Controlling the Morphology of Carbon Nanotube Films by Varying the Areal Density of Catalyst Nanoclusters Using Block-Copolymer Micellar Thin Films**

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In spite of much research progress in the science and synthesis of carbon nanotubes (CNTs),[1] control over the location and orientation of CNTs on substrates remains a major challenge. A key breakthrough was the synthesis of vertically aligned CNT (VA-CNT) arrays using thermal chemical vapor deposition (CVD)[2–7] and plasma-enhanced CVD,[8] where the CNTs self-orient perpendicular to the substrate surface due to initial crowding and continue to grow upward in this direction. These CNT arrays have wide-ranging applications, including membranes, heat dissipation, electrical interconnects, and nanoelectronics.[9–13] The catalysts for synthesis of VA-CNTs are commonly prepared by sputtering or evaporating a thin metal film onto a substrate,[14,15] which dewets to form catalyst nanoparticles at an elevated temperature prior to growth.[16–18] While these catalysts are easily prepared and patterned by shadow masking or lithography,[7,14] these approaches are not easily able to create nanocluster catalysts that have monodisperse diameters and quantifiable areal densities. In thin metal films, both the nanocluster size and areal density are coupled to the film thickness, and the annealing procedure affects the size, density, and the chemical state of the nanoclusters. Recently, Huh et al.[19] demonstrated a route for controlling the density of CNT growth using varying densities of colloidal cobalt nanoparticles; however, due to nanoparticle coalescence their route does not enable precise quantification of nanocluster areal density and leads to a broad distribution of CNT diameters. Zhang et al.[20] also recently demonstrated the control of CNT growth by varying the density of Co–Mo nanoparticles, although their route is unable to independently vary the diameter and the areal density of nanoparticles.

We employ a methodology for synthesizing iron oxide nanoclusters that utilizes micelles formed by the amphiphilic block copolymer, polystyrene-b-poly(acrylic acid) (PS-b-PAA).[21,22] This catalyst system has significant value because it enables the creation of nanocluster arrays of a chosen metal species, with independent control of the nanocluster diameter and areal density.[22] In previous work, nanocluster diameters were varied between 5 and 16 nm and the areal density was varied from $6.0 \times 10^{10}$ to $1 \times 10^{9}$ cm$^{-2}$, although variation outside of these ranges is easily accessible. At higher areal densities the nanoclusters are hexagonally ordered. Further, as we have presented separately, the nanocluster arrays can be patterned on the micrometer length scale using microcontact printing.[23]

Here, we utilize this system to create arrays of uniform-diameter iron oxide nanoclusters, with quantifiable areal densities that can be varied over more than an order of magnitude. We achieve vertical CNT growth from our catalyst system through appropriate selection of the substrate, catalyst preparation procedure, and reaction conditions. To the best of our knowledge, our work is the first example of vertical growth of CNTs from a block-copolymer-based catalyst. Because this catalyst system allows for precise quantification of the nanocluster areal density, we can estimate the percentage of nanoclusters that nucleate the growth of a CNT. By uniformly varying the areal density of iron oxide nanoclusters on the substrate surface, we manipulate the morphology of the CNT film from a tangled and sparse arrangement of individual CNTs, through a transition region with locally bunched and self-aligned CNTs, to rapid growth of thick vertical CNT films.

