Catalyst Nucleation and Carbon Nanotube Growth from Flame-Synthesized Co-Al-O Nanopowders at Ten-Second Time Scale

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Abstract: Flame-synthesized $(\text{CoO})_x(\text{Al}_2\text{O}_3)_{1-x}$ spinel nanopowders with primary particles of ~20 nm were used to grow small diameter carbon nanotubes (CNTs). The nanopowder with $x \leq 0.35$ grew few CNTs whereas that with $x = 0.65$ grew CNTs efficiently. Low crystalline and large-diameter multi-wall CNTs grew by annealing and chemical vapor deposition (CVD) at 800 °C for ~10 min, whereas single-wall CNTs with high crystallinity (G-band to D-band intensity ratio of 20–100 by Raman spectroscopy) grew by annealing and CVD at ≥ 1000 °C for ~10 s. The excess Co in the spinel reduced and segregated to form multiple Co nanoparticles on the surface of the single primary alumina nanoparticles in ~10 s, yielding SWCNTs in ~10 s. Such flame synthesized nanopowders, reduced and activated by H_2 , provide CNTs from C_2H_2 , all in ten-second time scale, and as such are promising for practical, high-through-put production of small-diameter CNTs.

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1. Introduction

Carbon nanotubes (CNTs) are attractive one-dimensional carbon nanomaterials offering diverse properties including excellent electrical and thermal conductivities, carrier mobility, chemical and thermal stability, light-weight, mechanical flexibility and compatibility with solution processing. Utility in various applications are anticipated including transparent electrodes [1,2], flexible transistors [3], integrated circuits [4,5], electrochemical capacitors [6,7] and rechargeable batteries [8,9]. Many prototype devices have demonstrated excellent performance, however, efforts are still needed to establish methods of low cost production of highly crystalline CNTs to realize their practical and wide use in society.

Chemical vapor deposition (CVD) has been studied extensively for practical production of CNTs, in which carbon source gases are catalytically decomposed typically around 600–1200 °C. Metal nanoparticles are crucially important as templates controlling CNT diameter and as catalysts promoting CNT formation vs non-catalytic soot formation. There are two ways to employ catalysts, one is by suspending the catalyst in the gas flow [10–13] and the other is by supporting catalysts on flat substrates [14–17] or ceramic powders [18–21]. The former catalyst is used typically for ≤ 10 s due to the limited residence time of the gas flow whereas the latter catalyst is used typically for 10 min–a few hours until deactivated by carbonization [22,23], oxidation [24], and/or coarsening [22,25]. Catalysts are used for much shorter times in CNT syntheses than in conventional chemical processes such as petrochemistry (typically several months), and therefore it is crucially important to prepare good catalysts quickly via practical processes.

In this paper, we demonstrate rapid CVD growth of CNTs in ten-second time scale using flame synthesized $(\text{CoO})_x(\text{Al}_2\text{O}_3)_{1-x}$ nanopowders as supported catalysts. Fe [16,17,24] and Co [26] nanoparticles supported on AlO_x are excellent catalysts growing single- and few-wall CNTs (SWCNTs and FWCNTs) at a few $\mu\text{m/s}$. And we have developed liquid-feed

flame spray pyrolysis (LF-FSP) which provides single phase but mixed-metal oxides with primary diameter of 10–30 nm over a wide composition range for various metal oxides including the Co-Al-O system [27]. Metalloorganic precursors of Co and Al are dissolved in organic solvent, aerosolized with O₂, and combusted to produce off-stoichiometric (CoO)_x(Al₂O₃)_{1-x} nanopowders with different ratios of x by controlling the ratio of the metalloorganic precursors. We have targeted forming Co/Al₂O₃ catalysts via *in situ* reduction of the metastable nanopowders.

