Morphology and chemical state of Co-Mo catalysts for growth of single-walled carbon nanotubes vertically aligned on quartz substrates

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ABSTRACT

Bimetallic catalysts (Co:Mo ≈ 2 in atomic ratio) were prepared on quartz substrates from metal acetate solutions using a procedure of dip coating, followed by calcination and reduction. High-purity single-walled carbon nanotubes (SWNTs) 1–2 nm in diameter were grown densely (1.5×10^17 m^-2) and vertically on these substrates during an alcohol catalytic chemical vapor deposition process. To clarify the mechanism of the high selectivity and activity of these catalysts, we studied the morphology and chemical state of the Co-Mo catalysts during their preparation using transmission electron microscopy and X-ray photoelectron spectroscopy. The results showed that the stable existence of well-dispersed (~1.3×10^17 m^-2) nano-sized (1–2 nm) catalyst particles composed of Co molybdates and metallic Co plays an important role in the SWNT growth. Based on these results, we propose a model to understand the good dispersion and high stability of these nano-sized catalyst particles against agglomeration during calcination and reduction.

Keywords: Co; Mo; Molybdate; Quartz; Single-walled carbon nanotubes; Catalytic chemical vapor deposition; Raman; XPS; TEM
1. Introduction

Single-walled carbon nanotubes [1] (SWNTs) exhibit superior chemical reactivity, electrical conductivity, optical activity, and mechanical property [2]. In contrast to arc discharge [3] and laser ablation [4] methods, catalytic chemical vapor deposition (CCVD) can produce large-scale SWNTs at low cost [5, 6]. Bimetallic Co-Mo catalysts, which have been studied for decades due to their high activity in hydrodesulfurization [7, 8], attract much attention owing to their high selectivity [9-12] for the SWNT growth. Especially, Co-Mo catalysts prepared from metal acetate solutions followed by an alcohol CCVD process [13] can directly produce high-purity SWNTs randomly [14] or vertically aligned [15] on quartz glass substrates without supporting materials. These achievements will definitely promote the innovation of glass- and silicon-based SWNT device systems.

The mechanism of high selectivity and activity for Co-Mo catalysts in controlling the growth and structure of SWNTs has not been fully clarified yet. For catalysts with different compositions, their catalytic performances in the SWNT growth have the following order: Co-Mo acetates > Co acetates >> Co (nitrides)-Mo (acetates) >> Mo acetates [16]. Although it is suggested that at an optimum Co/Mo ratio, Co molybdate upperlayers stabilize Co species during reduction, and Mo carbides release active carbon to catalytic metallic Co particles from which SWNTs selectively grow during the CVD reaction [17-19], the correlation between the morphology and the chemical state of Co-Mo catalysts during their preparation and activation has never been verified.
The effect of Mo in bimetallic catalysts on the growth of SWNTs still remains to be clarified.

In this study, to resolve these questions, we prepared Co-Mo catalysts on quartz substrates from metal acetate solutions using a procedure of dip coating, followed by calcination and reduction, instead of using single crystals or porous materials as catalyst support. This permits us to quantitatively characterize the catalyst morphology at the nanoscale using transmission electron microscopy (TEM), and the chemical state of metal species using X-ray photoelectron spectroscopy (XPS). Based on critical evidence discovered in our experiment, a model was then developed to understand why Co-Mo catalysts prepared with the above method show high selectivity and activity for the growth of high-purity SWNTs densely and vertically aligned on quartz substrates during the alcohol CCVD process.

2. Experimental

2.1 Catalyst preparation and SWNT growth

Co-Mo catalysts were prepared on fused quartz glass substrates using a procedure of dip coating, followed by calcination and reduction [14]. Firstly, as-delivered quartz substrates (25×25×0.5 mm³) were baked in air at 500 °C for 5 min in an electric furnace just before the supporting process. Then, Co acetate (CH₃COOH)₂Co-4H₂O and Mo acetate (CH₃COOH)₂Mo (Co:Mo = 0.01%:0.01% in metal weight, and = 1.6:1 in atomic ratio) in ethanol solution were dip-coated onto these substrates at a withdrawal speed of 4 cm min⁻¹. Assuming that the liquid film had a thickness of ~50 µm, metal catalyst
layers ~1 nm in thickness, i.e., a few monolayers (MLs), were formed on the substrate surfaces, calculated from the concentrations of metal acetate solutions and the bulk densities of metallic Co and Mo. After drying in air at room temperature (r.t.), the substrates were calcined in an open furnace at 400 °C for 5 min. These substrates are referred to as calcined catalysts/substrates hereafter.

