Chemical Vapor Deposition Growth of Well-Aligned Carbon Nanotube Patterns on Cubic Mesoporous Silica Films by Soft Lithography

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Carbon nanotubes (CNTs) exhibit unique electronic, mechanical, and chemical properties that make them attractive for a wide range of novel applications including advanced scanning probes,[1] electron field emission sources,[2] hydrogen storage materials[3] and building blocks of molecular electronics.[4,5] Therefore, developing controlled synthesis methods of carbon nanotubes, which could be applied to nanoscopic integrated circuits using nanotubes, have attracted a great deal of interest. Recent research into the preparation of carbon nanotube patterns with aligned nanotubes have been undertaken.[6,7] Fan et al. reported the self-oriented regular arrays of nanotubes on the porous silicon substrate and patterned with Fe film by electron beam evaporation through shadow masks,[6] and Huang and co-workers prepared the perpendicularly aligned carbon nanotube patterns by pyrolyzing expensive iron(II) phthalocyanine (FePc) onto a quartz substrate prepatterned with a photoresist film.[8] However, the use of physical masks and photomasks with features on the order of micrometers leads to a rather limited resolution for the resulting nanotube patterns. More recently, H. Dai and coworkers reported directed growth of nanotubes parallel to the plane of a silicon substrate using printing of the catalyst precursor materials onto the tops of towers or pillars on the substrate from a lithographically etching patterned silicon wafer;[9] L. Dai and coworkers prepared the region-specific growth of aligned nanotubes by pyrolysis of FePc using dizaonaphthoquinone (DNQ)−novolak photoresist patterns by the solvent-assisted micromolding (SAMIM) method.[10] We wish to find a process for growth of the aligned nanotube submicro-/nanopatterns that would simplify fabrication and reduce costs.

Previous studies show that the support materials for the catalysts play a key role in the type of nanotubes produced (such as the number of walls, the diameter, and the graphitization). A good catalyst material for CNTs synthesis necessarily exhibits strong metal−support interactions and possesses a high surface area and large pore volume. And it should retain these characteristics at high temperature without sintering.[11] The ordered mesoporous silica materials are excellent catalyst supports because they are mechanically and thermally stable and have strong interactions with metal catalysts such as Fe, Ni, and Co and also because they have a large pore size similar to the diameter of CNTs.[12] Herein, we use the micromolding in capillaries (MIMIC) technique[13,14] combined with three-dimensional (3D) cubic mesoporous silica films containing iron nanoparticles as catalysts to fabricate microscopically ordered carbon nanotube patterns with aligned orientation. This provides a new, easy method to control the orientation of aligned CNTs by the transition metal catalysts incorporated into ordered mesopores with a molecularly well-defined structure.[15] The open large pore allows efficient diffusion of reactant and intermediate hydrocarbon species and more efficiently promotes nanotube yield and purity.[12]

According to a MIMIC procedure (see Supporting Information), the patterned ordered mesoporous film catalysts were prepared: A poly(dimethylsiloxane) (PDMS) mold having a patterned relief structure on its surface was placed on the surface of a substrate to form a network of channels between them. A prepared solution[16] was placed at the open ends of the channels; the liquid spontaneously filled the channels by capillary action. After the solvent was evaporated, the PDMS mold was carefully removed; a patterned film of mesoporous silica material remained on the surface of the substrate. The film was calcined at 550 °C in air for 6 h to remove the block copolymer species and thereby produced patterned mesoscopically ordered porous solids.[17,18] Then, the substrate was placed in a quartz furnace tube and heated to 700 °C in flowing nitrogen at 400 cm^3/min, followed by a reduction at the same temperature in a flowing stream of 10% H_2/N_2 (220 cm^3/

