Growth of single-walled carbon nanotubes from size-selected catalytic metal particles.

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) were synthesized using size-controlled catalyst nanoparticles created by the pulsed laser ablation method. Specifically, the alloy particles (Co/Mo or Co/Pt) were prepared by ablation of the target alloy materials in an inert gas atmosphere. Size selection was performed using a differential mobility analyzer (DMA). The obtained nanoparticles were deposited on a quartz substrate and from which SWNTs were grown by the alcohol catalytic CVD (ACCVD) technique that was developed by the authors' group. AFM and Raman scattering analysis revealed that SWNTs were successfully synthesized. It seems the Co/Mo alloy catalyst was more effective for the synthesis of SWNTs than the Co/Pt catalyst, though this is a preliminary result to be further investigated.

Introduction

The discoveries of multi-walled carbon nanotubes (MWNTs) [1] in 1991 and single-walled

carbon nanotubes [2] in 1993 launched a new field of science and technology due to the outstanding potential of this specially elongated fullerene structure as a future material. In order to fully appreciate this fascinating carbon material, establishment of large scale, high-purity, and size-controlled synthesis of SWNTs has been strongly sought. In addition to the initial laser-furnace [3] and arc-discharge [4] techniques, the catalytic chemical vapor deposition (CCVD) approach [5-8] has been proposed for improved mass-productivity. In the CVD processes, methane [5-6], acetylene, [7] or carbon monoxide [8] are being considered as suitable precursors for synthesis of SWNTs. However, the authors' group found that alcohols (e.g. methanol, ethanol) are a rather favorable carbon source that can synthesize large amounts of high-quality SWNTs at low temperatures [9,10]. From the viewpoint of diameter control of carbon nanotubes (CNTs), size-controlled nanoparticles have sometimes been employed as catalysts. Zaretskiy et al. [11] found that the outer diameters of MWNTs were ruled by, and roughly equal to, the size of the nanoparticle. Y. Li et al. showed that the diameter of their mono-dispersed catalytic particles has a certain correlation to that of the produced SWNTs [12]. However, since most of their nanoparticles were prepared in a liquid solution using a chemical process, it is difficult to avoid impurities in the process. On the their hand, the laser ablation method in a low-pressure inert gas atmosphere is one of the novel approaches for producing very high purity nanoparticles [13]. We have previously demonstrated the synthesis of size-controlled pure silicon nanoparticles by laser ablation with a differential mobility analyzer (DMA) [14-15].

In this study, we attempted to produce SWNTs from size-selected nanoparticles formed by pulsed laser ablation using the alcohol CCVD method, expecting the diameter of the produced SWNTs to have some correlation with the nanoparticles' size. After the size selection by DMA, the bimetallic either Co/Mo or Co/Pt alloys nanoparticles were deposited on the surface of a quartz substrate before the alcohol CCVD process. The presence of SWNTs was confirmed by resonance

Raman scattering and AFM measurements.

Experiment

Details of the preparation of size-selected nanoparticles is described in our previous report [14-15]. The experimental system was composed of a laser ablation chamber, an annealing chamber, a DMA, and a deposition chamber. All of the preparation processes were preformed in an atmosphere of He gas. Nanoparticles were generated by irradiating the surface of target wafer with a focused pulsed laser beam (Spectra-Physics INDI-40, fluence 4.8J/cm^2, wavelength 532nm, 20Hz). The generated nanoparticles were removed from the laser ablation chamber with a He gas flow, and passed through a quartz glass tube heated to 800℃ by an electric furnance for a post annealing process (PAP). The PAP acted to crystallize coalescent species of primary particles, and prevent from interfering with the size-selection process of the DMA. Following the annealing process, the nanoparticles were introduced into a size classifier, a DMA. The size-selected nanoparticles (10±1nm) were ejected from the nozzle of the DMA and deposited on the quartz substrate for 5 minutes.

Figure 1 shows the schematic of our alcohol CCVD apparatus that is composed of an ethanol reservoir placed in a hot water bath, a 1m quartz tube with a 26 mm inner diameter, an electric furnace 30 cm in length, and a rotary pump to evacuate inside of the quartz tube. The sample to undergo the CVD reaction is placed in the central position of the quartz tube. Ar/H_2 (3% H_2) was flowed while heating-up the electric furnace with only the sub-drain path kept open so that the inside of the quartz tube was maintained around 300 Torr. The use of H_2 is for the purpose of pre-reduction of the catalytic metals, which would otherwise be slowly reduced by the alcohol during the CVD reaction. After the reaction temperature of 800 °C was reached, ethanol vapor was supplied from the

temperature-controlled reservoir so that the pressure measured at the entrance of the quartz tube is constant. After the CVD reaction, the ethanol vapor was stopped and the electric furnace was turned off before cooling to room temperature with a 100 sccm flow of Ar or Ar/H_2.

