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LETTER TO THE EDITOR

Film growth of pillars of multi-walled carbon nanotubes

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Abstract

Using ferrocene as the catalyst and xylene as the precursor, films of multi-walled carbon nanotubes (CNTs) that are well aligned can be synthesized on flat substrates by chemical vapour deposition. Here we report that, by controlling the growth speed of CNTs at specific catalyst/carbon ratios, vertically aligned pillars of densely packed nanotubes with uniform diameters (within 10–30 μm) and lengths of up to 0.3–0.4 mm can be fabricated on a large scale on planar SiO_2 substrates, forming a continuous film. The growth mechanism of the pillars was also investigated by observing the growth of CNTs at different growth stages.

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted much research effort due to their unique properties and possible applications in nanodevices [1–4]. For example, CNTs have outstanding electrical and mechanical properties and offer the potential to serve as field emitters [5–7] and building blocks for future device architectures [8–10]. An essential prerequisite for realizing these applications is to devise ways to grow CNTs in a controlled manner (location, orientation, length, diameter, etc) on flat substrates on a large scale. This has been the research focus in recent years in this field, and has aroused tremendous interest in investigating the growth mechanism of individual nanotubes and films of densely packed CNTs [11–14].

Arrays or films of CNTs can now be fabricated on planar substrates by chemical vapour deposition (CVD) with hydrocarbon as the carbon source and transition metal particles, either pre-patterned on substrates [7] or introduced together with hydrocarbon, as the catalyst [15]. CNTs in arrays or films are well aligned to each other and densely packed, and sometimes tightly bonded by the van der Waals interaction into long cylindrical structures, namely pillars consisting of tens of thousand of CNTs or more [16]. The pillars of CNTs can be quite useful in energy storage, electrodes and field emission sources. They have also attracted interest to

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investigate the growth mechanism of the pillars in order to devise ways to control the growth of pillars [17].

An efficient way to grow CNTs is the CVD of ferrocene and xylene [15], with which arrays of CNTs can be prepared on flat substrates via the substrate–site selective growth approach along one, two or three directions [13]. With this approach it is also possible, i.e. by varying the ratio of ferrocene over xylene in the deposition, to grow pillars of CNTs on a large scale [17].

Here we report a simple method for growing continuous films of pillars of CNTs, i.e. adjusting the speed of growth of CNTs at a defined ratio of ferrocene over xylene during deposition, as well as the investigation on the growth mechanism of the pillars.

CNTs were grown on Si(001) substrates, covered by a 100 nm-thick SiO_2 cap layer, by CVD of xylene and ferrocene at ∼800 °C in a quartz tube furnace that was first pumped down to $\sim 10^{-3}$ Torr and then backfilled with flowing argon to a pressure of ∼100 Torr. The ferrocene was dissolved into xylene to form a solution to a ratio of 0.01 g ml^{-1}, then the solution was introduced into the quartz tube by an injector when the temperature stabilized at ∼800 °C. To grow pillars of CNTs, a 10 ml solution was injected into the tube via two stages, i.e. first at a fast injection speed of ∼2 ml min^{-1} and then at a slow speed of ∼0.5 ml min^{-1} until the whole solution was injected. The growth morphology and structure of the CNTs were examined and characterized by SEM and TEM, respectively. To investigate the growth mechanism of the pillars, the deposition was stopped at different growth intervals.

CNTs synthesized by the two-speed deposition approach formed a continuous film on the substrate surface. Figure 1 shows typical SEM micrographs of the film of pillars, broken with sharp tweezers. This film, unlike what we reported earlier [13, 14], was not built up by aligned individual nanotubes. Instead, it was formed by densely packed, long (>400 μm) cylindrical structures, namely pillars, as shown by figure 1(a). The pillars that form the film are quite well aligned and each pillar consists of tens of thousands aligned CNTs or more. These are ∼400 μm long (figure 1(b)), ∼10–30 μm in diameter (figure 1(c)), and vertically aligned. Note that the pillars produced by this approach (see figure 1(a)) are covered by a thin film which, as we will see later, was deposited on the substrate at the very first stage of deposition and consists of mainly carbon and catalyst particles. When the thin connecting film was removed, one can clearly see the uniformity of the diameter of the pillars and their alignment (figure 1(c)). The nanotubes forming the pillars, as shown by figure 1(d), are multi-walled, with diameters of ∼30–50 nm.

