manually into powders (1–50  $\mu m$ ; determined by SEM) and then heated at various temperatures in static air to produce carbon nanotubes. Separation of CNTs from the gel matrix was carried out in an ultrasonic water bath. Dilute nitric acid (0.1 M, 60 °C) solutions were also used to remove matrix oxides, followed by washing with deionized water and drying. Thin-film gel matrixes on glass substrates were also prepared by spin-coating (3000–5000 rpm). With dilutions of the above-prepared sol (with 2-propanol) at various concentrations, gel thin films with thickness of 100–245 nm (determined by Alpha-Step 500) had been prepared with heating. The heated film gels were separated from the glass substrates in the ultrasonic bath with deionized water or with dilute nitric acids. Other posttreatments were the same as those adopted in the powdered gels.

To understand synthetic processes, the CNTs and gel materials were further investigated with Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer, model 2000), X-ray diffraction (XRD, Shimadzu XRD-6000, Cu K $\alpha$  radiation), differential thermal analysis (DTA, Perkin-Elmer DTA-7), thermogravimetric analysis (TGA, Perkin-Elmer TGA-7), X-ray photoelectron spectroscopy (XPS, VG ESCALAB-MKII; Al K $\alpha$ , 1486.8 eV; analyzer pass energy at 20.0 eV), scanning electron microscopy (SEM, JEOL JSM-T220A), and high-resolution transmission electron microscopy (TEM, Philips FEG CM300; at 300 kV).



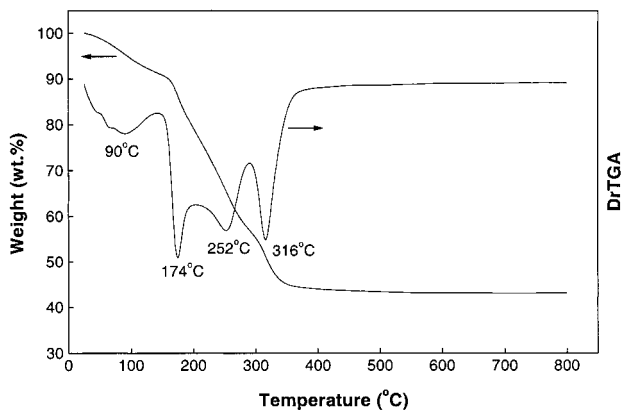
**Figure 2.** FTIR spectra for a Co– $Al_2O_3$  (weight ratio of Co:  $Al_2O_3$  = 30:100, i.e., 30 wt %) xerogel with various heat treatments in static air: (a) the as-prepared xerogel (b) heated at 200 °C for 2 h, (c) heated at 300 °C for 2 h, and (d) heated at 400 °C for 2 h. The heating rate was fixed at 5 °C/min. The absorption peaks at 1763, 1384, and 826  $cm^{-1}$  belong to nitrate ions ( $\nu_2 + \nu_5$ ,  $\nu_3$ , and  $\nu_2$  modes, respectively).

## Results and Discussion

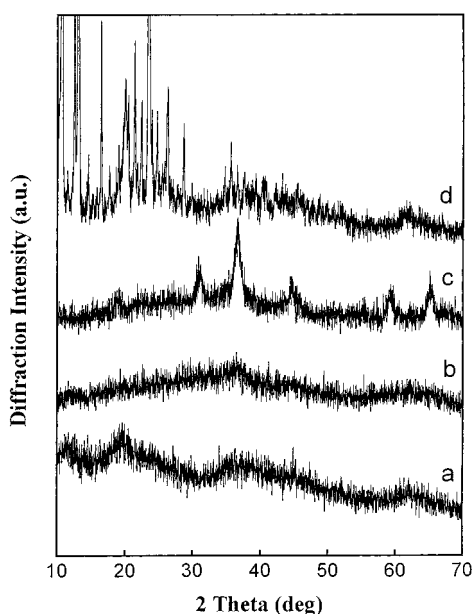
Figure 2 shows the evolution of FTIR spectra for a Co-doped  $Al_2O_3$  xerogel (weight ratio of Co: $Al_2O_3$  = 30:100) heat-treated at 200–400 °C. The presence of acetylacetonate is clearly indicated in the characteristic IR absorptions (spectrum a) of the metal–acetylacetonate complexes (1st insert, Figure 1),<sup>13</sup> noting that the peaks at 1763, 1384, and 826  $cm^{-1}$  belong to nitrate

