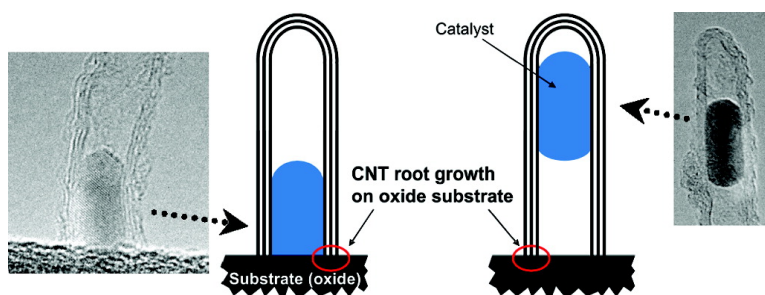Communication

Oxide-Driven Carbon Nanotube Growth in Supported Catalyst CVD

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Oxide-Driven Carbon Nanotube Growth in Supported Catalyst CVD

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The multifaceted promise that carbon nanotubes (CNTs) bring is enormous, potentially offering entirely new tools and capabilities. However, to fully exploit their potential an improved understanding of their nucleation and growth mechanisms is required. Owing to the success of catalyst particles for CNT formation, most investigations on their synthesis focus primarily on the catalyst particles. Generally, it is argued that transition metals are required as catalysts for CNT nucleation *and* growth. In situ HREM studies confirm this can occur for various transition metals.[1] In the case of chemical vapor deposition (CVD) it is also argued that these catalysts are catalytically active in the decomposition of the hydrocarbon feedstock. However, there are an ever-increasing number of works that show this picture is incomplete. For example, studies have shown the potential of various novel metallic catalysts,[2] while others show CNT formation from nonmetal catalysts.[3] Notably, in many studies, oxygen appears to play an important role in CNT growth. In laser ablation it has been shown that oxygen activates metals as catalysts for CNT synthesis[2a,b] and recent CVD studies confirm oxygen-based activation for nonstandard metal catalysts[2c,d] by heating in air prior to synthesis. The preheating air treatment is also key to the CVD synthesis of CNTs using semiconductor catalyst particles.[3a] In the case of semiconducting particles for the synthesis of CNTs on SiC at high temperatures,[3b,c] CNTs are only obtained with nominal amounts of oxygen in high vacuum. Oxygen chemically bound to CNTs is shown to be involved in the growth process.[4] Further, metal-free templated synthesis of CNTs is also possible when using porous Al_2O_3 structures.[5] CNTs can even be synthesized without catalyst particles in oxy-fuel flames when sufficient oxygen is provided.[6] In addition, oxides typically used as catalyst supports in CNT-based CVD synthesis can themselves form graphitic carbon layers.[7] In this Communication, detailed HREM studies on CNTs synthesized via CVD from nanoengineered catalyst particles are presented. Our studies show the (growing) root of a CNT lying at the support (oxide) interface rather than at the catalyst particle. The catalyst particles were Fe and the CNTs were synthesized in a vertical CVD reactor at 800 °C with cyclohexane serving as the feedstock.[8] HREM was carried out using a Tecnai F30 transmission electron microscope operated at 300 kV.

The use of nanoengineered catalyst particles enables tailored CNTs in terms of their mean diameter and number of walls.[8] Figure 1a shows a typical overview of the CNT obtained via this route. Figure 1b shows a direct correlation between the pristine catalyst size and the resultant CNT diameter. Further, it shows that the number of walls increases with increasing catalyst particle size. The correlation between catalyst diameter and CNT diameter is well-known. The increasing number of walls with catalyst size is attributed to volume to surface area dependencies,[9] namely, once
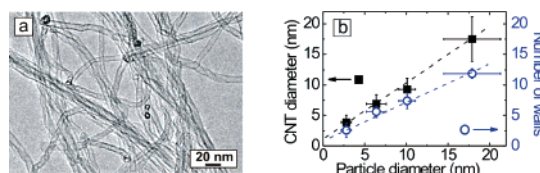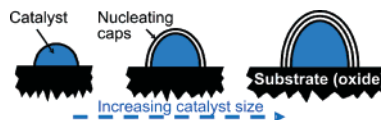

Figure 1. (a) Typical TEM overview of the CNT. (b) Relationship between pristine catalyst particle diameter and CNT diameter, and number of walls.

Scheme 1. Catalyst Size and Cap Formation Constraints at Nucleation

nucleation is triggered, the carbon-saturated catalyst particle precipitates its carbon and the number of nucleation caps formed will depend on the catalyst volume-to-surface area ratio. The process is illustrated in Scheme 1 and shows how the number of nucleating caps increases with increasing catalyst particle size. The outer cap nucleates first and consecutive caps then nucleate within the previously formed cap. Hence, the inward consecutive formation of concentric graphene caps inherently constricts the catalyst particle, thus, elongating it.