Then, the activation of these calcined Co-Mo catalysts was performed with a reduction process prior to the CVD reaction. These freshly calcined substrates were immediately transferred from the furnace into a tubular CVD reactor that was then evacuated to less than 2×10⁻² Torr by a rotatory pomp. They were heated from r.t. to 800 °C in 30 min in an Ar/H₂ (3% H₂) stream of 300 sccm at 300 Torr. These substrates are referred to as reduced catalysts/substrates hereafter.

Finally, the growth of SWNTs was performed with an alcohol CCVD process [15]. Immediately after reduction, ethanol vapor was supplied as a carbon source (3 Torr) mixed with an Ar/H₂ (3% H₂) stream (300 sccm, 7 Torr) at 800 °C. After reaction for 1 h, the substrates were cooled to r.t. in an Ar/H₂ stream. These products are referred to as as-grown SWNTs hereafter.

2.2 Characterization of SWNTs and catalysts

The quality and structure of the as-grown SWNTs were investigated using micro-Raman scattering and scanning electron microscopy (SEM). The Raman scattering measurements were done using a Chromex 501is spectrometer and an Andor DV401-FI CCD system equipped with a Seki Technotron STR250 optical system. The morphology of the as-grown SWNTs was observed using a Hitachi S-900 SEM.
The morphology of the calcined and reduced Co-Mo catalysts was characterized using TEM and the chemical state using XPS. To decrease the influence of oxidation and contamination during these ex-situ analyses, the samples were sealed in a plastic box filled with Ar gas as soon as they were removed from the furnace or the CVD reactor. TEM observations were done using a JEOL JEM-4000EX at 400 kV. For TEM specimens, a 10-nm SiO₂ layer was grown onto the substrates by sputter deposition to avoid structural variations occurring during TEM specimen preparation and observations. Then, TEM specimens were prepared using conventional mechanical grinding, polishing, and dimpling, followed by Ar ion milling. XPS measurements were done using a PHI 1600 X-ray photoelectron spectrometer equipped with an Mg Kα (1253.6 eV) source at 300 W. Binding energies (BEs) were referenced to the C 1s peak at 284.6 eV to compensate for the charging effect. The BE curves were fitted using a mixed Gaussian/Lorentzian curve after subtracting the background using the Shirley algorithm [20], in which spin-orbital-splitting intensities were fixed at their theoretical ratios. The surface atomic ratios of the calcined and reduced quartz substrates coated with Co-Mo catalysts were estimated from peak intensities in the XPS spectra and atomic sensitivity factors.

3. Results

3.1 Structure and morphology of as-grown SWNTs

Figure 1 shows the Raman spectra of the as-grown SWNTs on the quartz substrates measured with 488-nm excitation. The strong peak at 1590 cm⁻¹ (G-band) arises from
an in-plane oscillation of carbon atoms in the sp² graphene sheet. The weak peak at 1340 cm⁻¹ (D-band) reflects the degree of defects or dangling bonds contained in the sp² arrangement of graphene sheet. The G/D ratio as high as ~20 indicates the highly selective growth of high-purity SWNTs. Moreover, the absence of multi-walled carbon nanotubes (MWNTs) and amorphous impurities has been confirmed by previous TEM observations [15]. As indicated by the Raman spectrum of “radial breathing mode” (RBM) of these as-grown SWNTs, these SWNTs had diameters of 1–2 nm, which was estimated according to the relationship \( d = \frac{248}{\nu} \), where \( d \) (nm) is the diameter and \( \nu \) (cm⁻¹) is the Raman shift of a SWNT [21, 22].

