

Fabrication of Vertical Carbon Nanotube Arrays from Self-Assembled Block Copolymer Films

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Highly uniform vertical carbon nanotube arrays were prepared by a novel hybrid approach combining a plasma-enhanced chemical vapor deposition (PECVD) process with self-assembled block copolymer nanotemplate. Monodisperse catalyst nanoparticles were prepared on a substrate using self-assembled nanoporous block copolymer templates. The subsequent PECVD growth of vertical CNTs from the nanopatterned catalyst particles provided highly oriented vertical CNT arrays, which are potentially useful for device integration of CNTs.

Keywords: Carbon Nanotube, Block Copolymer, PECVD.

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1. INTRODUCTION

Discovery of carbon nanotubes (CNTs) opened a new world of research in the ideal one dimensional structure.¹ Their exceptional structural, electrical and mechanical properties^{2–3} have been validated many potential applications such as field emission⁴ and nanoelectronics,⁵ and stimulated a large amount of researches to optimize the synthesis and properties of CNTs. For the practical applications of CNTs, it is highly required to grow vertical CNTs having desired properties.^{6–7} In an ideal approach, vertical CNTs having a well-defined length, diameter and chirality should be grown at the desired locations. Although there are several synthetic methods for CNTs such as arc-discharge, laser ablation and chemical vapor deposition (CVD), CVD is the most widely used method for vertical CNTs, because of its facile operation and easy scale-up.⁷ In a CVD method, metal particles deposited on a substrate surface catalyze the vertical growth of CNTs.⁸ Thus the control of the areal density, regularity and size of the catalyst particles is a key element to achieve uniformly ordered CNT arrays.

The catalysts for CNT growth are generally prepared by sputtering or evaporating a thin metal film on a substrate.^{9–10} The subsequent heat treatment leads to the agglomerated particles of the deposited film.^{11–13} Although the average size of catalyst particle can be controlled by adjusting the thickness of the deposited film and the heat treatment conditions, the diameter of prepared catalyst particles is usually polydisperse and their distribution is random over the substrate surface. The diameter and the

spacing of the catalyst particles can be adjusted by applying a nanopatterning technique such as E-beam lithography. However, the serial processing of E-beam lithography does not allow for the mass production of the nanopatterned catalyst particles.

In this study, we report a hybrid approach combining PECVD process with self-assembled block copolymer nanotemplate for the fabrication of highly uniform vertical CNT arrays. Block copolymers, consisting of the covalently linked two or more chemically distinct polymer chains, may provide a variety of periodic nanoscale morphologies having feature sizes ranging from 5 to 50 nm.^{14–20} In our approach, the catalysts for CNT growth were nanopatterned by lifting-off process using a self-assembled nanoporous block copolymer nanotemplates. Since this lifting-off process resulted in a highly monodisperse catalyst nanoparticles following the nanoscale morphology of the block copolymer template, the CNT arrays grown by the subsequent CVD method were also highly uniform.

2. EXPERIMENTAL DETAILS

2.1. Materials

An asymmetric block copolymer, polystyrene-block-poly(methyl methacrylate)s (PS-*b*-PMMA)s forming cylindrical nanostructures (molecular weight: PS/PMMA-140k/60k, PMMA cylinder diameter: 43 nm, center to center distance between neighboring cylinders: 72 nm) were purchased from Polymer Source Inc. The iron and the nickel sources for E-beam evaporation (purity: 99.95%) were purchased from Thifine. Pure ammonia and acetylene gases

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were purchased from Showa Denko K.K., and Kyungin Chemical Industrial, respectively.

