A review: controlled synthesis of vertically aligned carbon nanotubes

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Abstract
Carbon nanotubes (CNTs) have developed into one of the most competitively researched nano-materials of this decade because of their structural uniqueness and excellent physical properties such as nanoscale one dimensionality, high aspect ratio, high mechanical strength, thermal conductivity and excellent electrical conductivity. Mass production and structure control of CNTs are key factors for a feasible CNT industry. Water and ethanol vapor enhance the catalytic activity for massive growth of vertically aligned CNTs. A shower system for gas flow improves the growth of vertically aligned single walled CNTs (SWCNTs) by controlling the gas flow direction. Delivery of gases from the top of the nanotubes enables direct and precise supply of carbon source and water vapor to the catalysts. High quality vertically aligned SWCNTs synthesized using plasma enhance the chemical vapor deposition technique on substrate with suitable metal catalyst particles. This review provides an introduction to the concept of the growth of vertically aligned SWCNTs and covers advanced topics on the controlled synthesis of vertically aligned SWCNTs.

Key words: vertically aligned carbon nanotubes, chemical vapor deposition, Ethanol based CVD, Water assisted CVD, Plasma enhanced CVD

1. Introduction

Carbon nanotubes (CNTs) consist of rolled graphene sheets built from sp² hybridized carbon atoms; they have extraordinary mechanical [1-15], thermal [10,16-28] and electronic [29-43] properties and hold great promise for future applications. Their remarkable properties have attracted intense scientific interest as numerous theoretical and experimental studies of their properties [1-15,17-28] have put forward possible electronic [33,44-50], field emission [51-55], electrochemical device, battery [56-59], molecular sensor [60-64], and gas storage [65-70] applications. The one dimensionality of the nanotube structure has given rise to exceptional physical and chemical properties and potential applications. For different applications, desired characteristics and different properties are needed. A single walled CNT (SWCNT), especially, can behave as a well-defined metallic, semiconducting or semi-metallic tube depending on the chirality and diameter, although there is no difference in the chemical bonding or any doping or additional functionalization between them. To accomplish the precisely controlled synthesis of an SWCNT structure in terms of the diameter, chirality, orientation, position and density, chemical vapor deposition (CVD) techniques [71-77] are becoming a strong manufacturing route compared to other synthesis methods such as electric arc-discharge, laser vaporization and electrolysis [78,79]. Arc discharge and laser vaporization processes can produce only randomly tangled CNTs mixed with various impurities. Research on CNT growth using CVD techniques has been initiated by Ren and Huang [80] and was first used to demonstrate the control of the synthesis of aligned and ordered large diameter multi walled CNT (MWCNT) structures on the top surface of glass substrates by plasma enhanced CVD (PECVD). CNTs can self-align vertically during the CVD process, and can be made into patterns perpendicular to the substrate surface. The mechanism of
nanotube self-alignment typically involves van der Waals interactions between CNTs. CNTs interact with their neighboring tubes via van der Waals forces to gain rigidity, and that allows the nanotubes to self-align and grow perpendicular to the substrate surface. To synthesize vertically aligned MWCNTs and SWCNTs, various CVD techniques have been developed. In this review, we review ethanol based CVD, water-assisted CVD and PECVD for the synthesis of vertically aligned SWCNTs.

