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## V.G.5 Modeling Catalyzed Growth of Single Walled Carbon Nanotubes

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### Program Scope

Understanding and controlling synthesis processes are key scientific challenges which are needed to achieve significant advances in the field of nanomaterials. Single-walled carbon nanotubes (SWCNTs) have unusual physical-chemical properties that make them promising materials for a large number of innovative applications in electronics, biomedicine, micro and nano separations among others. Their structure, diameter, and degree of helicity (also known as chirality) are responsible for their specific physical-chemical behavior. SWCNTs may be synthesized by catalytic decomposition of a carbon containing species over metallic nanoparticles using chemical vapor deposition methods. Many advances have been achieved in the last decade tuning this synthesis process aiming toward products with specific properties, and there is nowadays a consensus regarding the role of the catalyst on the associated growth of specific carbon structures on its surface. In previous work we (and others) have demonstrated the existence of structural correlations between the nanocatalyst and the nascent nanotube at different growth stages. Such correlations can be dominated by either the nanotube (inverse template effect) or the nanoparticle (template effect). We have shown that achieving chirality control depends on determining synthesis conditions where crucial structural features of the nanoparticles are maintained during growth (i.e., favoring a template effect). Thus, we have advanced in understanding the factors that influence specific growth behaviors and the next challenge must be oriented toward controlling these factors via smart synthesis procedures.

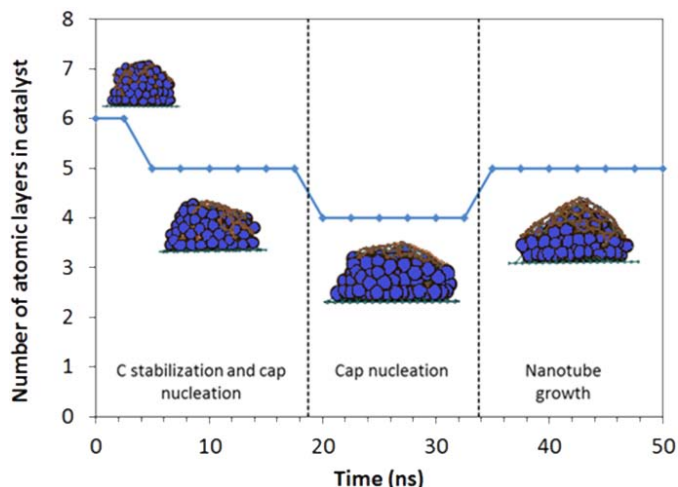
In our current studies we focus on the overall catalytic system that includes catalyst and support. We aim to elucidate the role of the support material on the nanocatalyst structure and composition, and therefore, on the growth of specific chiral carbon nanotubes. These studies will

allow a systematic search of nanotube growth conditions where the nanoparticle stability can be optimized thus allowing template effect and selective growth. Moreover, our systematic fundamental study of catalyst–support interactions will be useful for other catalytic processes and is a first step to elucidating nanocatalyst synthesis.

### FY 2016 Highlights

#### Changes in Nanocatalyst Shape and Composition during Nucleation of SWCNTs

This work was done in collaboration with the group of Dr. Renu Sharma at the National Institute of Standards and Technology, who has experimental capabilities of obtaining real-time atomic-resolution videos taken in an environmental transmission electron microscope during SWCNT growth. Thus, the dynamic evolution of supported Co carbide nanoparticles ( $\text{Co}_2\text{C}/\text{MgO}$ ) during the nucleation stage of single-walled carbon nanotube growth was explored using reactive- and ab initio-molecular dynamics simulations coupled with in situ environmental transmission electron microscopy imaging. Changes in the nanocatalyst shape and composition were examined throughout the nucleation process beginning with carbon dissolution, diffusion and formation of carbon chains on the surface until a cap is fully formed and the nanotube structure defined (Figure 1). The amount of carbon dissolved in the carbide-like nanoparticle decreases as C atoms precipitate at the surface. Once nucleation of the surface C atoms begins, a steady state global C concentration is reached. Changes in the nanoparticle shape occur linked with changes in the dynamics of C atoms according to experiments and RMD simulations: a decrease of the nanoparticle height and spreading over the substrate is observed while the C composition is stabilized, no changes occur as the cap is being formed, and subsequent elongation and shape recovery take place due to interactions with the cap as it lifts off. The main two factors influencing nanoparticle shape and C distribution can thus be summarized as: interactions with the substrate and interactions with the nascent nanotube. The nanoparticle evolution in relation to its interaction with the substrate from AIMD studies reveals that the nanoparticle–substrate interface is dominated by interactions between Co atoms located atop O atoms in the substrate. Strong nanoparticle–substrate interactions were characterized by electron transfer and re-arrangement of Co atoms at the interface stemming from a given  $\text{Co}_2\text{C}$  surface termination, i.e., (020) and (210). The interactions of the nanocatalyst with the cap are responsible for the C gradient observed along the direction perpendicular to the substrate in both simulations



and experiments. This suggests that the catalyst topmost layer is a primary source of C atoms for the formation of the nanotube cap. Overall, the combination of atomistic simulations and in situ observation of SWCNT growth provides insights into the fundamental phenomena driving the observed changes in the nanoparticle and allows the identification of key aspects for the formulation of models and mechanisms to better understand and control the catalytic process.

**FIGURE 1.** Shape evolution of the catalyst nanoparticle during nucleation and growth stages. Reactive MD simulations illustrate that during carbon stabilization, the metal layer in contact with the substrate tends to wet the substrate. Carbon nucleation starts before carbon stabilization is reached and leads to further reduction in the number of layers of the nanocatalyst particle. The slight vertical elongation of the nanocatalyst particle coincides with the beginning of the growth stage.