2.2. Nanopatterned Catalyst Particle Preparation

The entire process for synthesizing CNT arrays is schematically described in Figure 1. A silicon wafer surface was treated by a random copolymer brush to make a neutral surface. A thin film (thickness: 60 nm) of the block copolymer was spin-coated onto the neutral treated wafer surface. After a high temperature annealing at 190 °C for 3 days, the substrates were irradiated with UV and subsequently rinsed with acetic acid and water. This procedure removes PMMA cylinder cores and crosslinks the PS matrix.^{21–27} The substrate was further treated in oxygen plasma for 10 s to remove any remnant cylinder cores. Iron or nickel catalyst films having a thickness of 7 nm were deposited over the block copolymer template. After the deposition process, the remaining PS nanoporous template was lifted-off by sonication in toluene. Through this procedure, uniformly distributed catalyst nanoparticles having a narrow polydispersity were formed on a silicon wafer.

2.3. CVD Growth of Vertical CNTs

CNT growth was carried out on the catalyst-deposited substrates by a CVD method. The substrate was first heated to 750 °C under an ammonia gas flow of 100 sccm and the pressure of the chamber was kept at 1.3 torr. When the substrate temperature reached 750 °C, the substrate was heat-treated (usually less than 3 min) to reduce the size of the catalyst particles. The chamber pressure was increased to 30 torr by controlling the throttle valve. For PECVD,

additional DC plasma was activated with an anode DC voltage of 650 V relative to the grounded substrate. After acetylene gas was admitted at a flow rate of 25 sccm for 1 min, the substrate was covered by a dense multi-walled nanotube arrays grown from the catalyst nanoparticles.

2.4. Measurement of CNT Diameter

The mean diameter of CNTs was measured from the TEM analysis. The sample was prepared as follows. The as-grown CNTs were detached from the substrate and dispersed in ethanol. By applying ultrasonic treatment, the CNTs were individually dispersed. A drop of the CNT dispersion was deposited onto carbon supported TEM grid and air-dried. For the statistical analysis, the diameter of 300 randomly chosen CNTs was measured from TEM images.

3. RESULTS AND DISCUSSION

Figures 2(a) and (b) show the scanning electron microscopy (SEM) images of the iron catalyst particles prepared with or without a block copolymer nanotemplate, respectively. Figure 2(c) shows the statistical analysis results for the diameter of catalyst nanoparticles. The average diameter of agglomerated catalyst particles deposited without block copolymer nanotemplate was 89.3 ± 21.4 nm, which was relatively large^{28–29} due to the thick thickness (7 nm) of the deposited film. The agglomerated particles randomly distributed over the silicon wafer with the areal density of 3.5×10^9 cm⁻². The average diameter of catalyst particles patterned by block copolymer nanotemplate was 34.5 ± 1.97 nm after a heat treatment. The patterned catalyst particles were distributed in a hexagonal array with the areal density of 2.4×10^{10} cm⁻². As the catalyst particles were selectively deposited through the nanopores of the block copolymer templates, the hexagonal arrangement of the catalyst particles has the same morphology of the template.

In a CVD method, the growth of CNTs is significantly influenced by the chemical component of the catalyst particles. In particular, iron, cobalt, nickel and their alloys are frequently used to catalyze the CNT growth. As those transition metals have non-filled d shells in their orbitals, they can interact with hydrocarbons and show catalytic activity.³⁰ In previous researches, iron produced the highest density of CNTs,^{31–33} and nickel showed the highest growth rate and crystallinity^{34–35} among the three pure transition metals. Thus nickel and iron were chosen as catalysts for growing CNT arrays in this work. Figures 3(a) and (b) show the plane-view SEM images of the CNT arrays grown on nickel and iron catalyst nanoparticles, respectively. The catalyst particles were nanopatterned using block copolymer templates in both cases. In our work, nickel showed very low catalytic activity for CNT growth, which may be due to the oxidation of the