The synthesis of SWNTs was confirmed by micro Raman scattering spectra measured by a 488nm laser excitation. (Chromex 501is spectrometer and Andor DV401-FI CCD system with Seki Technotron STR250 optical system), as well as AFM observations (Seiko Instruments Inc., SPI3800N).

Results and Discussion

The existence of SWNTs after CVD was confirmed by analysis of resonance Raman scattering. Figure 2 shows Raman spectra of as-grown SWNTs from Co/Mo and Co/Pt alloy particles. As a comparison, Fe/Co particles were prepared in a liquid solution and supported by zeolite. The left panel is a magnification of the low-frequency regime (100 ~ 400cm^{-1}) of the spectra on the right. These Raman spectra were measured by 488nm laser excitation. The peak at 1350cm^{-1} is the “D-band” (indicated by the asterisk) and the peak at 1590cm^{-1} is the “G-band” (indicated by the arrow) of graphite. The splitting of the G-band, as shown in Fig. 2 (b) implies the existence of SWNTs [16-17]. The ratio of the D-band of the G-band (G/D ratio) represents the purity of SWNTs [18]. A higher G/D ratio indicates a higher purity of SWNTs. As the G/D ratio of SWNTs grown from Co/Mo catalyst is higher than in case of using Co/Pt catalyst, Co/Mo catalyst seems to perform better than the Co/Pt catalyst.

The radial breathing mode (RBM) peaks were observed and are shown in the left panel of Fig. 2. Here, the following correlation between the diameter *d* and the RBM Raman shift v was used for the diameter axis: $d/\mathrm{nm} = 248/(v/\mathrm{cm}^{-1})$. Although the signal to noise ratio of the Raman spectra

from Co/Mo or Co/Pt particles in Fig. 2 is not sufficiently high, it seems that the diameter distribution of SWNTs grown from Co/Mo or Co/Pt particle were narrower than that grown from Fe/Co particles supported by zeolite [9]. In particular, the peak at 203 cm^{-1}, which corresponds to SWNTs with a diameter of around 1.2 nm, were predominant. As we measured Raman spectra only by 488nm laser excitation in this study, a more detailed Raman spectroscopic study using several excitation wavelengths is necessary to discuss details of the diameter distribution of synthesized SWNTs.

In this study, we prepared size-controlled nanoparticle (10±1nm) as catalyst. However, the diameter of the synthesized SWNTs (around 1.2nm) was smaller than the size of catalyst particles. There are discussions whether or not the size of catalyst is key factor for SWNTs growth. Li et al showed that controlling the structure of the catalytic particle allows the control of nanotube diameter [19]. They pointed out that the size distribution of Fe nanoparticles and the diameter distribution of SWNTs were quite similar. On the other hand, Yoon et al synthesized SWNTs on silicon substrates using Co/Mo catalyst where the diameter of SWNTs and the size of catalyst particle were not proportional [20]. They pointed out that main effect of Mo addition to Co was the formation of small Co clusters in Co/Mo nanoparticles. Therefore, the small Co clusters act as an effective nucleation site for SWNT growth. There is a possibility that a similar phenomenon occurred during our CCVD process.

The synthesis of SWNTs on quartz substrates was also confirmed by AFM measurement. AFM images of as-grown SWNTs directly synthesized using (a) Co/Mo particles and (b) Co/Pt particles are shown in Fig. 3. The parts that look blackened in the images is due to cracks in the quartz. Bright white parts are also observed in the images, which we consider to be due to the aggregation of nano-particles during the CVD process. As our CVD process done at 800 °C, if the distribution of nanoparticle is dense, the aggregation of nanoparticles might occur. The white lines

(indicated by the arrow) are SWNTs. It is possible to determine the diameter of CNTs from height measurements[21-23]. According to height measurements, the height of these lines ranges around 3-5 nm, indicating the SWNTs are bundled. The amount of SWNTs grown from Co/Mo particles is larger than that grown from Co/Pt particles, which is consistent with Raman scattering measurements. From the preliminary experiments, the yield of SWNTs seems to strongly depend on the density of nanoparticles on the quartz substrate. High-density deposition of nanoparticles causes particle aggregation during the CCVD process; as a result the yield of SWNTs was reduced. We note that it is important to deposit nanoparticles in low density.