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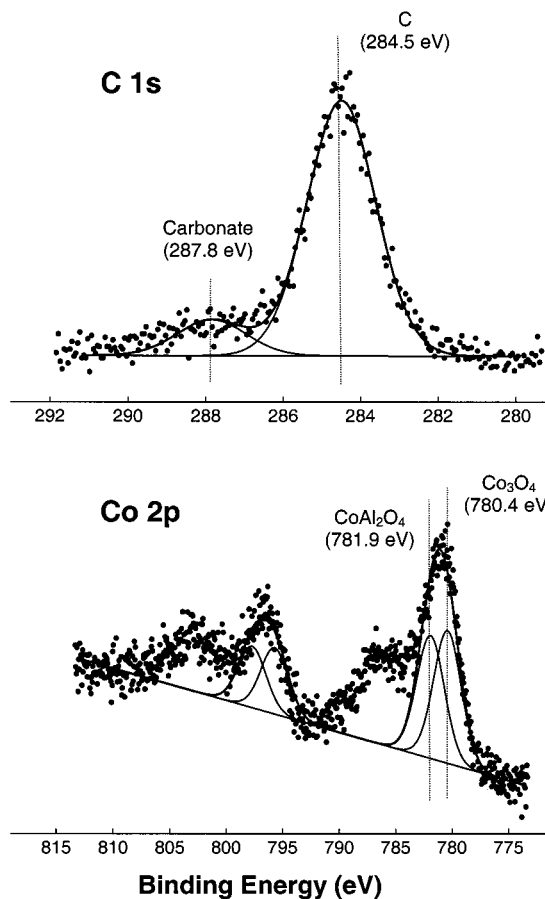
**Figure 3.** TGA scan (the weight loss and the first-order derivative (DrTGA) of weight loss with respect to temperature) in air for the as-prepared Co-Al<sub>2</sub>O<sub>3</sub> (Co:Al<sub>2</sub>O<sub>3</sub> = 30 wt %) xerogel. Heating rate: 2 °C/min.



**Figure 4.** XRD patterns for Co-Al<sub>2</sub>O<sub>3</sub> xerogel with various heat treatments in static air: (a) the as-prepared xerogel (b) heated at 300 °C for 2 h and (c) heated at 400 °C for 2 h; (d) the as-prepared xerogel *without* adding Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

anions.<sup>14</sup> When the xerogel was heated at 200 °C, the acetylacetonate (C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) groups were partially decomposed (spectrum b). At 300–400 °C (spectra c and d), acetylacetonate groups were decomposed completely (2nd insert, Figure 1) while oxide spinels of Co<sub>3</sub>O<sub>4</sub> and/or CoAl<sub>2</sub>O<sub>4</sub> were generated (more noticeable at 400 °C), as characterized by the two absorption bands at 670 and 562 cm<sup>-1</sup>.<sup>15</sup> The peak at 1642 cm<sup>-1</sup> is assigned to bending vibration of water ( $\delta_{\text{HOH}}$  mode) due to the encapsulated or adsorbed water molecules in the gel.<sup>15</sup>

In Figure 3, a representative TGA scan of Co-doped Al<sub>2</sub>O<sub>3</sub> xerogel (weight ratio of Co:Al<sub>2</sub>O<sub>3</sub> = 30:100) is shown to elucidate the thermal processes during the CNT formation. The peak at 90 °C (weight loss 8.9%) is attributed to evaporations of a small amount of water in the xerogel (also from dehydration of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O)