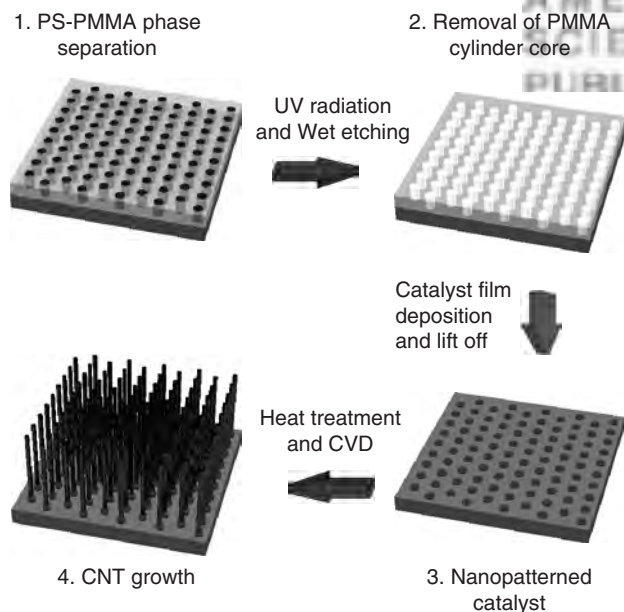


Fig. 1. Schematic illustration for the synthetic process of vertical CNT arrays.

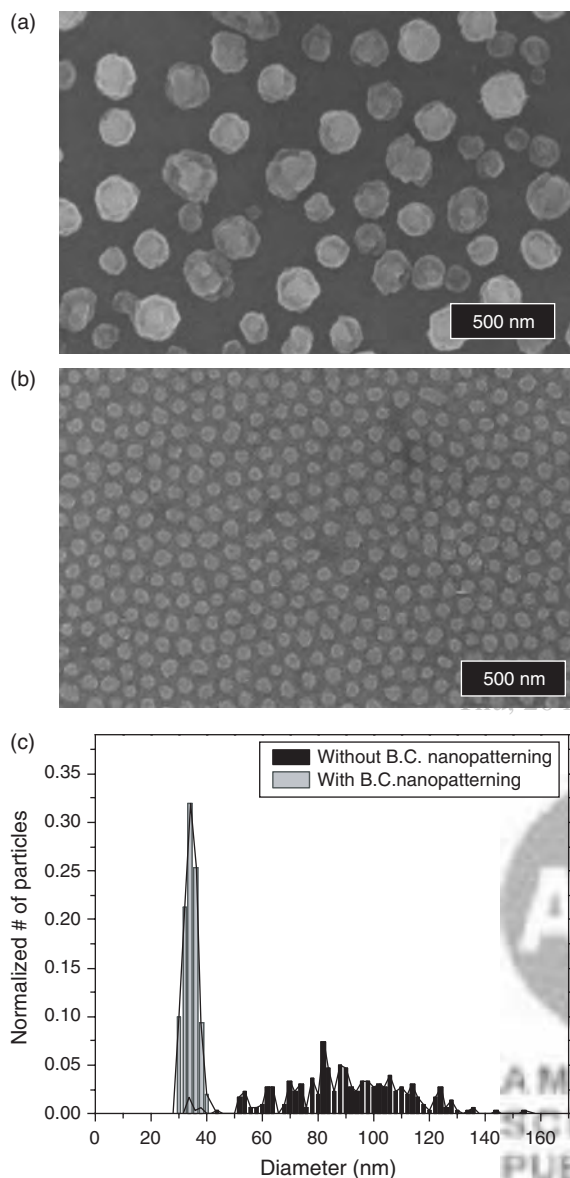


Fig. 2. High magnification plane-view SEM images of catalyst particle prepared (a) without or (b) with block copolymer nanopatterning process after heat treatment at 750 °C for 1 min. (c) The statistical size distribution of the catalyst nanoparticles after the heat treatment.

evaporated nickel during the lift-off process.³² In contrast, the iron oxide can catalyze the hydrocarbon source with a sufficiently high efficiency. As shown in Figure 2(b), a high density of CNT arrays was grown from the nanopatterned iron nanoparticles.