Conclusion

Single-walled carbon nanotubes (SWNTs) were synthesized using metal catalyst particles, whose size (10±1nm) was selected by DMA. The synthesis of SWNTs was confirmed by analysis of resonance Raman scattering and AFM observations. The Co/Mo catalyst was more effective than the Co/Pt catalyst for synthesis of SWNTs.

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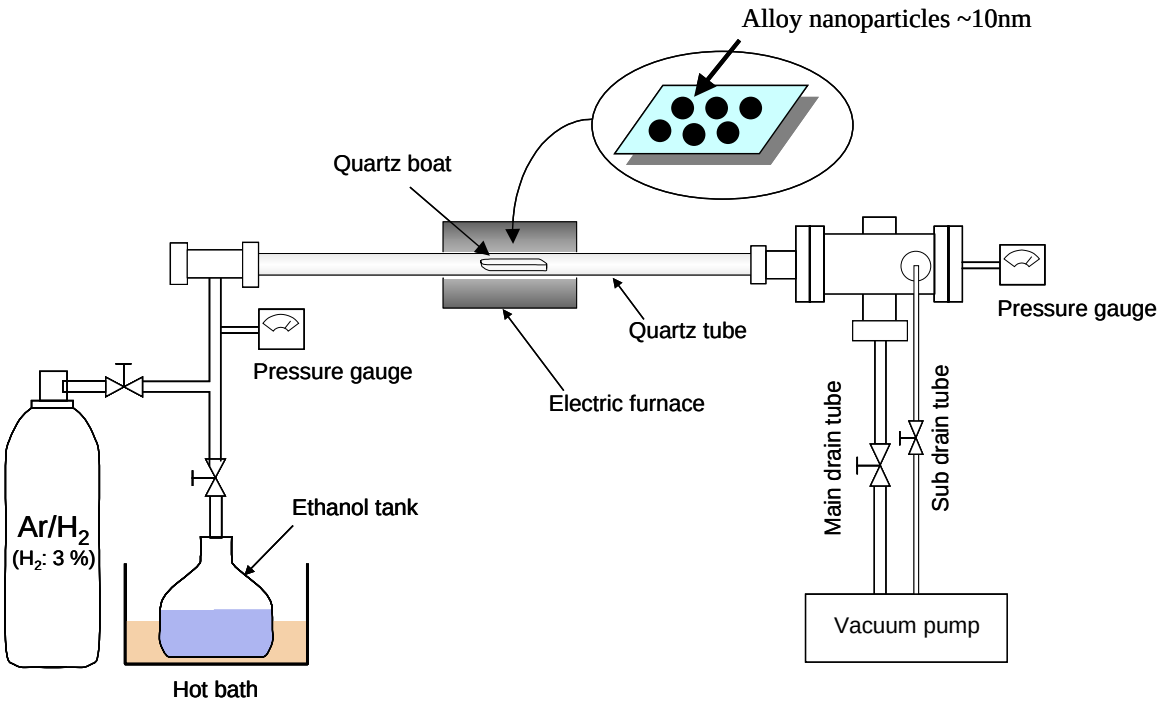
Figure Captions

