

Directed Growth of Free-Standing Single-Walled Carbon Nanotubes

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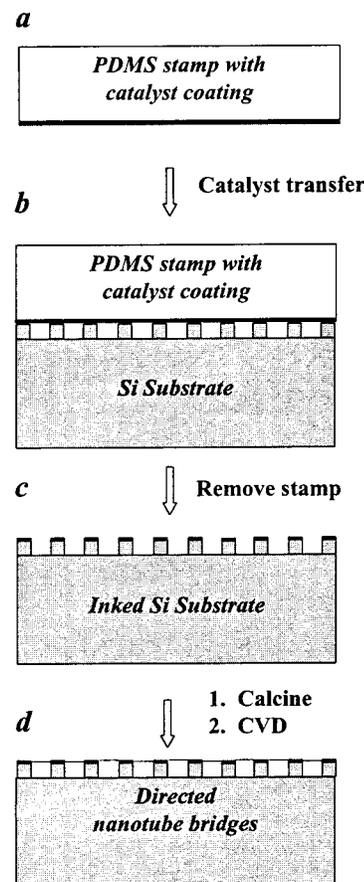
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The ability to controllably obtain ordered carbon nanotube^{1,2} architectures is important to fundamental characterizations and potential applications of novel molecular wires. Controlled synthesis involving chemical vapor deposition (CVD) has been an effective strategy to order multiwalled nanotubes (MWNTs) on surfaces.^{3–5} For instance, MWNTs self-oriented perpendicular to substrates and assembled into regular arrays were demonstrated recently.⁵ Single-walled nanotubes (SWNTs) are true molecular wires with their diameters in the range of ~ 1 –5 nm such that a SWNT is either metallic, semiconducting, or semimetallic depending on chirality.⁶ Synthesis of structurally perfect SWNTs has been demonstrated by a methane CVD method.^{7,8} This synthetic approach has allowed individual SWNT wires to be grown from controlled surface sites by catalyst patterning⁹ and has led to interconnecting SWNT electrical devices.^{10,11} However, obtaining SWNTs in aligned orientations perpendicular or parallel to surfaces has not been possible thus far.

In this communication, we report the first directed growth of single-walled nanotubes parallel to the plane of a silicon substrate. The SWNTs are suspended bridges grown from catalyst material placed on top of regularly patterned silicon tower structures. The key synthetic step in our approach involves developing a series of liquid-phase catalyst precursor materials. The liquid materials allow for uniform film formation and large-scale catalyst patterning. Contact printing techniques were used to selectively deposit catalyst precursor materials on top of the silicon tower arrays. Calcination led to the formation of catalyst particles confined on the tower tops and subsequent CVD growth yielded SWNTs emanating from the towers. Directed free-standing SWNT networks were formed by nanotubes growing to adjacent towers and becoming suspended above the surface. Rational design of tower arrangements within our approach could lead to a variety of directed SWNT architectures.

Our growth strategy begins with developing liquid-phase catalyst precursor materials consisting of three general components: inorganic chloride precursors, a removable triblock copolymer serving as the structure-directing agent for the chlorides, and an appropriate alcohol for dissolution of the

Scheme 1. Schematic Procedures for Directed Growth of Suspended SWNTs



inorganic and polymer compounds. The block copolymer¹² is P-103 or P-123 poly(alkylene oxide) $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_y(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ ($x \approx 22$, $y \approx 52$ for P-103 and $x \approx 24$, $y \approx 62$ for P-123). The inorganic chlorides include $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, SiCl_4 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and MoO_2Cl_2 , and the alcohol used is *sec*-BuOH, EtOH, or MeOH. In a typical preparation, 0.60 g (2.5 mmol) of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.42 g of SiCl_4 (2.5 mmol) are dissolved in 15 mL of an EtOH/MeOH mixture (2:1 by volume). Then, 0.50 g of P-103 triblock copolymer (MW = 4950) is added with vigorous stirring. Next, 0.084 g (0.31 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.003 g (0.015 mmol) of MoO_2Cl_2 are added to achieve a clear yellow solution, which afforded a catalyst precursor material.

Previously, the approach of using solutions of block copolymers, aluminum, and silicon chloride has been extremely successful in the synthesis of high surface area mesoporous alumina/silica oxides.^{13,14} With the addition of small amounts of iron and molybdenum chlorides, we find that the liquid precursor mixture led to a material containing iron oxide nanoparticles formed on a alumina/silica phase after solvent and polymer removal by calcination. This material has a high surface area (300 m^2/g) and large pore volume (0.67 mL/g) that are desired elements for an active catalyst for SWNT synthesis.⁸ Also, we find that the alumina/silica material derived by the block-copolymer approach is a useful support that upon metal impregnation and calcination leads to active catalysts for SWNT synthesis.