2. CVD for Growth of Vertically Aligned SWCNTs

2.1. Ethanol based CVD

The CVD method basically involves the decomposition of hydrocarbon molecules (e.g., methane, benzene, acetylene, naphthalene, ethylene, etc.) catalyzed by the transition metal. The synthesis process involves heating a thin film metal catalyst (e.g., Co, Ni, Fe, Pt or Pd deposited on substrates such as silicon, graphite or silica) to high temperature and flowing a hydrocarbon gas through the tube reactor. To synthesize vertically aligned SWCNTs, not only is it necessary to have highly dense and well-dispersed catalyst nanoparticles but it is also necessary to have high activity and long lifetime for the catalyst [81,82]. In the CVD method, growth of CNTs is seriously limited by the short lifetime and the low activity of the catalyst nanoparticles. The resulting short lifetime and low activity of the CNTs synthesis has not only reduced the availability of CNTs, but also the amorphous carbon covered catalysts remain as impurities in the as-grown materials. Maruyama and coworkers first reported the synthesis of high-purity SWCNTs using alcohols such as methanol and ethanol as carbon sources [83]. In the ethanol based CVD process, controlled amounts of ethanol molecules (C\textsubscript{2}H\textsubscript{5}OH) not only work as a carbon source to grow CNTs but also serve as a weak oxidizer that can selectively remove the amorphous carbon efficiently during CNT growth, leaving only pure CNTs as product [84]. Fig. 1 shows a schematic drawing of a typical ethanol based CVD system. In a typical ethanol based CVD procedure, a 20 nm thick Al film is deposited onto an Si/SiO\textsubscript{2} (1000 Å thick oxide) wafer by using a sputter coater or e-beam evaporator. Maruyama and coworkers first reported the synthesis of high-purity SWCNTs using alcohols such as methanol and ethanol as carbon sources [83]. 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Catalysts. Balancing the relative levels of ethylene and water is one of the critical factors to maximize catalytic lifetime for millimeter-scale growth of SWCNTs [81]. Hata et al. [81] also demonstrated ~1 cm long vertically aligned SWCNT growth on A4 paper size substrate using gas supply direction control, as shown Fig. 5 [85]. Under lateral gas flow growth, the gases can diffuse by typical molecular diffusion on the surface of the substrate. This typical diffusion allows a uniform and optimum supply of gases to the catalysts, as shown in Fig. 6a [85]. However, for top gas flow growth, the shower head forces the gases to flow into the gap of the SWCNTs with minimum flow around the vertically aligned SWCNTs, and this facilitates a uniform and optimum supply of carbon and of water vapor to the catalysts for growth of SWCNTs. The gases can also diffuse parallel to the SWCNT alignment direction and encounter minimal interruption, as depicted in Fig. 6 [85]. These results confirm the observed sensitivity, stability, uniformity, high carbon efficiency and high yield of top-flow growth. Noda et al. [86] reported millimeter thick SWCNT forest growth using an aluminum oxide supported Fe catalyst system and a water assisted CVD process. They demonstrated the hidden role of Fe catalyst support. Their CVD was carried out by using C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2}/H\textsubscript{2}O/Ar. Fig. 7 shows the effect of the catalyst supports on vertically aligned SWCNTs, resulting in vertically aligned CNT arrays. After a 30 min reaction time, the quartz tube is cooled to room temperature.

Hahm and coworkers recently reported the millimeter scale synthesis of highly dense vertically aligned SWCNTs using ethanol based the CVD process depicted in Fig. 3. Fig. 3a shows a cross-sectional optical image of vertically aligned SWCNTs synthesized with the ethanol based CVD process. Figs. 3b-d show representative scanning electron microscope (SEM) images of a highly dense and vertically aligned SWCNT forest (Figs. 3b and c are a low magnification SEM image and a high magnification SEM image, respectively) and a micro patterned growth of vertically aligned SWCNT wall structures (Fig. 3d). It can be clearly seen that the ethanol based CVD system is very effective in growing CNTs.