Figure 2 shows the morphology of the as-grown SWNTs on the quartz substrates at a titled angle. The SWNTs self-assembled into bundles ~1.5 \( \mu \)m in length, and these bundles were densely and vertically aligned on the substrates. The number density of these SWNTs was estimated to be ~1.5\( \times 10^{17} \) m⁻² from the density of bundles and the number of SWNTs per bundle [15]. The average growth rate of these vertically aligned SWNTs was calculated to be 0.4 nm s⁻¹.

3.2 Morphology of calcined and reduced Co-Mo catalysts

Figure 3 shows plan-view TEM images of the calcined and reduced Co-Mo catalysts on the quartz substrates. For both samples, as shown in Figs. 3(a) and 3(d), well-dispersed nano-sized particles with diameters of 1–2 nm can be observed. Figures 3(b) and 3(e) show that the Co-Mo catalyst particles after reduction seemed to shrink to a smaller size. The decrease in particle size suggests that during reduction, these nano-sized catalyst particles might partially de-wet on the substrates, while remaining
good dispersion without agglomerating into larger ones. The number density of these uniformly distributed catalyst particles after reduction was estimated from the TEM images to be as high as $\sim 1.3 \times 10^{17} \text{ m}^{-2}$.

Selected area electron diffraction (SAED) patterns shown in the insets of Figs. 3(a) and 3(b), and high-resolution TEM (HRTEM) images shown in Figs. 3(b) and 3(e) revealed that most of the nano-sized catalyst particles were amorphous, and some of them were crystalline. As indicated in Figs. 3(c) and 3(f), these crystalline particles exhibit lattice distances of 2.13–2.38 Å, which are approximately consistent with CoO (200) lattice constant (2.13 Å), but significantly differ from those of Co (111) (2.05 Å), Co$_2$O$_4$ (311) (2.44 Å), MoO$_2$ (110, 111) (3.41 Å), MoO$_3$ (021) (3.26 Å), and CoMoO$_4$ (002, 220) (3.36 Å) lattices. Because the bimetallic acetate solutions had a Co/Mo atomic ratio of 1.6, the amount of Co species should be in excess on the substrates. Therefore, we conclude that most of those nano-sized particles, whether crystalline or amorphous, might be mainly composed of CoO. This conclusion is supported with the surface composition analysis using XPS, which is shown in the next section.

The above results indicate that Co-Mo catalysts existed as well-dispersed nano-sized particles on the quartz substrates just before the CVD reaction. This morphology should be closely associated with the subsequent growth of densely and vertically aligned SWNTs. Further analyses of chemical state of Co-Mo catalysts using XPS provide us a more clear comprehension of the mechanism why these nano-sized catalyst particles with such a high number density can be formed and stably exist without agglomeration during calcination and reduction.

3.3 Chemical state of calcined and reduced Co-Mo catalysts
Figure 4 shows BEs of C 1s, Si 2p, and O 1s levels for the calcined and reduced catalysts on the quartz substrates. As indicated in Figs. 4(b) and 4(c), the BEs of Si 2p at 103.4–103.6 eV, and O 1s at 532.3–532.5 eV agree well with quartz references (Si: 103.3–103.7 eV, O: 532.1–532.7 eV) [23, 24]. This suggests that the BE shift due to the charging effect has been corrected well with the C 1s BE as a reference. The spectra of C 1s and Si 2p indicate the absence of acetate residues (288.2–289.3 eV) [25, 26], metal carbides (282.7–283.1 eV) [27, 28], and metal silicides (99.1–99.6 eV) [29-31]. Moreover, the spectra of O 1s indicate the formation of metal oxide species (530.3–530.4 eV) [32].

Figure 5 shows BEs of Mo 3d levels for the calcined and reduced catalysts on the quartz substrates. Both spectra exhibit a pair of spin-orbit BEs at 232.4–232.5 and 235.4–235.5 eV, whereas a pair of new spin-orbit BEs appeared at 229.0 and 232.0 eV only for the reduced catalysts. The Mo 3d_{5/2} BE at 232.4–232.5 eV is attributed to Mo^{6+} in MoO_3 (232.2–233.0 eV) [17, 33-37] and/or non-stoichiometric Co molybdates, CoMoO_x (232.1–232.3 eV for stoichiometric Co molybdates where x = 4) [17, 36, 37]. The new Mo 3d_{5/2} BE at 229.1 eV is attributed to Mo^{4+} in MoO_2 (229.0–230.1 eV) [17, 33-36]. These results indicate that the decomposition of Mo acetates resulted in the formation of Mo^{6+} in MoO_3 and/or CoMoO_x, and the reduction of calcined catalysts converted Mo oxide species to MoO_y (y ≤ 2) or even metallic Mo that was not detected due to its oxidization during ex-situ XPS analyses.