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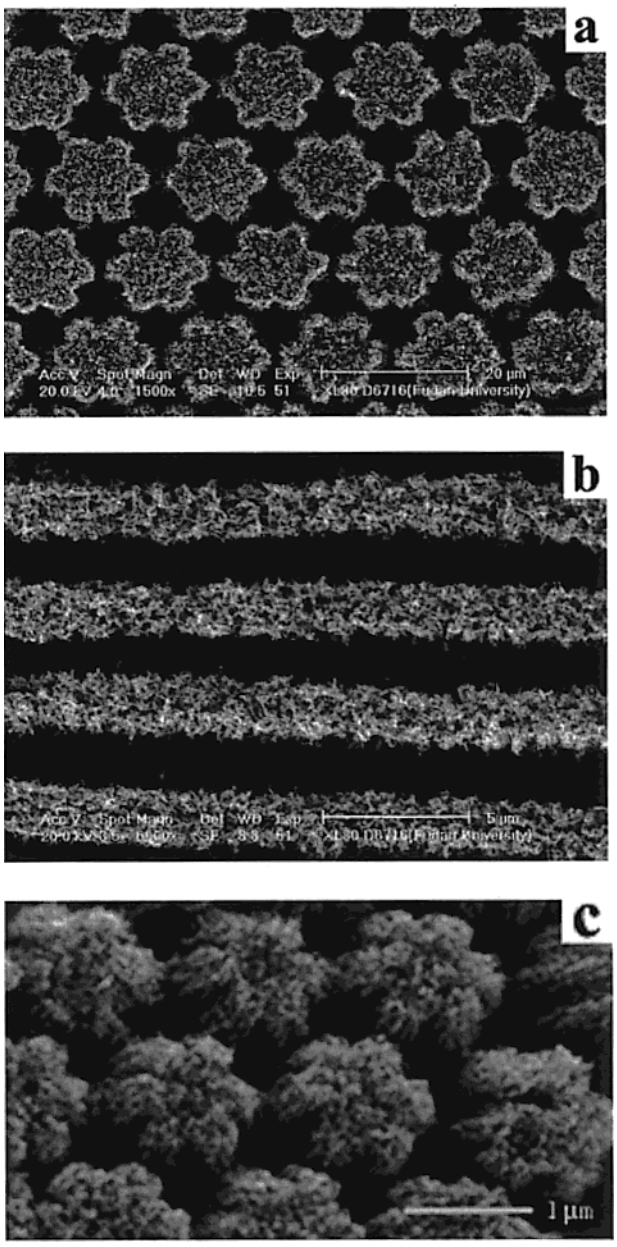

Figure 1. SEM images of aligned carbon nanotubes with different patterns grown from 3D cubic ordered mesoporous silica SBA-16 film containing an Fe catalyst (Fe/SiO_2 = 5.0 wt %). (a) Top view of patterned CNTs with a hexagonal pattern; (b) top view of CNTs with a strip-like pattern; (c) tilted view of CNTs with a hexagonal pattern.

min) for 5 h to obtain the reductive Fe nanoparticles in the pores. An acetylene−nitrogen mixture (2.5% mole ratio) was passed over the tube at a total rate of 205 cm^3/min for 10 min to deposit CNTs.

Patterned CNTs can be well prepared with high yield by the chemical vapor deposition (CVD) method on 3D cubic mesoporous silica films containing iron. The CNTs

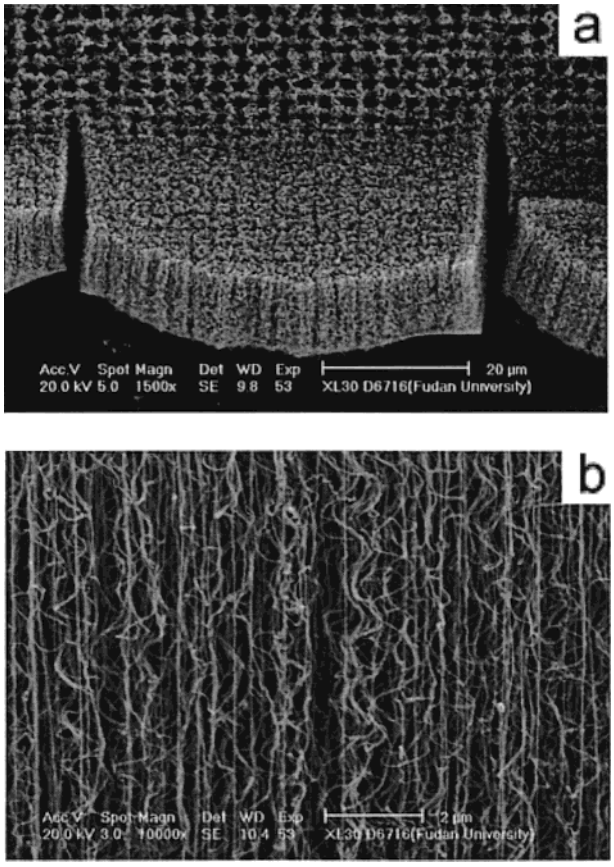

Figure 2. SEM images show the well-aligned carbon nanotubes with a square pattern grown from Fe-containing ordered mesoporous silica SBA-16 films (Fe/SiO_2 = 5.0 wt %) with different magnifications: (a) low; (b) high. In the top portion of (a), the top view of the square patterned CNTs is clearly shown. It is the side view of the well-aligned CNTs in the bottom of (a) where the catalyst films curve. (b) is the side view of aligned CNTs with high magnification.