Our ultimate goal is to suspend the nanopowders in the gas flow and feed the gas to the reactor continuously to mass-produce CNTs. But it is not easy to study the reaction processes of gas-suspended nanopowders. In this work, as the first step, we studied such reactions at ten-second time scale fundamentally by fixing the nanopowders on Si substrates; the nanopowders are exposed to our previously developed electrical current heating method of Si substrates which enables quick heating and cooling in one-second time scale [28,29]. Such short annealing times likely suppresses coarsening of catalyst nanoparticles [22,25], a common problem for CNT production. In addition, the amount of CNTs per catalyst support can be increased because the nanopowders have the high specific surface area of 20–60 m²/g [27]. Such nanopowders would be promising as inexpensive supported catalysts for practical CNT production.

2. Experimental

2.1. Catalyst nanopowders used as supported catalysts for CNTs

(CoO)_x(Al₂O₃)_{1-x} nanopowders with different compositions were used as supported catalysts. The elemental compositions of the nanopowders were analyzed by scanning electron microscopy (SEM; Hitachi S-4800, Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS; EDAX Genesis, AMETEK, Elancourt, France). The nanopowders were

also analyzed by inductively coupled plasma (ICP)-optical emission spectroscopy (OES) (Agilent Technologies ICP-OES 5100, Hachioji, Japan) following the method explained in Supplementary data. The results are summarized in Table 1, which shows good agreement between the two methods. Hereafter, the nanopowders are named with the x value calculated from the composition by SEM-EDS using the equation: $x = \text{Co}/(\text{Co}+0.5\text{Al})$.

The as-synthesized nanopowders with $x = 0.05, 0.08, 0.35$ show blue color while that with $x = 0.65$ shows black color (Fig. 1a). From the phase diagram for the CoO and Al₂O₃ system [27], the stoichiometric source with $x = 0.50$ should yield CoAl₂O₄ spinel at the temperature of the LF-FSP method. Al-rich source with $x < 0.50$ should yield spinel unsaturated with CoO, some of which may phase-separate into spinel and Al₂O₃. Whereas Co-rich source with $x > 0.50$ should yield spinel oversaturated with CoO, some of which may phase-separate into spinel and CoO. Because the spinel, Al₂O₃, and CoO show respective colors of blue, white, and black, the Al-rich sources with $x = 0.05, 0.08$, and 0.35 should have yielded nanopowders composed of the spinel and Al₂O₃ while the Co-rich source with $x = 0.65$ should have yielded nanopowder containing CoO. Actually, CoO was detected by X-ray diffraction (XRD; SmartLab, Akishima, Japan) in addition to the spinel for the nanopowder with $x = 0.65$ (Supplementary data, Fig. S1).

Table 1 – Elemental composition of the as-synthesized nanopowders. Each nanopowder was analyzed at 8–14 points by SEM-EDS. Average and standard deviation values are shown in at%.

Sample	Co	Al	O	x by ICP-OES
$x = 0.05$	1.2 ± 1.1	46.7 ± 8.4	52.1 ± 8.8	0.041
$x = 0.08$	2.2 ± 0.9	48.9 ± 7.3	49.0 ± 8.2	0.089
$x = 0.35$	11.4 ± 2.2	42.0 ± 4.2	46.6 ± 4.8	0.34
$x = 0.65$	27.2 ± 18.4	29.6 ± 4.5	43.2 ± 15.3	0.62
$x = 0.41$	12.9 ± 5.0	36.7 ± 4.2	50.3 ± 6.8	–

2.2. Catalyst activation and CNT growth by electrical current heating at ten-second time scale

Each nanopowder (1 mg) was dispersed in C₂H₅OH (1 mL) for 1 min by using an ultrasonic bath (VS-F100, AS ONE, Osaka, Japan) (Fig. 1b). A SiO₂ (50 nm)/Si substrate (phosphor-doped, 1.2 mΩ cm, 15 × 15 mm²) was pretreated with a mixture of sulfuric acid and hydrogen peroxide (3:1 v/v) to remove contaminations and make the substrate surface hydrophilic, on which the dispersion (10 μL) was spin-coated (4000 rpm, for 20 s) (Fig 1c). The substrate was cut into three pieces of 5 × 15 mm² and fixed to the metal electrodes with screws in a quartz glass tube (inner diameter of 21 mm) (Fig. 1d). The substrate was annealed at 900–1230 °C for 10 s under ambient pressure by Joule heating of the Si substrate using a DC power supply [28,29]. The gas composition during the annealing was H₂ (12.5 vol%)/CO₂ (3.8 vol%)/Ar (83.7 vol%) and the total flow rate was 300 sccm. Then, CNTs were grown for 10 s by adding C₂H₂/Ar while keeping the temperature and the flow rate of other gases (Fig. 1e). The gas during the growth was C₂H₂ (0.5 vol%)/H₂ (10 vol%)/CO₂ (3.0 vol%)/Ar (86.5 vol%) and 375 sccm. The temperature profile measured by a radiation thermometer (Chino IR-CQI 20C, Itabashi-ku, Japan) showed that the temperature for annealing and growth was controllable at the one-second time scale.