Figure 6 shows BEs of Co 2p levels for the calcined and reduced Co-Mo catalysts on the quartz substrates. The reduced samples showed remarkable differences from calcined ones in two aspects. One is the appearance of a new BE at 777.8 eV, which is
attributed to metallic Co (777.8–778.5 eV) [17, 36, 38, 39]. The other is the decreased distance between the 2p_{3/2} and 2p_{1/2} spin-orbit BEs by as large as 1.6 eV, while the 2p_{1/2} BE remained almost unchanged. This should result from the change in chemical state of Co oxide species during reduction, rather than from the charging effect due to particle sizes [40] or layered structures [41] with different dielectric properties.

To clarify the above changes, we decomposed and fitted the Co 2p_{3/2} BEs, as shown in Fig. 7. The spectra for calcined and reduced catalysts are composed of two 2p_{3/2} components at 780.9–781.0 eV and 783.3–783.5 eV, and two distinct shake-up satellites at 786.9–787.0 eV and 790.2–790.6 eV. The two 2p_{3/2} BEs are attributed to Co^{2+} oxide species based on these intense shake-up satellites 6.0–6.5 eV higher than the primary spin-orbit BEs [37, 42]. The two 2p_{3/2} BEs at 780.9–781.0 eV and 783.3–783.5 eV are further assigned to Co^{2+} in CoO and Co^{2+} in CoMoO_x, respectively, due to their agreement with CoO (780.0–780.7 eV) [17, 38, 39, 43, 44] and CoMoO_4 (780.5–781.2) [36-38, 45] references. The relatively large BE deviation of Co^{2+} in CoMoO_x from Co^{2+} in CoMoO_4 might result from the polarization effect or the non-stoichiometry when Co^{2+} ions are incorporated into highly oxidized MoO_3 matrix [38, 45, 46]. The BE intensity ratio of Co^{2+} in CoMoO_x to that in CoO increased from 1.3 to 2.6 after reduction, indicating that more CoMoO_x was formed at the expense of CoO and MoO_3. This change leads to the seemingly decreased distance between Co 2p_{3/2} and 2p_{1/2} BEs shown in Fig. 6. Therefore, we conclude that the calcination of dip-coated substrates decomposed Co acetates into Co oxide species existing as CoO and CoMoO_x, and the subsequent reduction resulted in the formation of metallic Co and more CoMoO_x.

Table 1 shows the surface atomic ratios of the calcined and reduced quartz substrates coated with Co-Mo catalysts. The quantity of metals as low as less than 10% of the total
composition supports the approximate estimation in the experimental section that the quartz substrates might be covered with the metallic catalyst layers as little as a few monolayers (~1 nm). The calcined and reduced samples had Co/Mo atomic ratios of 2.1–2.3, approximately consistent with the initial ratio of 1.6 in metal acetate solutions, so that only excess Co species were observed in TEM images. It is noteworthy that the atomic ratios of Co and Mo to total elements decreased by 63% and 68% after reduction, respectively, which could be explained from the decrease in catalyst coverage, i.e., the decrease in catalyst particle size, as confirmed in TEM images.