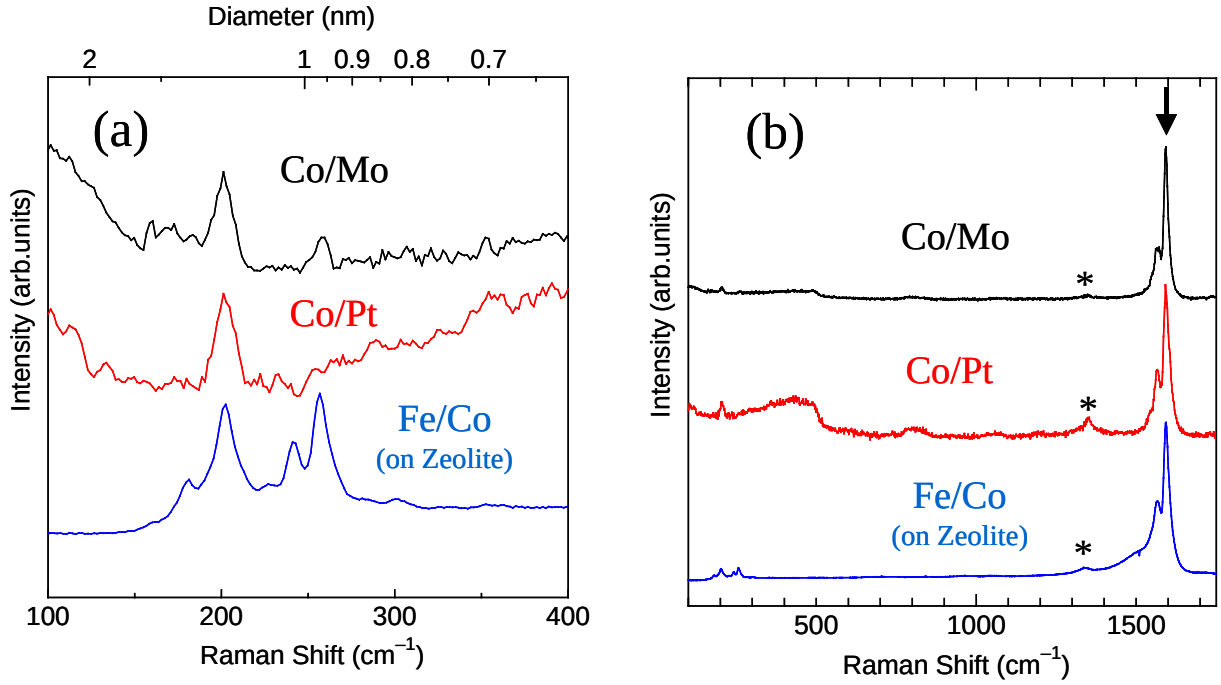
Figure 1. A schematic of the alcohol catalytic CVD apparatus.

Figure 2. Raman spectra of as-grown SWNTs from ethanol on various alloy particles at 800℃. The left panel (a) is a magnification of the low-frequency area of the right (b). These Raman spectra were measured by 488nm laser excitation.

Figure 3. AFM images of as-grown SWNTs from ethanol on (a) Co/Mo particles and (b) Co/Pt particles.

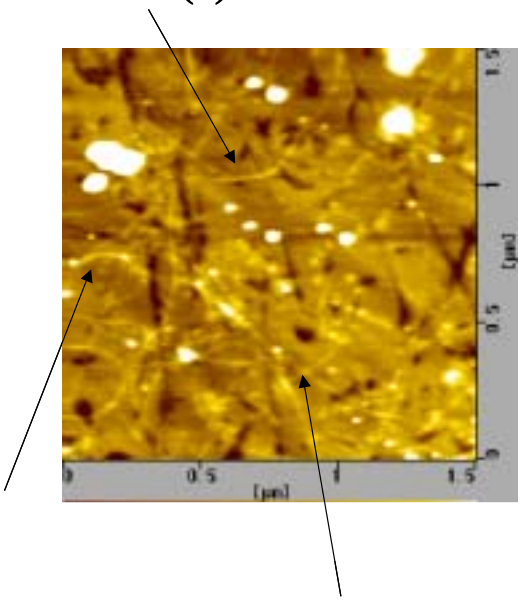


M.Kohno et al. Figure 1

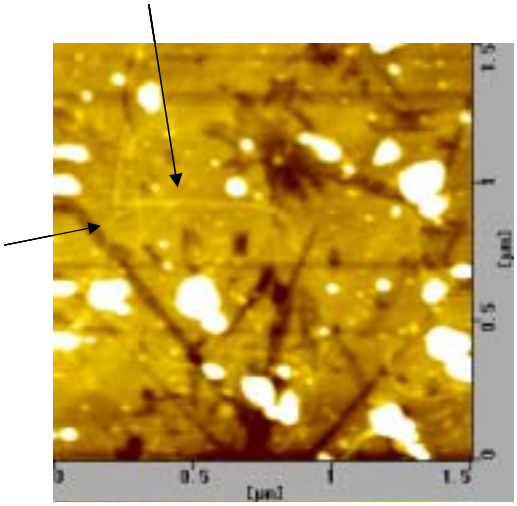


M.Kohno et al. Figure 2

(a) Co/Mo



(b) Co/Pt



M.Kohno et al. Figure 3