2.3. CNT growth by conventional thermal CVD

CNTs were also grown by conventional thermal annealing and growth, each for 10 min in a horizontal quartz glass tube (inner diameter 34 mm and hot zone length of 300 mm) [22,24]. The nanopowder with $x = 0.65$ was spin coated on an Si substrate. The nanopowder was annealed at 800 or 900 °C for 10 min in H₂ (11 vol%)/CO₂ (3.4 vol%)/Ar (85.6 vol%) with a total flow rate of 440 sccm, then CNTs were grown for 10 min by adding C₂H₂/Ar while keeping the temperature and the flow rate of other gases. The gas composition during growth was C₂H₂ (0.3 vol%)/H₂ (10 vol%)/CO₂ (3.0 vol%)/Ar (86.7 vol%) at 500 sccm.

2.4. Characterization of nanopowders and CNTs

As-grown CNTs were characterized by SEM-EDS. The crystallinity was estimated by calculating the intensity ratio of the G band ($\sim 1590\text{ cm}^{-1}$) to the D band ($\sim 1350\text{ cm}^{-1}$) by micro-Raman scattering spectroscopy (HR-800, Horiba, Kyoto, Japan) excited with an Ar^+ laser (488 nm). Also, typical as-grown CNTs were shaved off together with SiO_2 using a diamond pen and characterized by transmission electron microscope (TEM; JEOL JEM-2100F, Akishima, Japan).

Fig. 1 – Materials and apparatus for CNT growth experiment. (a) Optical image (OM) of the $(\text{CoO})_x(\text{Al}_2\text{O}_3)_{1-x}$ nanopowders. (b) OM of 1 mg of the nanopowders dispersed for 1 min in 1 mL $\text{C}_2\text{H}_5\text{OH}$. (c) SEM of nanopowder ($x = 0.65$) spin-coated on SiO_2/Si substrate. (d) Schematic illustration of the apparatus for electrical current heating CVD. (e) Typical time profile of the substrate temperature during electrical current heating CVD.

3. Results and discussion

3.1. CNT growth from nanopowders at ten-second time scale by electrical current heating CVD

Fig. 2 shows SEMs and Raman spectra of the CNTs grown from the nanopowders with $x = 0.05$ – 0.65 under the standard condition of electrical current heating CVD. Most nanopowders with $x = 0.05$, 0.08 , 0.35 (the dark sub- μm -sized dots) did not grow CNTs (Fig. 2a–c), whereas CNTs grew well from the nanopowder with $x = 0.65$ (Fig. 2d). The existence of excess Co in the nanopowder with $x = 0.65$ should be responsible for its high catalytic activity for the CNT growth.

Fig. 2 – SEMs of as-grown CNTs from the nanopowders by annealing for 10 s with H_2 (10 vol%)/ CO_2 (3 vol%)/Ar and CVD for 10 s with C_2H_2 (0.5 vol%)/ H_2 (10 vol%)/ CO_2 (3 vol%)/Ar. Powder composition and temperature are indicated on the images. The nanopowders with $x =$ (a) 0.05, (b) 0.08, (c) 0.35 were inert whereas that with $x =$ (d) 0.65 was active for CNT growth.