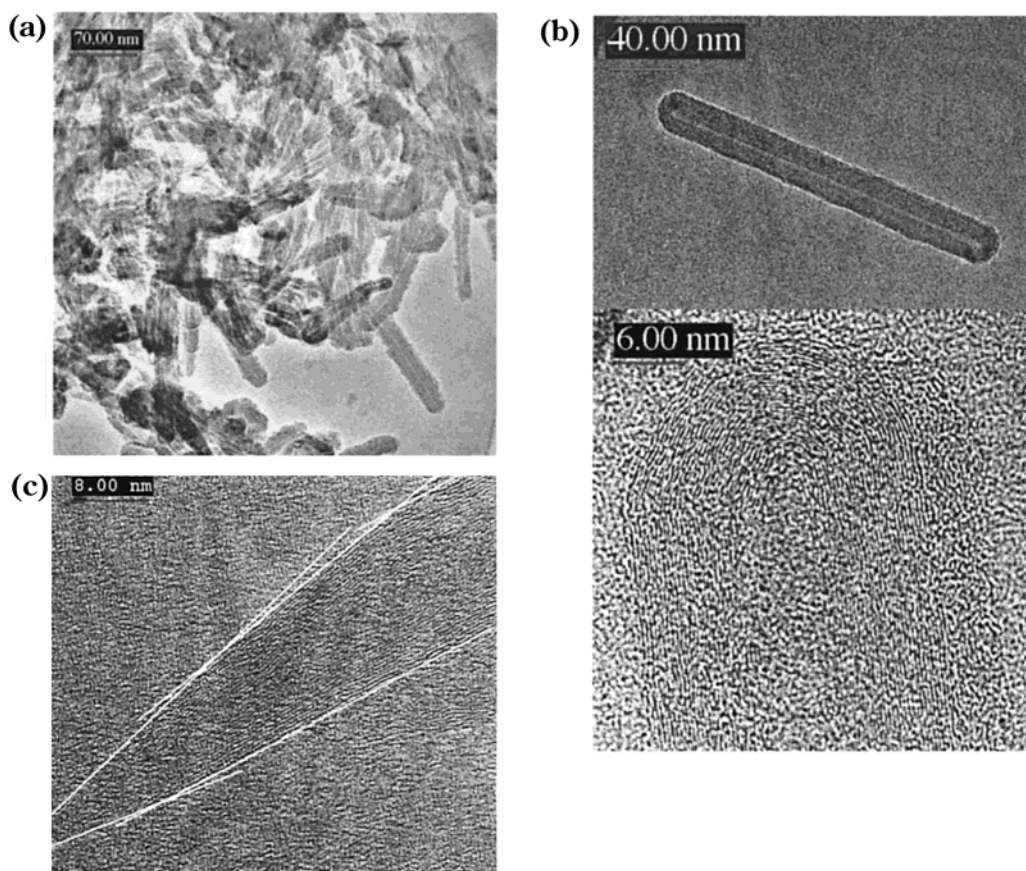
**Figure 5.** XPS spectra for the Co-Al<sub>2</sub>O<sub>3</sub> (Co:Al<sub>2</sub>O<sub>3</sub> = 30 wt %) xerogel after 2 h heating at 400 °C in laboratory air. Cobalt 2p spectrum: The Co 2p<sub>3/2</sub> peak at 781.9 eV is assigned to CoAl<sub>2</sub>O<sub>4</sub> while the peak at 780.4 eV to the Co<sub>3</sub>O<sub>4</sub>. Two Co 2p<sub>1/2</sub> peaks (spin-orbit coupling) are located at 15.5 and 15.0 eV higher than their respective Co 2p<sub>3/2</sub> peaks. The undeconvoluted areas are shake-up satellites for the CoAl<sub>2</sub>O<sub>4</sub> phase. Carbon 1s spectrum: The C 1s peak at 284.5 eV is assigned to elemental carbon (graphite-like) while the peak at 287.8 eV is assigned to carbonate ions.

and of residual alcohol solvent and products from the sol-gel synthesis. After the above dehydration and solvent depletion (i.e., 8.9% as a new reference), the gel composition can be approximately described at molar ratios of Co(NO<sub>3</sub>)<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:acacH = 23:45:32 and acacH:(Co<sup>2+</sup> + Al<sup>3+</sup>) = 32:(23 + 2 × 45) = 0.28 to get a rough TGA estimation. The peak at 174 °C with weight loss of 11.3% can be assigned to the partial decomposition of the nitrate ions (from Co(NO<sub>3</sub>)<sub>2</sub>) in the solid,<sup>15</sup> as it was the only weight loss if the acacH was not added. The weight loss data is lower than the theoretical value of 21.0% if we assume final decomposed product is CoO (noting that CoO and Al<sub>2</sub>O<sub>3</sub> can further form CoAl<sub>2</sub>O<sub>4</sub> that causes no weight difference). The third weight loss (peaked at 252 °C; 22.9% in this case) is generally long-lasting and proportional to the contents of acacH and cobalt cations added to the matrixes. It can thus be attributed to the catalytic cracking of the anchored C<sub>5</sub>H<sub>7</sub>O<sub>2</sub> that produces solid carbonaceous species and gaseous hydrogen. The small loss of 13.5% (peaked at 316 °C and up to 400 °C) is always with a sharp turn, which can be assigned to the loss of H<sub>2</sub> generated from some CH<sub>x</sub> species during their conversion to nanocarbons. In good agreement with this assignment, a large