4. Discussion

Based on the above results, we propose a model, as shown in Fig. 8, to describe the evolution in morphology and chemical state of Co-Mo catalysts on the quartz substrates during calcination and reduction. We assume that a layer of bimetallic catalysts (Co:Mo \( \approx 2 \)) a few MLs (~1 nm) in thickness is formed on the quartz substrates after the dip coating from dilute metal acetate solutions. After calcination in air at 400 °C, metal acetates are decomposed into CoO, CoMoO\(_x\) (\(x = 4\) for stoichiometric Co molybdates), and MoO\(_3\), which exist as well-dispersed nano-sized particles. After reduction in Ar/H\(_2\) up to 800 °C, existing CoMoO\(_x\) remains unchanged, whereas CoO and MoO\(_3\) are reduced into Co and MoO\(_y\) (\(y \leq 2\)), and more CoMoO\(_x\) are formed at the expense of Co and MoO\(_3\). During this process, no distinct agglomeration occurs although catalyst particles partially de-wet into smaller sized ones. Finally, the growth of SWNTs starts with the reaction of the ethanol vapor and metallic Co particles.
We deduce that when Mo and Co species uniformly coexist on SiO₂ surfaces during calcination, Mo preferentially promotes the formation of metal oxides at catalyst/SiO₂ interfaces, because Mo has a stronger affinity to oxygen than Co [47]. Because of the Co/Mo atomic ratio of ~2, the excess Co easily diffuses into MoO₃ [45], and forms CoMoOₓ underlayers/boundaries, whereas the residue Co exists as CoO particles either located on CoMoOₓ underlayers or attached to CoMoOₓ boundaries.

The formation of well-dispersed nano-sized catalyst particles during calcination is attributed mainly to the decomposition of metal acetates as little as a few MLs (~1 nm) on oxide substrates. It is suggested that the strong coordination of carboxylic groups with metal ions mediates the decomposition of metal acetates to prevent the formation of large particles [48, 49]. As a result, compared with metal nitrides, metal acetates form better dispersed nano-sized particles during calcination [48, 49], thereby accounting for their best performance for the growth of SWNTs [16].

As the temperature rises from r.t. during reduction, CoO and MoO₃ in Ar/H₂ start to be reduced into metallic Co and MoOₓ, respectively, whereas CoMoOₓ remains unchanged due to their extreme stability against reduction [50, 51]. The firstly reduced Co might diffuse into and react with residue MoO₃ or existing CoMoOₓ to further form CoMoOₓ. Then, the formation of metallic Co possibly competes with that of Co molybdates, and finally becomes dominant over the latter above a critical temperature.

The stable existence of well-dispersed nano-sized Co particles during reduction is attributed to the immobilization effect of CoMoOₓ underlayers. Although metallic Co particles vigorously migrate on SiO₂ surfaces [39], they should be easily trapped on CoMoOₓ underlayers, owing to the strong interactions between MoO₃ and metallic Co [45]. Although these Co particles de-wet partially on CoMoOₓ, their interfacial
interactions are strong enough to limit their mobility and prevent them from agglomerating into large particles. Therefore, we conclude that the role of Mo in bimetallic Co-Mo catalysts is to stabilize well-dispersed nano-sized metallic Co particles from agglomeration. Without Mo [16, 39] or CoMoO4 [19, 37], the catalyst selectivity for the growth of SWNTs decreases or even disappears due to the agglomeration of Co particles.

Generally, the growth of SWNTs requires catalyst particles with diameters less than 2–3 nm [52-55]. These well-dispersed Co particles with diameters of 1–2 nm and a number density of \(1.3 \times 10^{17} \text{ m}^{-2}\) directly confirmed in HRTEM images correlate well with the selective growth of high-purity vertically aligned SWNTs with diameters of 1–2 nm and a number density of \(1.5 \times 10^{17} \text{ m}^{-2}\). This proves convincingly the extremely high catalytic activity and efficiency of these nano-sized particles.