Fig. 3 shows typical TEMs of as-synthesized nanopowder with $x = 0.65$ (without annealing and growth). The bright-field image and the histogram (Fig. 3a,b) show μm size secondary particles composed of gray-colored primary particles 20 ± 8 nm. Some black

particles can also be observed on some primary particles, showing uneven distribution and some segregation of CoO. We note that the bright field image shows the heavy element (Co) as a dark contrast. On the other hand, the dark field image and the elemental mapping results show quite similar patterns, showing that Co, O, and Al typically co-exist uniformly in the nanopowder (Fig. 3d–f). When we carefully compare the elemental mapping results of Co and Al, we can find some regions with high Co contents and low Al contents (indicated by white circles in Fig. 3e,f). Such regions possibly correspond to the segregated CoO nanoparticles found in the bright-field image (Fig. 3a) and XRD spectrum (Fig. S1). Other nanopowders were also analyzed by SEM-EDS and ICP-OES. The compositions of all samples are summarized in Table 1. Co content in the stoichiometric CoAl_2O_4 spinel is 14.3 at%, and only the nanopowder with $x = 0.65$ had excessive Co. Such excessive Co possibly segregates and forms Co nanoparticles on the spinel primary particles on annealing and catalyzes CNT growth during CVD. Co contained in the spinel primary particles at $\text{Co} < 14.3$ at% possibly does not segregate to the surface on annealing for ~ 10 s and yielded few CNTs during CVD.

Fig. 3 – TEM analysis of the as-synthesized nanopowder with $x = 0.65$ (before annealing/CVD). (a) Bright field TEM image. (b) The diameter distribution with average diameter and standard deviation of the primary particles. (c) Dark-field image and (d–f) TEM-EDS element mappings. White circles in (e) and (f) show the regions with high Co contents and low Al contents.

Next, as-grown CNTs on the nanopowder with $x = 0.65$ were observed by TEM (Fig. 4). The images show formation of SWCNTs (Fig. 4a–c), FWCNTs with diameters of 5–10 nm (Fig. 4d), and multi-wall CNTs (MWCNTs) with diameters > 10 nm (Fig. 4e). The CoO particles on the primary particles in the as-synthesized nanopowder (Fig. 3a) had diameters ≥ 10 nm, likely responsible for the MWCNT growth. We also observed multiple Co nanoparticles on a single primary nanoparticle (Fig. 4f). Excess Co contained in the

as-synthesized nanopowder (Fig. 3e,f) possibly segregated and reduced to form multiple Co nanoparticles without aggregation in 10 s (Fig. 4d) promoting growth of SWCNTs in successive 10-s CVD (Fig. 4a–c). Actually, we observed that nanoparticles (possibly CoO) segregated to the surface of the primary particles by the annealing for 10 s under pure Ar without reduction at 1000 °C (Supplementary Information, Fig. S2). Thus it is probable that the Co first segregated as CoO on primary particles and then was reduced with H₂ to form Co nanoparticles.

Fig. 4 – TEMs of CNTs grown from the nanopowder with $x = 0.65$ at ten-second time scale by current-heating CVD method (annealing for 10 s with H₂ (10 vol%)/CO₂ (3 vol%)/Ar, CVD for 10 s with C₂H₂ (0.5 vol%)/H₂ (10 vol%)/CO₂ (3 vol%)/Ar at 1170 °C). (a–c) SWCNTs, (d) FWCNTs, (e) MWCNTs, and (f) multiple Co nanoparticles on a single primary nanoparticle. White arrows in (b,c) show SWCNTs.

3.2. CNT growth from nanopowder at ten-minute time scale by conventional thermal CVD

Above we find that the nanopowder with $x = 0.65$ exhibit high catalytic activity for the

SWCNT growth with 10-s annealing and 10-s CVD by the electrical current heating method. We compare these results with conventional thermal CVD which generally takes tens of minutes. Fig. 5 shows SEMs and Raman spectra of as-grown CNTs produced by thermal annealing for 10 min followed by growth for 10 min. This conventional thermal CVD produces either wavy short CNTs or large-diameter, long CNTs at 800 °C (Fig. 5a), which show Raman spectra with large D- and broad G-band peaks without any radial breathing mode (RBM) peak, showing MWCNTs of low crystallinity (Fig. 5c). Whereas it produces longer and straighter CNTs at 900 °C (Fig. 5b), which showed Raman spectra with small D- and sharp G-band peaks with some RBM peaks (Fig. 5c). The TEM shows many MWCNTs with a few SWCNTs (Fig. 5d). These results show that the $(\text{CoO})_x(\text{Al}_2\text{O}_3)_{1-x}$ nanopowder with $x = 0.65$ can yield CNTs including some SWCNTs (by conventional CVD) in 10 min at 900 °C, and CNTs with SWCNTs (by pulse-current heating CVD) in much shorter time of 10 s at 1000 °C or above.