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**Figure 6.** TEM images for the straight carbon nanotubes (1D) formed from the Co–Al<sub>2</sub>O<sub>3</sub> (Co:Al<sub>2</sub>O<sub>3</sub> = 30 wt %) xerogel: (a) general overview of the CNTs synthesized at 400 °C (2 h) in laboratory air; (b) high-resolution TEM image of a half of a fullerene-capped CNT synthesized at 300 °C (2 h) in laboratory air; (c) tube closure with an angle of 19.2° (prepared by thin film method). The specimen for TEM imaging was prepared by suspending 1 mg of the heated gel powder with deionized water and sonicating in an ultrasonic bath for 30 min.

exothermic peak is observed at this temperature by DTA, which corresponds to the formation of CNTs (TEM results) that will be reported shortly. The sum of above experimental weight losses (11.3% + 22.9% + 13.5% = 47.7%) is close to a theoretical value of 47.2% assuming all acacH were combusted to CO<sub>2</sub> and H<sub>2</sub>O after 400 °C. Nonetheless, these weight loss data should not be over addressed, because the dynamical heating (2 °C/min) used in TGA is different from the constant-temperature heating adopted in our actual synthesis. For example, CNTs could also be obtained after 2 h heating at 300 °C, noting the weight loss at this temperature (44.0% – 8.9% = 35.1%, Figure 3) is then much lower than the theoretical maximum 47.2%. Furthermore, the reference point at 8.9% is not sufficiently high to represent a *dry* mixture of Co(NO<sub>3</sub>)<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and acacH, since Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and alumina xerogel are not necessarily dehydrated at this temperature range. In fact, aluminum oxide hydroxides (Al<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O, 0 < x < 1; γ-Al<sub>2</sub>O<sub>3</sub>) can only be formed at 400 °C and the truly “dried” Al<sub>2</sub>O<sub>3</sub> (or corundum α-Al<sub>2</sub>O<sub>3</sub>) at 1000 °C using the similar precursor system.<sup>12c</sup> Therefore, the above weight estimation indicates that there are some carbons retained in the matrixes after heat treatments.

The XRD investigation reported in Figure 4 reveals that the as-prepared xerogel remained its amorphous state prior to the formation of the spinel phases at 300–400 °C (pattern a).<sup>16</sup> Without addition of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O

to the gel synthesis, aluminum tri-*sec*-butoxide (ASB) would react with acacH and form an Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> phase which could be detected by XRD (pattern d).<sup>16</sup> The observed amorphous state thus suggests that the added Co<sup>2+</sup> also competed with Al<sup>3+</sup> for the acacH to form Co-(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> in the gel, noting that the molar ratio of acacH to total metals (Co<sup>2+</sup> + Al<sup>3+</sup>) was only 0.28 in the sample. Similar to the FTIR results, XRD intensities of the spinel phase are generally weak and broad (patterns b and c), which indicates that only nanometer-sized crystallites were formed in the gel matrix (confirmed with TEM). Since the XRD patterns of Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> are very similar,<sup>16</sup> the XPS method was further employed. In Figure 5, the peak at 781.9 eV in Co 2p is assigned to CoAl<sub>2</sub>O<sub>4</sub> phase while the peak at 780.4 eV was assigned to Co<sub>3</sub>O<sub>4</sub>.<sup>17</sup> The assignment for CoAl<sub>2</sub>O<sub>4</sub> is further supported with the strong shake-up satellite peaks (undeconvoluted) observed at about 6 eV higher than their respective main peaks.<sup>17</sup> The C 1s spectrum shows a huge carbonaceous peak at 284.5 eV (graphitic; i.e., formation of CNTs) and a small carbonate ion peak at 287.8 eV due to atmospheric adsorption of CO<sub>2</sub>.