The growth mechanism of the film of pillars via this approach is intriguing. According to our previous studies, CNTs can organize themselves into well-shaped growth units at an early stage of growth, based on which a continuous film was developed over prolonged deposition [14]. This suggests that the formation of a film of CNT pillars by this approach might also be related to the early growth stages of CNTs, which could be determined by the injection speed (or growth speed of CNTs) at this specific ratio of ferrocene over xylene, i.e. 0.01 g ml^{-1}. We therefore conducted two series of experiments to clarify the influence of the injection speed on the growth morphology of the CNT film, at an early stage of growth, by using two injection speeds, i.e. ∼0.5 and 2 ml min^{-1}, respectively. It was found that the injection speed did influence greatly the early growth stages of CNTs.

At the very first stage of deposition in both experiments, a thin film containing carbon and catalyst particles was deposited on the substrate surface. The catalyst particles and carbon were formed through the decomposition of ferrocene and xylene at ∼800 °C, respectively. This film was actually the film covering and connecting the CNTs pillars after prolonged deposition, as shown in figure 1(a). At this stage, dimples of approximately several microns in diameter were also observed in the thin film in both experiments (see figure 2(a)). The dimple is the origin of the pillars. From the trace of the dimple, broken with sharp tweezers

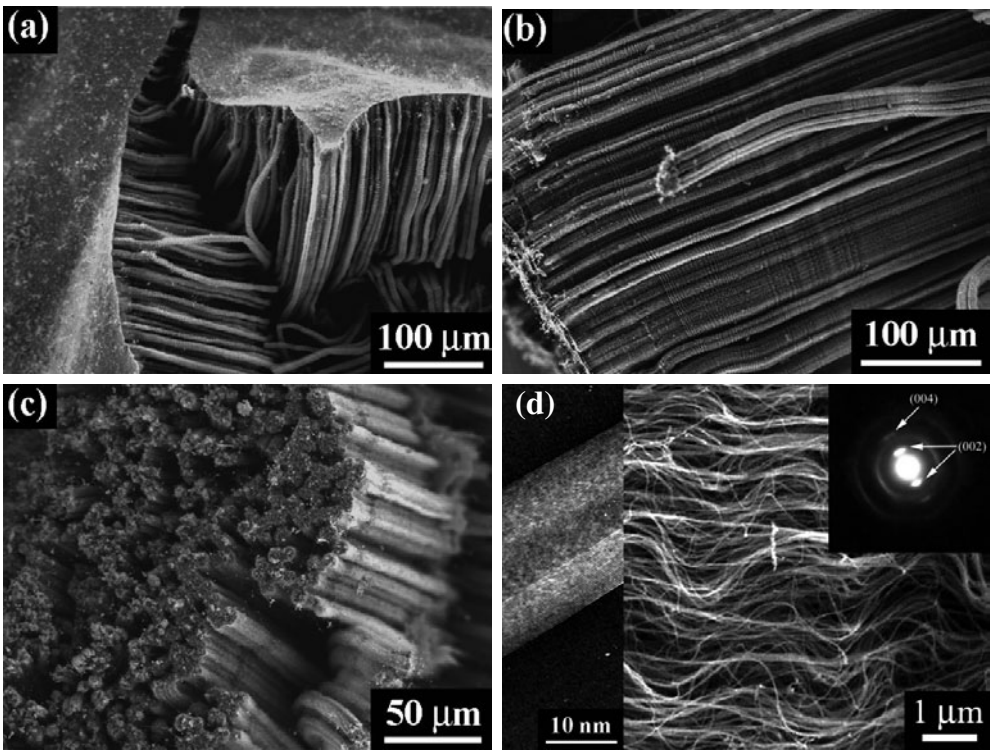

Figure 1. SEM and TEM images of a CNT-pillar film grown by a two-speed injection approach: (a)–(c) show the diameter, length and alignment of CNT pillars forming the film; (d) shows the diameter, structure and alignment of CNTs forming the pillars. The insets of (d) are an HRTEM image and the SAD pattern of individual CNTs.

(see figure 2(b)), one sees that aligned nanotubes had already developed there, while there is almost no observable growth outside. The reason for the preferred nucleation of CNTs within the dimple is that there are more catalyst particles than at other sites. The insets of figure 2(b) show the distribution of catalyst particles inside (upper right) and outside (lower right) the dimple. One can clearly see the difference in the density of catalyst particles in both regions. Naturally, nanotubes first started to nucleate and develop in the regions with more catalyst particles, and their development in these areas led to the formation of dimples in the thin film, which served as the origins of the pillars due to the vertically aligned growth of CNTs. The reason for the preferred partition of the catalyst particles is not clear and needs further investigation.