Fig. 5 – (a,b) SEMs, (c) Raman spectra, and (d) a TEM of as-grown CNTs by conventional thermal CVD ($x = 0.65$, annealing for 10 min with H₂ (10 vol%)/CO₂ (3 vol%)/Ar, CVD for 10 min with 0.5 vol% C₂H₂ (0.5 vol%)/H₂ (10 vol%)/CO₂ (3 vol%)/Ar at 800 or 900 °C). The Raman spectra were taken at three different points for each sample. The peak at 300 cm⁻¹ in (c) originates from the SiO₂ layer on Si substrates. The white arrows in (d) indicate SWCNTs.

3.3. Optimization of growth conditions

From the results described above, short-time annealing of ~10 s followed by CVD was found effective for SWCNT growth from flame synthesized nanopowders. Next, growth conditions were optimized to enhance yields and CNT crystallinity using the nanopowder with $x = 0.65$, which showed the highest catalytic activity.

Fig. 6 shows SEMs of CNTs grown under different H₂ (3–20 vol%) and CO₂ (0–14 vol%) concentrations. The addition of H₂ is intended to reduce the cobalt oxide, while addition of CO₂ is intended to maintain the catalytic activity by etching carbonaceous byproducts by reaction of $C + CO_2 \rightleftharpoons 2CO$ [12]. With small amounts of H₂ (3 vol%) (Fig. 6f–i), CNTs grew well only when CO₂ was added at 3 vol% (Fig. 6g). CNTs grew better with higher H₂ content (Fig. a–e) and/or longer annealing time (Fig. 6a,b), and CNTs grew well even without CO₂ when annealed with 20 vol% H₂ for 10 s (Fig. 6a). Compared with conditions without CO₂, addition of 3 vol% CO₂ improved both the quality (G/D ratio) and quantity of CNTs regardless of H₂ content (Fig. 6b,d,g). Excess CO₂ at ≥ 10 vol% resulted in fewer CNTs with lower G/D ratio, possibly due to the etching grown CNTs and/or inhibited reduction of the Co catalysts (Fig. 6e,h,i). Because the temperature fluctuates run by run, the repeatability of the CNT growth is examined at the standard CVD condition with 10 vol% H₂ and 3 vol% CO₂ (Fig. S3). The temperature fluctuation of ≤ 50 K caused some fluctuation in CNTs, but the H₂ and CO₂ concentrations showed more significant effects on the CNT yield and I_G/I_D ratio.

Fig. 6 – SEMs of CNTs grown with H₂ and CO₂ at various concentrations and ~1100 °C ($x = 0.65$, annealing for 5–10 s with H₂/CO₂/Ar, CVD for 10 s with C₂H₂ (0.5 vol%)/H₂/CO₂/Ar). H₂ concentration (a,b) 20, (c–e) 10, and (f–i) 3 vol% and CO₂ concentration (a,c,f) 0, (b,d,g) 3, (e,h) 10, and (i) 14 vol%. Actual temperature and G/D ratio of resulting CNTs are shown for each image. Raman spectra were taken at three different points for each sample.