The CNTs grown by CVD method orient perpendicularly to the substrate surface due to the initial crowding among them and continue to grow upward.³⁶ However, the conventional thermal CVD method did not yield a highly oriented vertical morphology due to the thermal fluctuations and the gas stream inside the chamber.^{28,37} A highly oriented morphology of CNTs is very important for the device application. We used PECVD method to introduce the electric field alignment of CNTs having a

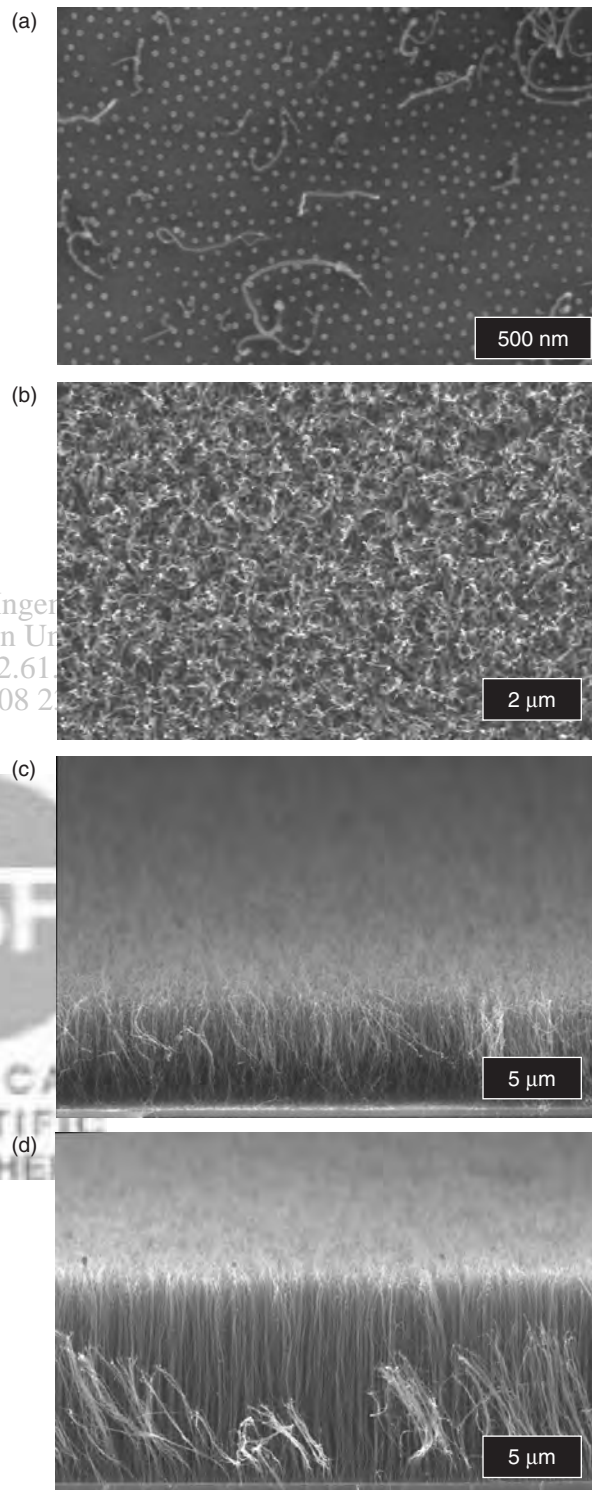


Fig. 3. Plane-view SEM images of the CNT arrays grown from the nanopatterned (a) nickel and (b) iron nanoparticles via thermal CVD methods. The lateral SEM images of CNT arrays grown from the nanopatterned iron catalyst particles by (c) thermal CVD and (d) PECVD methods.

high polarizability.^{37–39} The large induced dipole moments led to large aligning torques on the CNTs and enhanced the vertical alignment of CNT.³⁹ Figures 3(c) and (d) show CNT arrays grown by thermal CVD and PECVD

methods, respectively. The CNT array grown by thermal CVD method was curly, whereas the CNT array grown by a PECVD method was highly oriented to the vertical direction.