The procedure for synthesizing the iron oxide nanocluster arrays utilized spherical micelles formed by PS-b-PAA in toluene, which were loaded with FeCl$_3$, and then spin-cast onto a substrate (see Experimental Section).[21,22,24] The polymer thin film was then treated in oxygen plasma to remove the organic components, leaving an iron oxide nanocluster array, as shown in Figure 1A. Previous studies have demonstrated that the iron oxide nanocluster structure is Fe$_3$O$_5$.[22,25] The molecular weight and metal-loading ratios of Figure 1A led to iron oxide nanocluster arrays with diameters of $16 \pm 1.6$ nm that were arranged in a quasihexagonal array with an areal density of $6.0 \times 10^{10}$ cm$^{-2}$.[22] The root-mean-square roughness of the nanocluster arrays was 2.2 nm, as determined from using atomic force microscopy (AFM).
Because of the flexibility of this catalyst system, we were also able to synthesize iron oxide nanocluster arrays with diameters of 8.0 ± 0.7 nm and an areal density of $8.2 \times 10^{10}$ cm$^{-2}$. We observed that the 8 nm diameter iron oxide nanocluster arrays catalyzed significantly fewer CNTs than the 16 nm diameter iron oxide nanoclusters at each of the growth conditions shown in Figure 1, and vertical CNT growth from the 8 nm diameter nanoclusters was not observed. Thus, for a given CVD growth condition, nanocluster diameter has a direct effect on the density and the uniformity of the resulting CNT growth. The increased activity of the 16 nm diameter nanoclusters (producing CNTs with outer diameters of 12 ± 2 nm, discussed later) versus the 8 nm diameter nanoclusters reinforces the notion of a catalyst particle “size window” for growth at a certain CVD condition.[22] Our previous study of CNT growth from a thin-film catalyst at identical CVD conditions demonstrated growth of CNTs with 8 nm outer diameters and a much broader diameter distribution. Further characterization would enable assessment of surface and support effects that may govern the precise relationship between nanocluster size and CNT diameter, and determine the suitability of a particle for growth. Because this catalyst system enables the synthesis of iron oxide nanoclusters with diameters smaller than 5 nm, we believe that this approach will also be applicable for growing smaller diameter CNTs such as single-walled CNTs (SWCNTs) and double-walled CNTs (DWCNTs). Future research will involve optimizing CVD growth conditions to facilitate the growth of CNTs with tailored diameters and a specific number of walls, along with controlling the film morphology and packing density, as suggested by our results presented here. For the remainder of this report, we focus on MWCNT growth from the 16 nm diameter micellar-templated nanoclusters.

During the spin-casting of polymer thin films, non-uniformities at the edge of the substrate lead to polymer films that are thicker at the substrate edge than in the center of the substrate.[28] Depending on the shape of the substrate and other experimental variables, these non-uniformities can extend substantially from the substrate edge. The substrates from Figure 1B and C were created by spin-casting the micellar solution onto a 1 cm $\times$ 1 cm Al$_2$O$_3$-coated Si substrate, followed by oxygen plasma etching prior to CNT growth. While these substrates had a monolayer of iron oxide nanoclusters in the center of the substrate, the edge regions had a substantially higher areal density of nanoclusters as a result of the spin-casting non-uniformities. For the 1 cm $\times$ 1 cm Al$_2$O$_3$-coated Si substrates we always observed denser CNT growth along the substrate edges, which was consistent with the higher areal density of nanoclusters at the edges. We previously observed that the yield is affected by the local areal density of catalyst on the substrate, and that under limiting CVD conditions the reactant supply can be depleted at the edges of the substrate surface.[29] Therefore, it was important for the micellar-based catalyst system to have a uniform micellar film thickness over the entire substrate surface.
To eliminate the non-uniformities in the thickness of the micellar thin film, the micellar solution was spin-cast onto 2.5 cm × 2.5 cm Al$_2$O$_3$-coated Si substrates. The edges of the substrates were then removed to leave a 1 cm × 1 cm substrate. This process leads to substrates with uniform micellar film thicknesses and to uniform areal densities of iron oxide nanoclusters over the entire substrate. Figure 1D shows CNTs grown from a uniform density nanocluster array on Al$_2$O$_3$-coated Si using CVD with 200/500/0 sccm C$_2$H$_4$/H$_2$/Ar at 750 °C. The activity of the catalyst and the density of the CNT growth substantially increased compared to the CNT growth shown in Figure 1C. The dense uniform vertical CNT growth, which is caused by the high density of CNTs simultaneously growing from the nanoclusters, was observed over the entire substrate surface.

The capability to systematically vary the areal density of iron oxide nanoclusters on the substrate is one of the key advantages of this catalyst system. By adding varying amounts of polystyrene (PS) homopolymer into the PS-b-PAA micelle solution prior to spin-casting, the areal density of iron oxide nanoclusters can be systematically decreased over more than an order of magnitude (see Experimental Section).[22] Because the areal density of the iron oxide nanoclusters can easily be varied and quantified, the morphology of CNT films can be controlled and studied using this catalyst system. The results from our catalyst system are shown in Figure 2, which demonstrates the effects of uniformly varying the areal density of the iron oxide nanoclusters on CNT growth. All of the substrates in Figure 2 were cut from a larger initial substrate to remove the non-uniform edge regions. In each level of the figure a TEM image of the catalytic nanoclusters is shown on the left, with the corresponding SEM image of the resulting CNT growth on the right. As discussed previously, an iron oxide nanocluster areal density of 6 × 10$^{10}$ cm$^{-2}$ results in a dense vertical growth of CNTs (Fig. 2B and G). By decreasing the spin-casting speed to 2000 rpm, thicker micellar thin films with multilayers of iron oxide nanoclusters were created. These films had a thickness of 50 nm, as measured by ellipsometry, and resulted in an iron oxide areal density of 1.5 × 10$^{11}$ cm$^{-2}$ (Fig. 2A). The CNT growth using this catalyst (Fig. 2F) resulted in a uniform and dense film of vertically grown MWCNTs that was similar to the CNT growth from the catalyst with an areal density of 6 × 10$^{10}$ cm$^{-2}$ (Fig. 2G). By decreasing the areal density of nanoclusters to 2.5 × 10$^{10}$ cm$^{-2}$ (Fig. 2C and H), the uniform vertical growth of CNTs was replaced with a more irregular vertical growth, where the average thickness of the CNT thin film was significantly reduced compared to the thickness in Figure 2G. These results suggest that the minimum areal density of iron oxide nanoclusters required to grow uniform and thick CNT films is in the range between 2.5 × 10$^{10}$ cm$^{-2}$ and 6.0 × 10$^{10}$ cm$^{-2}$ for this system.