In addition to the above analyses, our TEM investigation shows simultaneous formations of the nanometer-size metal catalysts (Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub>) and multi-

(16) Joint Committee on Powder Diffraction Standards; International Centre for Diffraction Data: Swarthmore, PA; CoAl<sub>2</sub>O<sub>4</sub> (No. 44–0160), Co<sub>3</sub>O<sub>4</sub> (No. 09–418), Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> (No. 22–1537).

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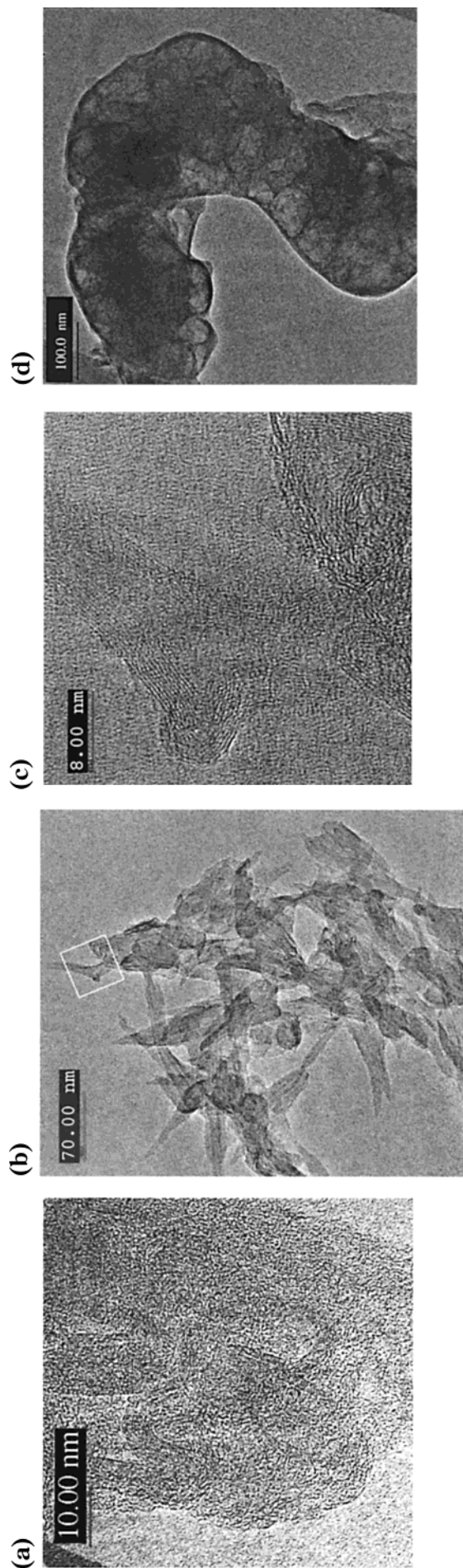
walled CNTs. The average particle size of the metal oxides is  $<10$  nm, and the interplane distances  $d_{111}$ ,  $d_{220}$ , and  $d_{400}$  of cubic spinel phase were clearly resolved.<sup>16</sup> It should be mentioned that the presence of cobalt oxide catalysts is important to the formation of CNTs (catalytic cracking of hydrocarbons). Without these cobalt oxides,<sup>12c</sup> the CNTs and their nanocarbon derivatives are not observed under the similar studied conditions.