Next, the annealing and growth temperatures were varied widely from 900 to 1230 °C under the standard gas conditions. Fig. 7 shows SEMs and the Raman spectra of grown CNTs. The SEMs show large amounts of CNTs covering the entire substrate at a low temperature of 900 °C. Also, 100 µm long CNT bundles grew from some parts of the nanopowders (Fig. S4). However, Raman spectra had I_G/I_D ratios as low as 0.69 without any RBM peaks, showing the growth of large-diameter MWCNTs. As the temperature increases, CNTs grew with higher crystallinity. The split G-band peak with the presence of RBM peaks show the growth of SWCNTs at ≥ 1000 °C. Especially, CNTs with high crystallinity (I_G/I_D ratio > 100 , e in Fig. 7g) were obtained at 1160 °C. However the amount of CNTs decreased at higher temperatures. The catalysts coarsen faster at higher temperature [22], possibly resulting in fewer catalyst particles of suitable size and thus fewer CNTs. The RBM peaks appear at various wavenumbers between 120 and 200 cm⁻¹ depending on the measurement positions, showing the broad diameter distribution of SWCNTs.

Fig. 7 – (a–f) SEMs and (g) Raman spectra of CNTs grown at different temperatures ($x = 0.65$, annealing for 10 s with H_2 (12.5 vol%)/ CO_2 (3.8 vol%)/Ar, CVD for 10 s with C_2H_2 (0.5 vol%)/ H_2 (10 vol%)/ CO_2 (3 vol%)/Ar). Raman spectra were taken at 3 positions for each sample and one of them was shown in (g) with I_G/I_D range.

Next, we investigated the effect of annealing time (from 0 to 60 s) on the CNT growth (Fig. 8). Few CNTs were observed without annealing (Fig. 8a), showing that any Co must be reduced prior to exposure to C_2H_2 to grow CNTs efficiently. Whereas CNTs grew much better with the annealing for ≥ 2 s, showing the Co reduction was rapid, require just a few seconds. SEMs and Raman spectra are similar with annealing times between 2–60 s. The segregated Co nanoparticles proved to be rather stable, for ~ 1 min at 1100 °C and ~ 10 min at 900 °C (Fig. 5b).

Fig. 8 – (a–e) SEMs and (f) Raman spectra of CNTs grown with different annealing time (shown as inset) ($x = 0.65$, annealing for 0–60 s with H_2 (12.5 vol%)/ CO_2 (3.8 vol%)/Ar at 1100 °C, CVD for 10 s with C_2H_2 (0.5 vol%)/ H_2 (10 vol%)/ CO_2 (3 vol%)/Ar at 1100 °C). Raman spectra were taken at 3 positions for each sample and one of them was shown in (f) with I_G/I_D range.

Finally, we tried to grow CNTs with small diameters by using a nanopowder with a lower CoO content ($x = 0.41$) than the standard one ($x = 0.65$). Fig. 9 shows the SEMs and the Raman spectra of CNTs grown with different annealing time from 10 to 60 s. CNTs did not grow with annealing for 10 s, while CNTs grew well with annealing for 20 s. The different time needed to activate nanopowders (2 s for $x = 0.65$ vs 20 s for $x = 0.41$) should have been caused by the different Co content (see Table 1) and the existence/absence of CoO in the as-synthesized nanopowders (Fig. S1). It has been known that only particles of specific sizes work well to grow CNTs and there is a gap in particle sizes between catalysts for SWCNTs and MWCNTs [31]. Annealing for 60 s resulted in very high G/D ratio, but fewer CNTs

without RBM peaks, suggesting narrower window for CNT growth with $x = 0.41$ than $x = 0.65$. Therefore, the annealing condition has to be carefully optimized for different starting nanopowders to nucleate properly sized Co particles for small-diameter CNTs.

4. Conclusions

CNTs with small and moderate I_G/I_D ratios grew at 800 and 900 °C, respectively, by a conventional thermal CVD process with annealing and CVD in ten-minute time scale. Whereas highly crystalline CNTs including SWCNTs with I_G/I_D ratio of 20–100 grew from the nanopowder by annealing and CVD in ten-second time scale at ≥ 1000 °C. Multiple Co particles with proper size for SWCNTs formed on single primary particles of the nanopowder in such a short time. H_2 addition at 3–20 vol% and CO_2 addition at 3 vol% to the CVD gas promoted the growth of SWCNTs with high crystallinity. The Co-Al-O supported catalyst rapidly synthesized by flame, rapidly reduced and activated by H_2 , and growing CNTs from C_2H_2 , all in ten-second time scale, is promising for practical, high-through-put production of small-diameter CNTs.

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