CNTs peeled off the substrate and subjected to HREM confirm the presence of capped ends (Figure 2a). Postsynthesis cleaving of substrates via focused ion beam (FIB) in which a coverage layer (Pt or polymer binder) is formed over the as grown CNTs was conducted. HREM studies of these FIB cleaved samples show the tops of the CNTs to be exclusively capped. These examples are instructive in that they imply a base growth mechanism in agreement with previous conclusions on these samples.[8] The HREM studies of the peeled CNT samples also showed catalyst particles residing along the length of the CNT core, even, at times, close to capped ends (Figure 2b). Many open ends with or without (elongated) catalyst material residing in the core were also observed (Figure 2 panels c and d, respectively). HREM of mechanically cleaved samples, for example, Figure 2e, show open-ended CNT with elongated catalyst particles at the interface of the substrate (Al_2O_3) confirming a base growth mechanism. These findings are in agreement with similar microscopy studies.[10] Despite persistent HREM investigations no CNT roots *on* catalyst particles were ever observed. Indeed, the consistent observation of elongated catalyst particles in the CNT core at an open end or further up the tube, suggest growth occurs on the substrate itself. It has been shown that oxide substrates typically used in supported catalyst CVD of CNTs can serve as an interface for ordered sp^2 carbon formation.[7] Further, much of the important interfacial chemistry on oxide surfaces does so at surface defect sites. In the present case of
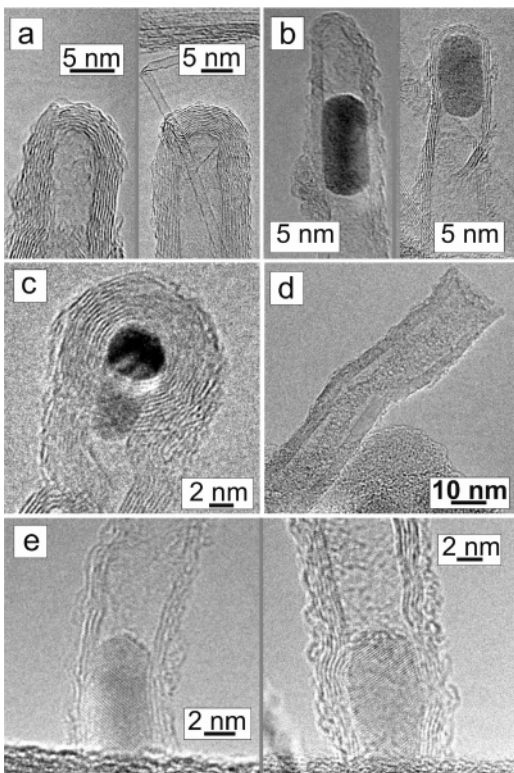
Figure 2. TEM micrographs of the CNT ends: (a) CNT capped ends; (b) CNT capped ends with encapsulated (elongated) catalyst particle; (c) CNT ends with compressed catalyst particle within the tube core; (d) open CNT tubes without catalyst; (e) root of CNT on the substrate with elongated catalyst particle in the tube core.

Scheme 2. Growth Model Showing CNT Root Growth on Oxide Support
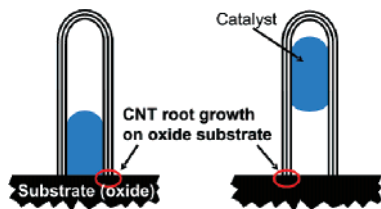
catalysts residing on an oxide support, it is our contention that the interface between the catalyst particle and the substrate (particle circumference) provides a circular defect site. Molecular oxygen could absorb on oxygen vacancies at the defect site that may then anchor the CNT to the substrate and enable C incorporation via rapid exchange reactions[11] between the support and CNT roots. Spillover mechanisms could provide the C (and oxygen) required for inner wall formation. Thus, the upward growth of cylindrical graphite structures can occur, namely, CNT. This substrate-driven growth is illustrated in Scheme 2. Such a scenario allows a catalyst particle to reside anywhere within the core of the CNT since it may no longer play a role in its growth. This implies that the catalysts role is primarily to provide the nucleation caps of the CNT.

This concept is radically different to that in which the catalyst both nucleates and grows CNT and in which the supports role is limited to merely stabilizing the catalyst particle. A catalytically active role by the support in the growth of CNT can also explain the success of oxidizers (H_2O or O_2) in enhancing the growth of substrate-based CVD synthesis of CNT.[12] Generally, it is argued that growth enhancement is due to the etching of amorphous carbon species via OH radicals, which helps prevent poisoning of the catalyst particles. Such poisoning of catalyst particles has not been demonstrated and has recently been questioned by Reilly and Whitten.[13] They also point out the contradiction in the argument that an amorphous carbon coating on the catalyst particle halts growth, yet these catalyst particles are able to grow nanotubes (ordered carbon) or even carbon nanofibers (disordered carbon). If however, the oxygen species at the surface of the support are directly involved in the growth of the CNTs, then it becomes crucial to maintain oxygen surface species, which will be depleted by hydrogen in the CVD reaction. Inclusion of a supplementary oxidizer in the CVD reaction effectively prevents passivation of the catalytically active oxide (support) surface by resupplying oxygen. The importance of surface hydroxide groups and surface oxygen in heterogeneous catalysis is well-known,[14] as is the catalytic graphitization of carbon by oxides.[7,15]

To conclude, we have shown that the pristine catalyst particle dictates the CNT diameter and number of walls at nucleation. Further, the consecutive inward formation of concentric graphene caps during nucleation constricts and elongates the catalyst particle within the tube core. Our findings evidence continued growth (after nucleation) at the oxide surface.

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