When the areal density was further decreased to 1 × 10$^{10}$ cm$^{-2}$ (Fig. 2D and I), the overall density of the CNT growth decreased significantly. This sample showed sporadic columns of vertical CNT growth (inset of Fig. 2I) surrounded by large areas with considerably less growth. The columns of vertically grown CNTs can be explained by a local variation in the iron oxide nanocluster areal density that results from the loss of hexagonal order of the nanoclusters as the PS homo-

Figure 2. Effects of varying iron oxide nanocluster areal density on the morphology of the CNT films. The left column (A–E) shows TEM images of the iron oxide nanocluster arrays with varying areal density prior to CNT growth. The right column (F—45° tilt, G—85° tilt, H—70° tilt, I—0° tilt, J—0° tilt) shows SEM images of CNT growths using iron oxide nanocluster arrays with a specified areal density on Al$_2$O$_3$-coated Si with C$_2$H$_4$/H$_2$/Ar flow rates of 200/500/0 sccm at 750 °C. The figures correspond to the following iron oxide nanocluster densities: A,F) 1.5 × 10$^{11}$ cm$^{-2}$; B,G) 6 × 10$^{10}$ cm$^{-2}$; C,H) 2.5 × 10$^{10}$ cm$^{-2}$; D,I) 1.1 × 10$^{10}$ cm$^{-2}$ (The inset in I shows a higher magnification image of one vertically grown CNT column); and E,J) approximately 1 × 10$^{9}$ cm$^{-2}$.
polymer is added. These results suggest that when the critical local areal density of nanoclusters is exceeded, columns of vertically grown MWCNTs are produced. When the areal density was decreased to $1 \times 10^9 \text{ cm}^{-2}$ (Fig. 2E and J), no vertical growth of CNTs was observed. Comparing Figure 2I and J shows that the density of the CNT growth was significantly reduced and the average distance between CNTs increased noticeably. For the sample in Figure 2J, the areal density was low enough that the local variations in the areal density did not exceed the critical local areal density; therefore, the vertical growth of MWCNTs was prevented altogether. The distribution of CNT diameters was nearly identical for each of the nanocluster areal densities tested, with CNT outer diameters of $12 \pm 2 \text{ nm}$. This result was expected because the diameters of the iron oxide nanoclusters remained constant as the areal density was varied.

