

スピコーティングを用いた触媒担持法の最適化による垂直配向単層カーボンナノチューブ膜の合成

Optimization of catalyst deposition by spin-coating for synthesis of vertically-aligned single-walled carbon nanotube arrays

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For morphology-tunable synthesis of vertically-aligned single-walled carbon nanotube (VA-SWNT) arrays, we present a spin-coating catalyst-deposition method as an alternative to dip-coating, where cobalt and molybdenum metals are deposited onto Si substrates by spin-coating a solution containing 0.01 %wt of each metal species dissolved in ethanol. The array height and yield of the VA-SWNTs from this method are higher than that from dip-coating, however the resonance Raman spectra in the radial breathing mode region are similar. The VA-SWNT array height was found to be independent of the thickness of the spin-coated film over the investigated range, and the uniformity was optimized by tuning the spin-coating conditions.

Key Words: single-walled carbon nanotube, SWNT, synthesis, spin-coating, catalyst deposition

1. Introduction

There are many methods to prepare catalysts for synthesis of single-walled carbon nanotubes (SWNTs). A liquid dip-coat method, which can deposit high-density catalysts, has been used widely in many applications. As for the direct growth of vertically aligned SWNTs (VA-SWNTs) by conventional alcohol catalytic chemical vapor deposition (ACCVD) on substrates [1-3], this method has been utilized to realize high yield and uniformity. In the ACCVD method [3], VA-SWNTs are synthesized from cobalt (Co) and molybdenum (Mo) binary catalyst nanoparticles deposited onto Si or quartz substrates [4]. We found that applying this method to small or large substrates produces SWNT arrays that are not uniform. Moreover, the array height and yield are usually limited. Therefore, in this study, we investigate spin-coating as a possible method to overcome these dip-coating limitations.

Although there are many reports of spin-coating for deposition of polymers [5], nanoparticles [6], or catalyst for synthesis of random SWNTs [7,8], multi-walled carbon nanotubes [5,9-15], to our knowledge there is no report of synthesis of VA-SWNT arrays from spin-coated catalyst. Therefore, in this work, we have investigated a spin-coating method as an alternative to dip-coating to produce more uniform and higher yield VA-SWNTs, and for morphology-tunable synthesis of SWNT arrays.

2. Experimental

Rectangular Si substrates annealed at 500°C were used to deposit Mo and Co metal catalysts by spin-coating a solution containing 0.01 %wt of each metal species dissolved in ethanol. The substrate was covered by the catalyst solution, and was then spun with a spin rate between 1000 and 5000 rpm. The spinning time at each condition was 0.5 seconds, and acceleration to the designated spin rate occurred in 0.4 seconds. Following spin-coating, the substrate was annealed in air at 400°C for 5 min. VA-SWNTs were grown using the ACCVD process [1-3], and were characterized by SEM and TEM

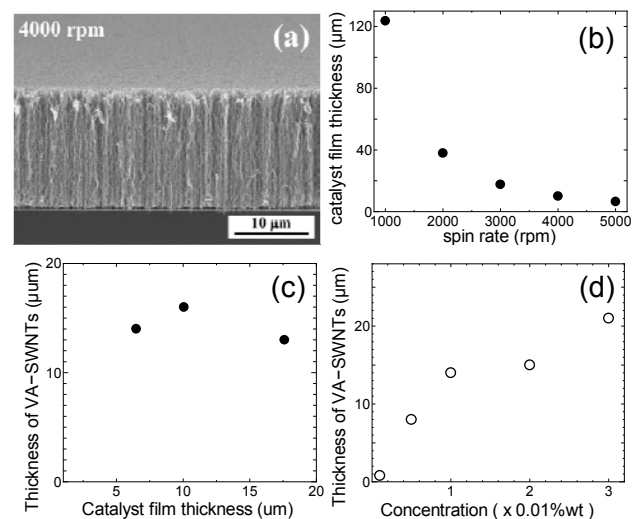


Fig 1. (a) SEM image of VA-SWNTs grown on a Si substrate from catalyst deposited by spin-coating method, (b) film thickness as a function of spin rate, (c) height of VA-SWNT arrays for different film thicknesses of spin-coated catalyst solution, and (d) concentration dependence.

observation, as well as resonance Raman spectroscopy. The thickness of the spin-coated film was calculated using the standard film thickness equation [16]

$$h = \frac{h_0}{\left[1 + \frac{4\rho\omega^2 h_0^2 t}{3\eta}\right]^{1/2}}$$

where h is film thickness at time t , h_0 is the initial film thickness, ω is angular velocity, ρ is density of the fluid and η is viscosity. The results from this method were compared with VA-SWNTs synthesized by our standard dip-coating method.