### 2.2. Water assisted CVD

The water assisted CVD process is one of the well-known techniques for synthesis of vertically aligned SWCNTs. Hata et al. [81] reported millimeter-scale vertically aligned SWCNTs using the water assisted ethylene CVD process. 2.5 mm long vertically aligned SWCNTs were synthesized using Fe/Al or aluminum oxide multilayers on Si wafers, as shown Fig. 4. They found that the water vapor acts as a promoting and preserving agent for the catalytic activity of the metal catalyst nanoparticles. Balancing the relative levels of ethylene and water is one of the critical factors to maximize catalytic lifetime for millimeter-scale growth of SWCNTs [81]. Hata et al. [81] also demonstrated ~1 cm long vertically aligned SWCNT growth on A4 paper size substrate using gas supply direction control, as shown Fig. 5 [85]. Under lateral gas flow growth, the gases can diffuse by typical molecular diffusion on the surface of the substrate. This typical diffusion allows a uniform and optimum supply of gases to the catalysts, as shown in Fig. 6a [85]. However, for top gas flow growth, the shower head forces the gases to flow into the gap of the SWCNTs with minimum flow around the vertically aligned SWCNTs, and this facilitates a uniform and optimum supply of the carbon and of water vapor to the catalysts for growth of SWCNTs. The gases can also diffuse parallel to the SWCNT alignment direction and encounter minimal interruption, as depicted in Fig. 6 [85]. These results confirm the observed sensitivity, stability, uniformity, high carbon efficiency and high yield of top-flow growth. Noda et al. [86] reported millimeter thick SWCNT forest growth using an aluminum oxide supported Fe catalyst system and a water assisted CVD process. They demonstrated the hidden role of Fe catalyst support. Their CVD was carried out by using C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2}/H\textsubscript{2}O/Ar. Fig. 7 shows the effect of the catalyst supports on vertically aligned SWCNTs.
Vertically aligned SWCNTs can be synthesized using the PECVD technique on substrates with suitable metal catalyst particles. Amaratunga and coworkers reported the growth of vertically aligned CNTs using a direct current PECVD technique with an Ni and Co catalyst system. Their results show that the alignment of vertically aligned CNTs depends on the electric field and that the growth rate can be changed depending on the CNT diameter, which reaches a maximum as a function of growth temperature. Dai and coworkers developed large scale ultra-high-yield synthesis of vertically aligned SWCNTs using a molecular oxygen-assisted PECVD technique on a full 4 inch wafer scale, as shown in Fig. 8. Their results show that PECVD also requires the formation of a dense and relatively uniform layer of catalyst nanoparticles. This layer is essential for vertically aligned SWCNT growth. For 10 min growth, the length of the vertically aligned SWCNTs is ~10 μm, as shown in Fig. 8d. Figs. 8e and f show that the vertically aligned CNTs are single walled. Kawarada and coworkers also reported a long, millimeter scale growth of vertically aligned SWCNTs using growth using the water assisted CVD process. Differences of height of vertically aligned SWCNTs are evident between the Fe catalysts with aluminum oxide (Al₂O₃) supports. SWCNT forests grow thick by using either of these two catalysts when Fe catalyst layer is wider than 0.6 nm. However, vertically aligned SWCNTs grow longer only with the Fe/Al₂O₃ catalyst when the Fe catalyst layer is thinner than 0.6 nm.

2.3. Plasma enhanced CVD

High quality SWCNTs and MWCNTs can be grown using high pressure arc-discharge, high pressure CVD and high pressure laser ablation. Vertically aligned SWCNTs can be synthesized using the PECVD technique on substrates with suitable metal catalyst particles. Amaratunga and coworkers reported the growth of vertically aligned CNTs using a direct current PECVD technique with an Ni and Co catalyst system. Their results show that the alignment of vertically aligned CNTs depends on the electric field and that the growth rate can be changed depending on the CNT diameter, which reaches a maximum as a function of growth temperature. Dai and coworkers developed large scale ultra-high-yield synthesis of vertically aligned SWCNTs using a molecular oxygen-assisted PECVD technique on a full 4 inch wafer scale, as shown in Fig. 8. Their results show that PECVD also requires the formation of a dense and relatively uniform layer of catalyst nanoparticles. This layer is essential for vertically aligned SWCNT growth. For 10 min growth, the length of the vertically aligned SWCNTs is ~10 μm, as shown in Fig. 8d. Figs. 8e and f show that the vertically aligned CNTs are single walled. Kawarada and coworkers also reported a long, millimeter scale growth of vertically aligned SWCNTs using...
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Breathing mode (RBM) peaks for semiconducting and metallic nanotubes. On the other hand, as-synthesized vertically aligned SWCNTs have the dominant Raman spectra of semiconducting SWCNTs in both RBM and G band regions [98]. In three different Raman RBM spectra with different laser wavelengths (488, 633 and 785 nm), RBM modes also show semiconducting nanotubes, as depicted in Fig. 10b.

3. Summary

CVD techniques are becoming a strong manufacturing route for the controlled synthesis of SWCNTs, especially with a view to controlling their structure (diameter and chirality) and building organized SWCNT networks with desired growth orientation, position and density. There have been great developments in nanotube growth techniques, and it is now possible to synthesize high quality vertically aligned CNTs. In this review, we reviewed the various growth techniques for controlled synthesis of vertically aligned SWCNTs, including ethanol based CVD, water assisted CVD and PECVD processes. We also introduced the hidden role of the OH radical and aluminum oxide buffer layers in the growth of highly dense vertically aligned SWCNTs.
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