Because the areal density of iron oxide nanoclusters created using our micellar route is readily available, the catalyst activity can be estimated for these vertically grown CNT thin films. The catalyst activity is defined as the ratio of the CNT areal density to the areal density of the iron oxide nanoclusters. Because the iron oxide nanoclusters do not coalesce during the CNT growth process (demonstrated in the inset of Fig. 1B), the only unknown quantity is the CNT areal density. To calculate the CNT areal density, we determined the mass of the CNT film using thermogravimetric analysis (TGA). The average CNT diameter was $12 \pm 2 \text{ nm}$, as determined from using high-resolution TEM (HRTEM), which is shown in Figure 3A. A histogram illustrating the distribution of CNT diameters is shown in Figure 3B. The length of each CNT was estimated by observing the height of the bulk CNT film (Fig. 1D) and the side view of the vertically grown MWCNT thin film (Fig. 3C) using scanning electron microscopy (SEM) imaging. Figure 3C clearly demonstrates that the MWCNTs are not highly aligned, and are therefore longer than the height of the bulk MWCNT thin film. From the curvature of the CNTs in Figure 3C, we estimate the length of the MWCNTs to be approximately 50 % longer than the bulk thickness of the MWCNT thin film. By combining the length of the CNTs with the diameter and the number of concentric walls of the CNTs, the mass of an individual CNT can be estimated. The ratio of the mass of the CNT film to the mass of an individual CNT gives the number of CNTs, which can be converted to the CNT areal density by dividing by the substrate area. By using this analysis for the CNT growth substrate containing a monolayer of iron oxide nanoclusters with uniform density (as shown in Fig. 2B and G), we obtained a CNT areal density of $2.2 \times 10^7 \text{ cm}^{-2}$ (0.363 mg cm$^{-2}$). By comparing with the known iron oxide nanocluster density of $6.0 \times 10^{10} \text{ cm}^{-2}$, we obtained a catalyst activity of approximately 4 %. This catalytic activity is very reasonable compared to the few percent catalyst activity observed in normal CVD growth, while considerably less than the 84 % activity calculated for highly efficient water-assisted CNT growth.[18] as expected. Using this analysis for a CNT thin film grown from a nanocluster array created from a multilayer micellar thin film (as shown in Fig. 2A and F), we obtained a CNT areal density of $5.2 \times 10^9 \text{ cm}^{-2}$ (0.879 mg cm$^{-2}$). By comparing the CNT areal density with the nanocluster areal density of $1.5 \times 10^{11} \text{ cm}^{-2}$, the catalytic activity for the multilayer nanocluster catalyst was determined to be approximately 4 %. This suggests that while the areal density of the CNTs grown on the substrate varies as a function of the areal density of iron oxide nanoclusters, the percentage of nanoclusters catalyzing the growth of a CNT remains approximately constant.

The yield of the catalyst can also be quantified as the ratio of the mass of MWCNTs produced to the mass of iron in the catalyst nanoclusters. We can estimate the mass of iron in the nanoclusters by using a micelle aggregation number of 150 and assuming that the ratio of carboxylic acid groups to iron ions within the micelles was 3:1. For the iron oxide nanocluster array with an areal density of $6.0 \times 10^{10} \text{ cm}^{-2}$ there was $1.7 \times 10^{-3} \text{ mg cm}^{-2}$ of Fe. By comparing this to the mass of MWCNT per area, the yield of the nanocluster array was $2.1 \times 10^4 \text{ mg MWCNT/mg Fe}$. This yield can also be determined for an evaporated iron thin-film catalyst subjected to identical CNT growth conditions.[7] The thickness (1.2 nm, as
measured by Rutherford backscattering spectrometry) of the iron thin film was used to determine that the catalyst contains approximately $9.4 \times 10^{-4}$ mg cm$^{-2}$ of Fe after deposition. From the measured mass of MWCNT and the substrate area, the yield of the iron thin film was determined to be $1.2 \times 10^{7}$ mg MWCNT/mg Fe. Comparing the yield of the nanocluster array versus the evaporated thin film suggests that the micelle-based nanocluster array more efficiently utilizes the iron molecules present on the substrate surface to convert the feed gases into MWCNTs.

In conclusion, our novel CNT catalyst system derived from spin-coated, iron-loaded PS-b-PAA micelles has significant advantages over other catalyst systems. This block-copolymer micellar catalyst system combines a unique ability to control the diameter, the areal density, and the composition of the nanoclusters, along with the ability to pattern the catalyst on a micrometer scale using microcontact-printing techniques. Through the variation of substrates and growth conditions, as well as the removal of spin-coating non-uniformities, we demonstrated the ability to catalyze vertical CNT growth from these iron oxide nanocluster arrays. Because these iron oxide nanocluster arrays have an easily quantifiable areal density, we were able to estimate that the catalyst activity for the vertical CNT growth was approximately 4%. The catalytic activity was approximately constant over a range of iron oxide nanocluster areal densities from $6 \times 10^{10}$ to $1.5 \times 10^{11}$ cm$^{-2}$. Furthermore, by varying the areal density of the iron oxide nanocluster arrays while maintaining a constant nanocluster diameter, we were able to control the morphology of the resulting CNT growth from dense vertical CNT films to an arrangement of sparse individual CNTs on the substrate surface. In our system, the critical areal density for growing a uniform vertical CNT film was between $2.5 \times 10^{10}$ and $6.0 \times 10^{10}$ cm$^{-2}$.