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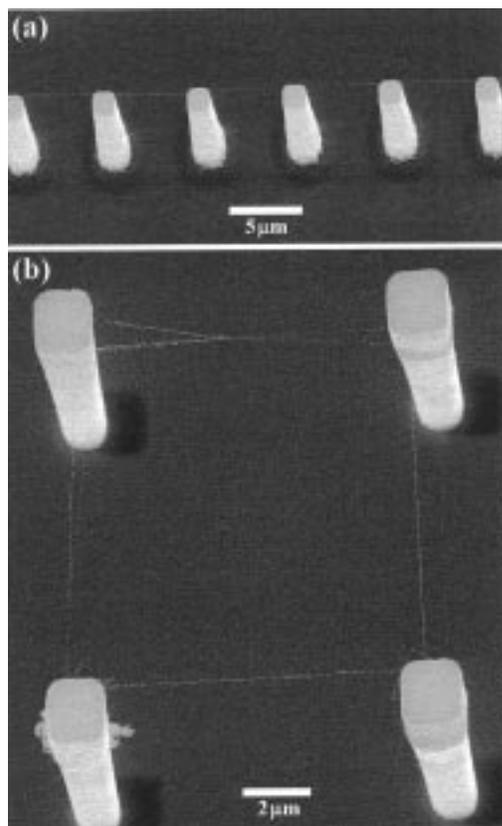


Figure 1. (a) SEM image of a suspended SWNT power line. (b) SEM image of a square of suspended SWNT bridges.

The procedure for directed growth of suspended SWNTs using the liquid catalyst precursors is schematically shown in Scheme 1. First, a flat piece of poly(dimethylsiloxane) (PDMS) elastomer stamp is etched in an oxygen plasma to render the surface hydrophilic,^{15,16} followed by spin coating the stamp with the catalyst precursor. The inked stamp is then printed onto a silicon substrate containing regular arrays of towers fabricated by

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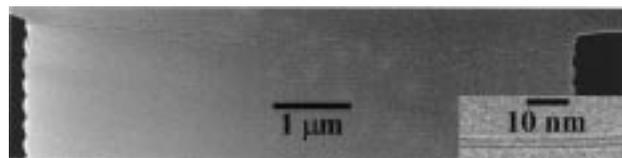


Figure 2. TEM image of a SWNT bridge suspended between silicon towers. Inset: A high magnification TEM image showing the structure of a synthesized SWNT.

photoresist patterning and anisotropic etching. The catalyst material is thus transferred to the tower tops and allowed to dry in an oven heated to 60 °C for 5 min. The substrate is then heated in air at 400 °C for 4 h followed by calcination in air at 700 °C for 30 min to remove the polymer component. SWNTs are then synthesized on the substrate by chemical vapor deposition of methane at 900 °C in a 1-in. tube furnace using a methane flow of 750 mL/min for 20 min.

Examining under a scanning electron microscope (SEM), we find that highly directional suspended SWNTs are formed on the synthesized sample. The directions of the suspended tubes are determined by the pattern of the towers. Well-aligned SWNT bridges are obtained in an area of the substrate containing isolated rows of towers as shown in Figure 1a, where suspended tubes forming a power-line structure can be seen. In an area containing towers in a square configuration, a square of suspended nanotube bridges is obtained (Figure 1b). Directionality of the suspended tubes is simply a result of the designed substrate. During the CVD growth, nanotubes emanate from the top of the towers. Nanotubes growing toward adjacent towers become suspended, whereas tubes growing toward other directions fall onto the sidewalls of the towers (not easily resolved under SEM). We have confirmed that the suspended bridges are individual or bundled SWNTs by transmission electron microscopy (TEM). Figure 2 shows a high-magnification TEM image of a SWNT and a low-magnification image of a suspended tube.

In summary, the directed growth of suspended SWNTs is demonstrated for the first time. Our approach involves developing a new type of catalytic material, contact-printing of catalyst onto rationally designed substrates and CVD synthesis. This approach should open new possibilities in fundamental characterization and device applications of organized nanowire architectures in a suspended state or after being transferred onto flat substrates.

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