During the alcohol CVD reaction, because Mo is catalytically inactive at ~800 °C [16], the SWNTs might only grow from metallic Co particles. These SWNTs interact with neighboring nanotubes via van der Waals forces to self-assemble into rigid bundles. These bundles are so populated that they have to grow only upright from the substrate surfaces due to the space restriction, similar to the case of vertically aligned MWNTs [56, 57]. As the SWNTs lengthen, their growth should be limited by the diffusion of ethanol vapor through the narrow space between nanotubes/bundles, which results in a growth rate \((0.4 \text{ nm s}^{-1})\) much lower than would be typically observed \((\sim 1 \mu \text{m s}^{-1})\) [58, 59]. The continuous supply of H2 together with ethanol vapor during the CVD reaction might enable Co particles to remain highly active throughout the nucleation and growth of SWNTs. Without feeding H2 during the alcohol CCVD process, the SWNTs only grow sparsely in a random orientation [14].
This study revealed that the stable existence of well-dispersed nano-sized catalytic metal particles is indispensable for the growth of SWNTs densely and vertically aligned on the quartz substrates. In addition to that, the CCVD process with ethanol as a carbon source also plays an important role in the selective growth of high-purity SWNTs. An appropriate amount of oxygen radicals generated from the decomposition of ethanol on catalytic metal particles removes amorphous carbon impurities with dangling bonds in the growing SWNTs [60]. The combination of the Co-Mo catalysts prepared from metal acetate solutions and the alcohol CCVD process satisfies the requirement of (1) strict control of chemical state and morphology of catalyst particle and (2) in-situ purification of produced SWNTs, thereby being able to fabricate vertically aligned SWNTs with high selectivity and high purity. However, some issues on the working state of these catalysts during the CVD reaction, such as the chemical state and its contribution to the growth of SWNTs, need further investigation.

5. Conclusions

High-purity SWNTs with diameters of 1–2 nm were grown densely (~1.5×10¹⁷ m⁻²) and vertically on the quartz substrates where bimetallic Co-Mo catalysts with a stoichiometry of ~2 were dip-coated from metal acetate solutions, followed by calcination and reduction. HRTEM and XPS studies on the morphology and chemical state of the calcined and reduced catalysts provided critical evidence for their catalytic mechanism.

The results show that calcination in air at 400 °C decomposes metal acetates into metal oxide species composed of CoO, MoO₃ and CoMoOₓ (x = 4 for stoichiometric Co
molybdates), which exist as well-dispersed nano-sized particles possibly due to the mediation of strong coordination of carboxylic groups with metal ions during the acetate decomposition. The excess CoO might be either located on or attached to CoMoO$_x$ underlayers/boundaries. After reduction in Ar/H$_2$ up to 800 °C, metallic Co, MoO$_y$ ($y \leq 2$) and more CoMoO$_x$ are formed at the expense of CoO and MoO$_3$. The strong interactions between metallic Co and CoMoO$_x$ underlayers prevent these well-dispersed (~1.3×10$^{17}$ m$^{-2}$) nano-sized (1–2 nm) catalyst particles against agglomerating into larger ones.

The good dispersion of nano-sized catalyst particles due to the acetate decomposition, their stability against agglomeration due to the interactions between Co and CoMoO$_x$, their high activity due to the continuous supply of H$_2$ throughout the CVD reaction, and the in-situ purification of growing SWNTs due to the oxygen radicals generated from the ethanol decomposition lead to the highly selective growth of high-purity SWNTs densely and vertically aligned on the quartz substrates.
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Figure legends

Figure 1. Raman spectra of as-grown SWNTs on quartz substrates measured with 488-nm excitation.

Figure 2. Cross-sectional SEM image of as-grown SWNTs on quartz substrates, observed at a fracture edge at a tilted angle.

Figure 3. Plan-view TEM images of (a) calcined and (d) reduced Co-Mo catalysts on quartz substrates, and HRTEM images of (b) (c) calcined and (e) (f) reduced Co-Mo catalysts. SAED patterns are shown in the insets of (a) and (d).

Figure 4. XPS spectra of (a) C 1s, (b) Si 2p, and (c) O 1s levels for calcined and reduced Co-Mo catalysts on quartz substrates.

Figure 5. XPS spectra of Mo 3d_{5/2} and 3d_{3/2} levels for calcined and reduced Co-Mo catalysts on quartz substrates.

Figure 6. XPS spectra of Co 2p_{3/2} and 2p_{1/2} levels for calcined and reduced Co-Mo catalysts on quartz substrates.
Figure 7. XPS spectra of Co 2p\textsubscript{3/2} levels for calcined and reduced Co-Mo catalysts on quartz substrates.

Figure 8. Chemical state and morphology of Co-Mo catalysts on quartz substrates after (a) calcination and (b) reduction.
Table 1. Surface composition of quartz substrates dip-coated with Co-Mo catalysts after calcination and after reduction.

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