The control afforded by this micellar catalyst system could be promising for both CNT applications as well as for improved understanding of the combination of chemical and mechanical conditions necessary for growth of uniform CNT films. Using this micellar catalyst system, we can create multi-component nanocluster arrays of interest in CNT growth, such as iron/molybdenum containing particles, particularly, we expect that the critical density for vertical growth depends on the catalyst composition and the CVD reaction conditions. Our approach could also be used to synthesize various other nanotubes and nanowires which grow from catalytic nanoparticles, including carbon nitride nanotubes[29] that are produced in alternative CVD atmospheres. Our micellar catalyst system is a step toward precisely engineering the position, orientation, and density of nanostructures on substrates.

**Experimental**

**Materials:** PS-b-PAA [number-average molecular weight ($M_n$) PS = 16 400 g mol$^{-1}$, $M_n$ PAA = 4500 g mol$^{-1}$, polydispersity index, PDI = 1.05] and PS homopolymer ($M_n$ = 8500 g mol$^{-1}$, PDI = 1.06) were used as received from Polymer Source. The following chemicals were also used as received: anhydrous FeCl$_3$ and toluene (HPLC grade, 99.8%) obtained from Sigma–Aldrich. The substrates were clean silicon wafers (p-type, Silicon Quest International) coated with a 1 μm layer of thermally grown SiO$_2$, or a 15 nm layer of Al$_2$O$_3$ deposited by electron-beam evaporation in Temescal VES-2550 with a FDC-8000 film deposition controller. The silicon nitride membrane window substrates were purchased from Structure Probe. Each substrate (surface area $4.5$ mm $\times$ 4.5 mm) consisted of a 100 nm thick amorphous, low-stress Si$_3$N$_4$ membrane supported on a 0.2 mm thick silicon wafer that had been back-etched in the center to create the electron-transparent Si$_3$N$_4$ window (surface area $0.2$ mm$^2$). The use of the electron-transparent silicon nitride substrates allows for direct TEM characterization without disturbing the spin-cast films.

**Preparation of Carbon Nanotube Growth Catalysts:** Details about synthesizing iron oxide nanocluster arrays have been published previously [21,22,24]. In brief, PS-b-PAA was mixed with toluene at a concentration of 10 mg mL$^{-1}$ and heated to 145 °C for 20 min in a sealed vial to create a spherical block-copolymer micellar solution. The PAA micelle cores were selectively loaded with iron by adding FeCl$_3$ to the micellar solution at a ratio of 5.4 metal ion equivalents per carboxylic acid group. Thin films were then created by spin-casting the metal-loaded micellar solutions onto the planar substrates at 2000–8000 rpm for 1 min at room temperature. The micellar thin film was removed by oxygen plasma etching (rf plasma, 8–12 MHz) for 20 min, leaving only the inorganic iron oxide nanocluster arrays remaining on the substrate. To create iron oxide nanocluster arrays with lower areal densities, PS homopolymer ($M_n$ = 8500 g mol$^{-1}$) was added to the micellar solutions with a PS-b-PAA to PS homopolymer ratio of 3:1, 4:1, and 50:1 prior to spin-casting. To reduce the viscosities of these solutions to acceptable levels for spin-casting monolayers, the solutions with a 3:1 and 4:1 ratio were diluted with toluene from 10 mg PS-b-PAA/mL of toluene to 5 mg PS-b-PAA/mL of toluene, while the solution with a 50:1 ratio was diluted to 1 mg PS-b-PAA/mL of toluene.

**Carbon-Nanotube Growth Procedure:** CNT growth was performed in a single-zone atmospheric pressure quartz tube furnace (Lindberg), with an inside diameter of 22 mm and a 30 cm long heating zone, using flows of Ar (99.999%, Airgas), C$_2$H$_4$ (99.5%, Airgas), and H$_2$ (99.999%, BOC). The substrate sample was rested in the furnace tube, 40 mm downstream of the control thermocouple. The furnace temperature was ramped to the set point temperature in 30 min and held for an additional 15 min under 400 scm Ar. The flows of Ar and H$_2$ used during growth were established 1 min prior to introducing C$_2$H$_4$, then the C$_2$H$_4$/H$_2$/Ar mixture was maintained for the growth period of 15–60 min. Finally, the H$_2$ and C$_2$H$_4$ flows were discontinued, and 400 sccm Ar was maintained for ten more minutes to displace the reactant gases from the tube, before being reduced to a trickle while the furnace cooled to below 100 °C.

**Characterization:** Transmission electron microscopy (TEM) was performed on a JEOL 2000FX operating at 200 kV. SEM was performed on a FEI NOVA in 3000 NanoScope IIIA scanning probe microscope operating in tapping mode using a silicon cantilever. The images were analyzed using NanoScope III software (version 5.12r3, Digital Instruments).

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