As can be seen in Figure 6a, CNTs were grown uniformly with a narrow hollow tubule in the center and an outer diameter of 15–25 nm. Unlike the vapor-phase growths, which normally give CNTs in the form of bundles, the CNTs obtained here are separated singularly in the solid matrixes. A cross-sectional examination of these straight nanotubes shows a stack of concentric onion rings, confirming a cylinder-wall structure ( $d_{002} = 0.34\text{--}0.37$  nm).<sup>18</sup> Because of the solid-state growth, the matrix oxide should exert certain mechanical stress on the external surface of CNTs. The separation of CNTs is thus relatively easy, as carried out in a sonicating process (Figure 6a). Figure 6b shows a straight short carbon nanotube. The tube is capped with half of a fullerene molecule in its both ends, and the wall thickness is about 8 nm. Although high aspect ratio in CNTs is generally preferred, CNTs with short tube lengths are also desirable in many cases. It has been proposed that CNTs with the length of 10–300 nm might be used as connectors and components for molecular electronic devices.<sup>19</sup> The as-prepared short, discrete CNTs (Figure 6a,b) might meet these applications. Furthermore, it is recognized that the in-situ-formed CNTs and cobalt-containing alumina matrix in fact comprise a fiber–ceramic nanocomposite system. Other CNTs with different types of closure (such as cone shape 19.2°), fullerenes, and nanopolyhedra are also observed in the heated matrix. In Figure 6c, an interesting tube closure is shown (prepared by thin film method; also see Figure 7b,c below); the tube changes from parallel wall to the cone shape at an angle of ca. 11° and then to 19.2° at the tip. It was estimated through a large number of TEM observations that the prepared CNTs have an inner diameter of 4–8 nm and an intergraphitic-layer distance ( $d_{002}$ ) of 0.34–0.37 nm. Like in other well-known techniques,<sup>2</sup> a small amount of amorphous carbon is also observed on external surfaces of CNTs that have a large number of walls (Figure 6b) while the surfaces of the CNTs with small wall number are almost quasi-free from amorphous carbon, noting that there have been several methods available for amorphous carbon removal.<sup>2</sup> However, unlike in the conventional catalytic methods, metal enclosure inside the tubes is not observed in all our TEM images.

It is important to recognize that the present preparation of CNTs is a constrained growth. Carbon nanotubes are grown inside both a composition-defined and dimension-defined solid solution (Figure 1). Within the gel, in fact, it is not surprising to see the growing CNTs

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**Figure 7.** TEM images for the CNTs formed within the Co–Al<sub>2</sub>O<sub>3</sub> (Co:Al<sub>2</sub>O<sub>3</sub> = 30 wt %) gel matrix: (a) interlinked CNTs synthesized at 300 °C (2 h) in laboratory air; (b) 2D nanotube assembly; (c) framed area of (b); (d) 3D growth according to the gel space provided: CNTs network synthesized at 400 °C (2 h) in laboratory air. The specimen for TEM imaging was prepared by suspending 1 mg of the heated gel powder with deionized water and sonicating in an ultrasonic bath for 30 min.



having a chance to meet one another and result in cross-linking (or branching). Figure 7a seems to elucidate this type of growth. These intricately linked nanotubes may find their application in the hydrogen storage that requires no particular orientation. As depicted in Figure 1, by the coating of the sol suspension onto a substrate, thin-film gel matrixes with a desired thickness can be prepared. With this film-matrix confinement, CNTs are allowed to propagate only in two dimensions. This is indicated in Figure 7b,c from our thin-film experiments that show the formation of 2D nanotube assemblies. Due to the limited film space, CNTs are indeed grown in the directions perpendicular to the surface and tube walls as thin as 8 graphitic layers have been observed. Similarly, when the sol suspension is cast into three-dimensional monoliths, networks (3D) of carbon nanotubes can be generated. In Figure 7d, the CNTs are grown according to the space that the bulk gel provided, generating a three-dimensional "sponge".

We have reported several unique features of the formation of CNTs inside gel matrixes and anticipated that the results of present investigation might lead to further development of solid-state synthesis of CNTs. On the basis of our more than 20 synthetic experiments for various Co-Al<sub>2</sub>O<sub>3</sub> (Co = 10–30 wt %) gels, the generation of CNTs in these matrixes is highly reproducible at  $\geq 300$  °C. Our recent work using other chelating agents also indicates the application potential of the present method.<sup>20</sup> However, the current work represents only an initial effort in this area. The further

design of precursor sols and posttreatment of gel matrixes remain challenging. For example, with help of micelles and other molecular templates, regularity of the CNTs in the matrixes may be improved. On the other hand, selection of reaction atmosphere (such as inert gases) and control of nucleation for the growth may help to reduce oxidation of hydrocarbons and improve growth orientation and nanotube alignment.

### Conclusions

In summary, carbon nanotubes can be prepared in the solid state from the organic functional groups or ligands that are chelated to catalytically active metal ions (such as cobalt in the present example) at low heating temperatures. Ceramic matrixes derived from sol-gel method can be used to store solid carbon source and metal catalysts for the synthesis. The resultant carbon nanotubes and oxide matrixes can be viewed together as carbon-ceramic nanocomposites. As the carbon nanomaterials are confined within the gel matrix space, the present method may be further developed to allow the formations of 1D, 2D, and 3D carbon nanotubes by controlling the shape and dimension of a gel matrix.

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