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Self-networking of carbon nanotubes

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Carbon nanotube self-assembly into honeycomb-networks *via* controlling the ratio of the catalyst over hydrocarbon in the vapor phase using a tunable chemical vapor deposition process.

There is intense interest in understanding the growth mechanism and controlling growth morphology of carbon nanotubules. Here we report an interesting self-networking behavior of carbon nanotubes by tunable, catalytic decomposition of hydrocarbon (differing from other processes in that the catalyst and hydrocarbon are introduced simultaneously, the growth of nanotubes being tuned by the ratio of catalyst to hydrocarbon). At specific ratios, the carbon nanotubes formed are self-organized into honeycomb networks. Prolonged deposition thickens the walls of the honeycombs, gradually filling the central holes and finally forming a packed film of vertically aligned carbon nanotubes. Our results provide a possible way to control the growth pathways of carbon nanotubes.

Carbon nanotubes are macromolecular structures, nanosized in diameter and microsized in length, with outstanding properties that are very attractive for nanotechnology, and intense effort has been directed towards producing aligned nanotube arrays for applications such as field emission.[1–7] Although packed films of carbon nanotubes can be produced by catalytic chemical vapour deposition (CVD) of hydrocarbons,[8–10] the initial growth stage of carbon nanotubes remains a mystery. Here, we report a fascinating nucleation and growth feature of nanotubes *via* a tuneable CVD process, which dominates the growth process of nanotubes films on planar silica substrates.

In our experiments carbon nanotubes are grown on thermally oxidized silicon wafers at ~ 800 °C by a tuneable CVD process using ferrocene ($FeC_{10}H_{10}$) and xylene (C_8H_{10}) as catalyst and carbon precursors; both are pre-heated, co-evaporated and fed *via* the vapour phase. By adjusting the ferrocene/xylene ratio one can tune the growth pathways of carbon nanotubes toward a packed film of vertically aligned nanotubes. As reported recently, a better control of the catalyst/hydrocarbon ratio may result in the formation of crystallites (at a ratio of <0.01 g ml^{-1}) and spherulites (at a ratio of >0.2 g ml^{-1}) of carbon nanotubes, which, at prolonged deposition, develop into a packed film through space filling the silica surface.[11] The progress of the nucleation and growth of nanotubes into a dense film can be monitored by observing the substrates at different CVD stages.

Fig. 1 shows SEM images representative of nanotube deposition sequences at a ferrocene/xylene ratio of 0.01 ~ 0.2 g ml^{-1}. Carbon nanotubes grown at this ratio are self-organized into honeycomb-like networks. Fig. 1(a) shows a SEM image of a typical nanotube honeycomb. The central hole of the honeycomb is several μm in diameter, and the hexagonal walls are < 1 μm thick. Fig. 1(b) is an invert of Fig. 1(a). From these we notice that carbon nanotubes are nucleated from circular centres and grow outwards horizontally. When the nanotubes from neighbouring centres meet, they stop growing horizontally and start to grow vertically together, thus forming the honeycombs perpendicular to the substrate (see Fig. 1(c)).

At prolonged deposition, additional carbon nanotubes nucleate from the central holes of honeycombs and grow outwards. They stop growing horizontally when meeting the walls of honeycombs and start to grow vertically (parallel to the walls), thus thickening the walls and gradually filling the central holes, finally forming a continuous film of vertically aligned carbon nanotubes. Fig. 1(d) shows an interface where the honeycombs of nanotubes developed into a packed film. An enlarged image of the interface, see Fig. 1(e), shows the evolution process at prolonged deposition. The carbon nanotubes forming the continuous film are multiwalled and of a diameter of 20 ~ 30 nm (see inset of Fig. 1(f)), and are well vertically aligned, see Fig. 1(f).

We also performed experiments using ferrocene only in the CVD precursor to see if Fe nanoparticles are deposited in any desired patterns that could act as templates for this honeycomb-networking growth, but no such evidence was found. In an early study, the authors found that the ratio of the catalyst over hydrocarbon played a key role in determining the early growth stages of nanotubes. For example, nanotubes first self-assemble into structures of spherulites and crystallites at a catalyst/hydrocarbon ratio of >0.2 g ml^{-1} and <0.01 g ml^{-1}, respectively, and then develop into a continuous film through space filling the substrate surface.[11] For these reasons, the honeycomb growth could possibly be a specific mode triggered at this catalyst and hydrocarbon combination by the tuneable CVD process. The nanotubes grown at different catalyst/

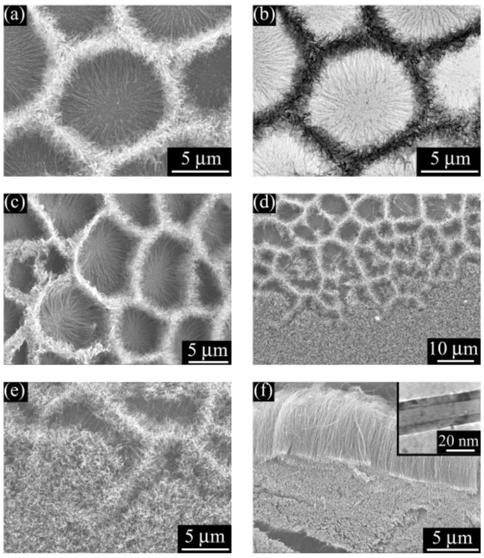

Fig. 1 SEM images showing the growth of carbon nanotubes honeycombs on silica substrates by CVD: (a) a typical honeycomb of nanotubes; (b) an inverse image of (a); (c) an image showing that the honeycombs are perpendicular to the substrate, taken by tilting the sample; (d) an interface where the honeycombs develop into a continuous film of nanotubes; (e) a high magnification image of the interface; and (f) alignment of nanotubes forming the continuous film. Inset is a TEM image showing the diameter of the nanotubes.

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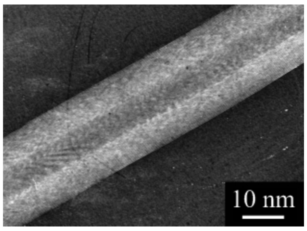

Fig. 2 A HRTEM image of the carbon nanotubes forming the honeycomb networks.

hydrocarbon ratios, though forming islands of different morphology at the beginning of the growth, *i.e.* crystallites, spherulites, honeycomb-networks, are no different in structure. Fig. 2 shows a typical HRTEM image of the carbon nanotubes.

This honeycomb networking behaviour of nanotubes is of great application interest; for example, one can stop the growth at desired stages to access either honeycombs with controlled thickness of walls or packed films of vertically aligned nanotubes for different application purposes such as field emission. The present study provides a clear picture of the nucleation, growth and organization procedure of nanotubes, and also a technique to tune the pathways by which nanotubes can assemble and grow.

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