Figures 4(a) and (b) show the transmission electron microscopy (TEM) images of the CNTs grown from the iron nanoparticles prepared without or with block copolymer nanotemplates, respectively. The diameter of

about 300 CNTs, which was randomly chosen among the dispersed CNT samples, was measured from the TEM images. Figure 4(c) shows the statistical analysis results for the measured diameter of CNTs. The diameter of CNTs prepared without block copolymer nanopatterning process was polydisperse. The average value was 52.9 ± 19.2 nm. The CNTs prepared from the nanopatterned catalyst particles were highly uniform and their average diameter was 15.5 ± 1.9 nm.

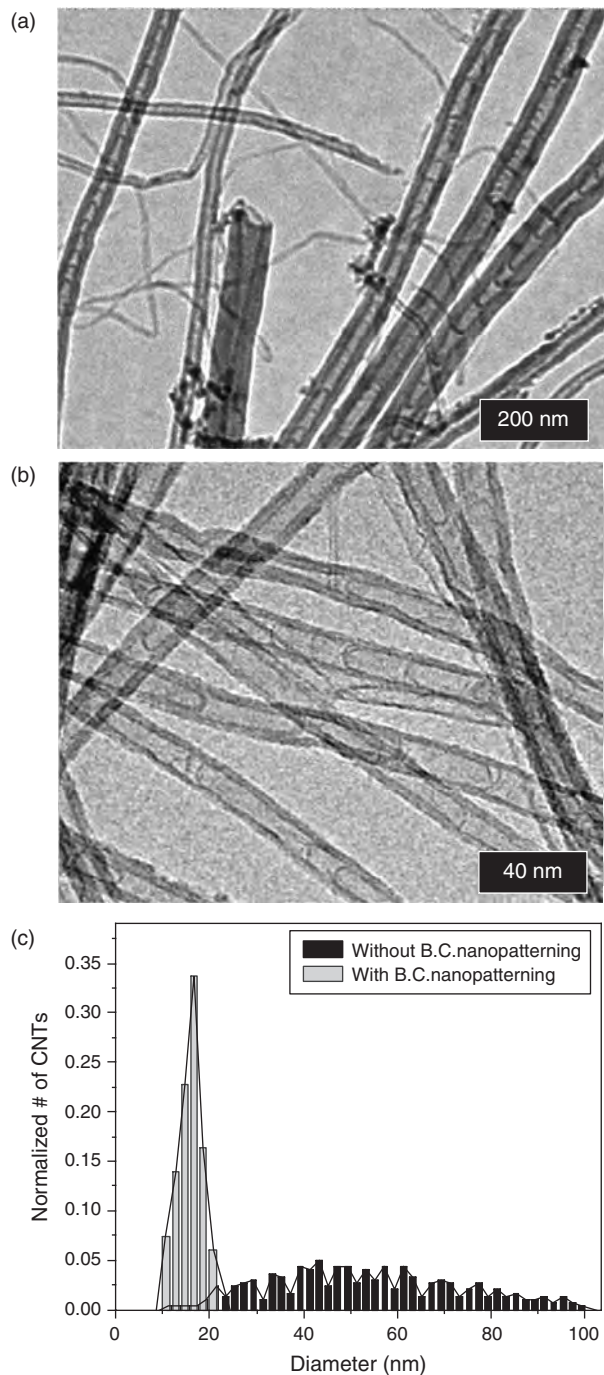


Fig. 4. TEM images of CNTs grown from the iron catalyst particles prepared (a) without or (b) with block copolymer nanopatterning process. (c) The statistical size distribution of the CNT arrays.

4. CONCLUSION

In summary, we have demonstrated a novel process for highly uniform CNT arrays combining PECVD and block copolymer self-assembly. The catalysts for CNT growth were nanopatterned by block copolymer lithography. DC plasma was introduced during the subsequent growth of vertical CNT arrays to enhance their vertical alignment. As a result, monodisperse and highly aligned vertical CNT arrays were prepared. We anticipate that our approach can be widely applied to synthesize various nanostructured materials which can be grown from catalytic nanoparticles.

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