Although the very first deposition stages observed for both experiments are very similar, prolonged deposition with both injection speeds however led to different morphologies of the CNTs film. Using an injection speed of $\sim$0.5 ml min^{-1} (as reported previously) resulted in a continuous film of aligned individual nanotubes, developed from the CNTs crystals originating from the dimples [14]. At a fast injection speed of $\sim$2 ml min^{-1}, different from that observed at a low injection speed of $\sim$0.5 ml min^{-1}, the dimples did not develop into crystal-like structures. Instead, nanotubes were grown vertically aligned beneath the film of the dimple at a relatively higher growth speed than at other places, thus forming embryos of CNTs pillars, as shown by figure 2(c). If deposition was continued at the same injection speed of $\sim$2 ml min^{-1}, as shown by figure 2(d), the fast growth of CNTs within the dimples flapped over the pillar embryos

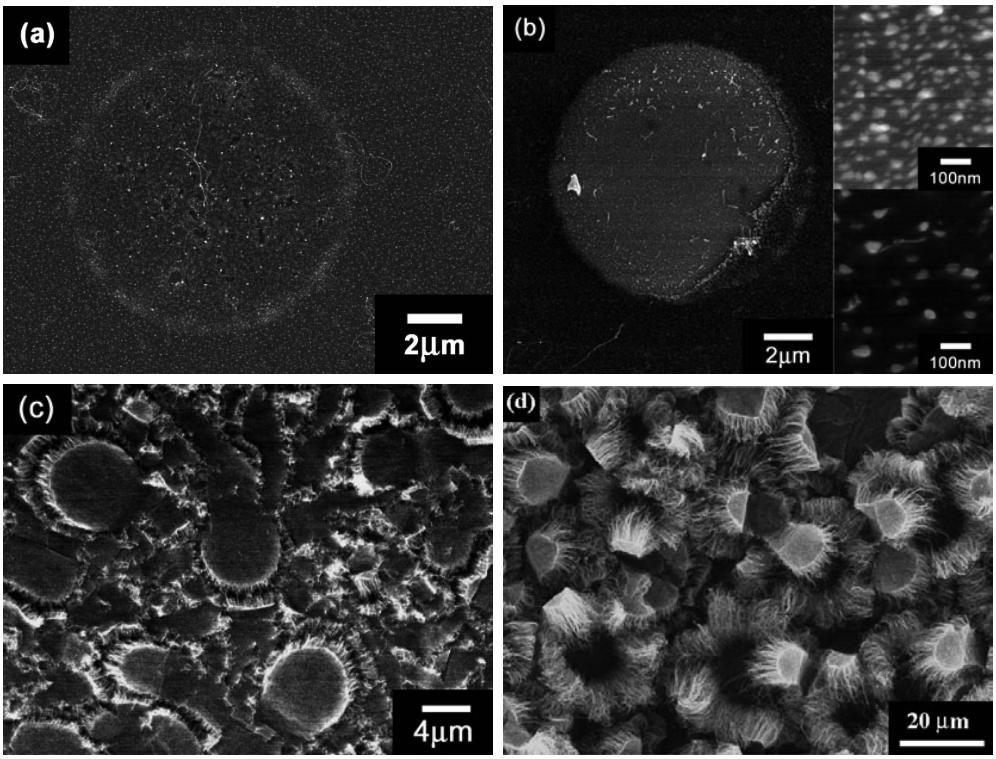

Figure 2. SEM images of CNTs deposited at a fast injection speed of ∼2 ml min^{-1}: (a) a typical dimple formed in the film at the initial stage of growth; (b) the trace of the dimple—the insets show the difference in the distribution of catalyst particles inside (upper right) and outside (lower right) the dimple; (c) the development of the dimples into embryos of the pillars; and (d) pillars flapped over at prolonged deposition at the fast injection speed of ∼2 ml min^{-1}.

and, obviously, could not lead to the formation of a continuous film of aligned pillars, shown by figures 1(a)–(c). Therefore, a lower growth speed is needed to flatten the pillar embryos, i.e. to avoid development into a morphology shown by figure 2(d) after they were developed (see figure 2(c)). This is why we used a two-step injection approach to form the film of CNTs pillars. It is thus concluded that the first fast-speed injection was used to form the embryos of CNTs pillars and the following low-speed injection was intended to avoid the flapping over of the embryos, thus leading to a continuous film after prolonged deposition.

In summary, we have demonstrated a simple two-speed injection method for the large-scale fabrication of pillars of CNTs on flat substrates. We have also demonstrated the growth mechanism of the CNTs pillars via this approach. The large-scale fabrication of CNT pillars on planar substrates could be useful for the application of CNTs in energy storage, field emission source, and electrodes etc.

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