3. Results and Discussion

The thickness of the liquid layer resulting from spin-coating is thicker than that formed by dip-coating.

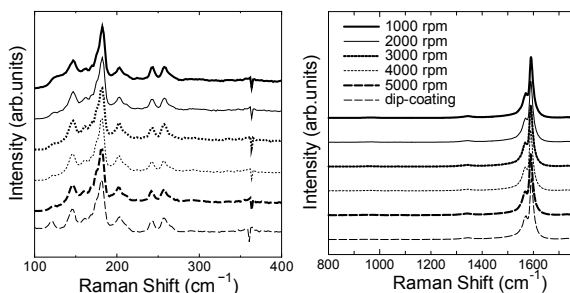


Fig 2. Raman spectra of VA-SWNTs grown on Si substrates from catalyst deposited by liquid dip-coating and spin-coating with different spin rates.

Therefore, a larger amount of catalyst should be deposited on the surface, particularly because all the catalyst contained in the liquid thin film is deposited during evaporation of the liquid. The amount of catalyst can therefore be adjusted by changing the film thickness (by changing the spin rate) and the solution concentration [17]. In contrast, when the substrate is withdrawn from a solution as in the dip-coat process, a thinner liquid layer forms on the surface, with a nonlinear thickness profile extending down to the meniscus [18].

Figure 1(a) shows a typical SEM image of VA-SWNTs obtained from catalyst spin-coated at 4000 rpm. The catalyst film thickness for different spin rates is shown in Fig. 1(b). Despite the exponential decrease in the thickness of the catalyst solution layer with increasing spin rate, the height of the resulting VA-SWNT arrays was unaffected [Fig. 1(c)]. The array height, however, was more sensitive to the solution concentration, as shown in Fig. 1(d).

As for the uniformity and yield of VA-SWNTs, we found that a spin rate of 4000 rpm results in the most uniform and highest yield of VA-SWNTs. Additionally, based on SEM observation, VA-SWNT arrays prepared from spin-coated catalyst were found to be more uniform than arrays synthesized from dip-coated catalyst. The spin-coating method also resulted in higher yield of VA-SWNTs than liquid dip-coating (~27% taller arrays). From resonance Raman spectra (Fig. 2), we found no appreciable differences in the radial breathing mode (RBM) regions (100-400 cm^{-1}) of VA-SWNTs synthesized from dip-coated catalyst, indicating SWNTs with similar diameters were produced.

TEM observation (Fig. 3) indicates that VA-SWNTs from spin-coating contain slightly more contamination compared with our previously reported observations [3], and some areas have much more contamination or small dots that appear to be catalyst particles. This indicates that more catalyst was deposited on the surface than in the dip-coating case. The average SWNT diameter, however, was 1.80 ± 0.70 nm, which is somewhat smaller than VA-SWNTs synthesized from dip-coated catalyst.

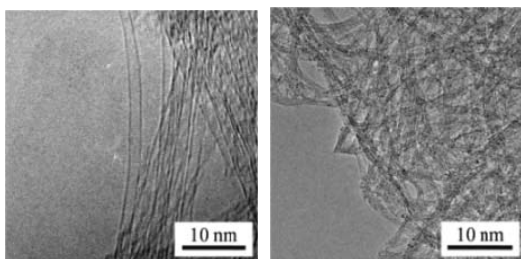


Fig 3. TEM images of VA-SWNTs synthesized from catalyst particles deposited by spin-coating at 4000 rpm.

4. Summary

We present a spin-coating method as an alternative to dip-coating catalyst preparation for synthesis of vertically-aligned single-walled carbon nanotube (VA-SWNT) arrays. The yield of the VA-SWNTs synthesized by this method is higher than from dip-coating, since this method deposits a larger amount of catalyst. The VA-SWNT array height was found not to depend on the thickness of the spin-coated film for the range shown in Fig. 1(c), and the uniformity was optimized by tuning the spin-coating conditions. Furthermore, the RBM region of the resonance Raman spectra (100-400 cm^{-1}) is similar to that of VA-SWNTs synthesized from dip-coated catalyst at the same catalyst concentration.

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