are almost pure, as shown in Figures 1 and 2; the yield for CNT is about 400% (weight ratio compared with catalysts). SEM images show the high selectivity of the deposition process: the catalytic pattern leads almost exclusively to the growth of carbon nanotubes. The carbon nanotubes grown on the patterned cubic mesoporous silica film show the same pattern as the PDMS stamp, as shown in Figure 1. In the region without a catalyst pattern, no carbon nanotubes were formed, clearly demonstrating that the carbon nanotubes are controlled by the distribution of the catalyst. With use of different stamps, carbon nanotubes arrays with different patterns, such as strip-like, petal-like, square, and hexangular patterns, were successfully grown.

Figure 2a represents the image of the carbon nanotube arrays; it clearly shows that the carbon nanotubes grown on the Fe-containing 3D cubic mesoporous silica films are perpendicular to the substrate. In the high-magnification SEM images (Figure 2b), it can be observed that the arrays are composed of thousands of carbon nanotubes, which are closely compacted. These carbon nanotubes have lengths of about 10 μm. The diameter of the CNTs is about 20−40 nm. Iron catalysis particles are found at the tips of most of the obtained CNTs. The ordered alignment of the CNTs demonstrates that the growth and the orientation of the nanotubes arrays are controlled and templated by the ordered

(18) 3D highly 3D ordered cubic mesostructure of SBA-16 films are revealed by X-ray diffraction (XRD), TEM, and N_2 adsorption/desorption measurements. The XRD for the cubic mesoporous SBA-16 films show a well-resolved diffraction pattern with at least seven reflection peaks that can be indexed to the $Im3m$ space group (a = 18.2 nm). TEM images and 2D XRD show the SBA-16 films have a well-ordered cubic mesostructure and preferred orientation whose (100) plane is aligned parallel to the substrate. Calcined cubic SBA-16 films have a large pore size of 12.0 nm, a high BET surface area of 1100 m^2/g, and a pore volume of 1.03 cm^3/g.

mesoporous silica substrate. The reason for the formation of nanotubes arrays may be related to the pore structure of the 3D cubic ordered mesoporous silica SBA-16. There are many nanopores perpendicular to the substrate,[17] and they may serve as the template of the nanotubes. The 3D cubic ordered mesoporous silica SBA-16 films are more efficient than other mesoprous silica films such as the 2D hexagonal structure SBA-15 with a 1D channel parallel to the substrate plane because the orientation does not provide easy accessibility to the substrate for efficient diffusion of hydrocarbon species.[12] Our experimental results show that the hexagonal mesoporous silica SBA-15 films can promote the directed growth of carbon nanotubes parallel to the substrate plane (see Supporting Information), clearly indicating that structures of ordered mesoporous silica films can control the orientation of the nanotubes.[11]

Transmission electron microscopy (TEM) (see Supporting Information) is used to determine the interior and wall structures of the carbon nanotubes. It shows a cross-sectional view of a typical thinner carbon nanotube. The outside diameter of this carbon nanotube is nearly 20−40 nm, in agreement with that obtained from SEM. TEM measurements also reveal that the nanotube is a multiwalled centrally hollow tube (Supporting Information). The fringe on each side of the tube represents an individual cylindrical graphilitic layer. This particular carbon nanotube has a structure with approximately 10 walls of graphitized carbon. However, the amount of the Fe catalyst embedded in the silica substrate can only relate to the yield of the nanotubes and not change the nanotubes diameter. As the amount of Fe catalyst increases, the yield of the nanotube improves greatly. Co catalyst incorporated in ordered 3D cubic mesoporous silica SBA-16 films can also be used to grow the well-aligned CNT patterned, but compared to Fe catalyst, the yield of the CNT is much lower. So it is still our goal to find new catalyst support materials for yielding a large amount of CNTs with small diameters.

In summary, we have proposed an easy method for growth of well-aligned patterned CNTs arrays using 3D cubic ordered mesoporous silica films as the catalyst support combined with a soft-lithographic technique. This synthetic approach shows fascinating possibilities for directed growth of CNTs that could be used for large-area, low-cost, flexible electronic and photonic devices.

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Supporting Information Available: Figures of the fabricating procedure of well-aligned nanotube patterns by the MIMIC method, CNTs grown from the 2D hexagonal structure SBA-15 parallel to the substrate, and TEM images showing the multiwalled carbon nanotubes grown from a SBA-16 film with different magnifications (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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