Role of the Metal Catalyst in the Formation
and Growth of Carbon Single-Wall Nanotubes

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Carbon single-wall nanotubes (C-SWNTs) can be produced by different techniques namely, arc discharge, solar furnaces, which are high temperature processes, and catalytic methods which are medium temperature syntheses. In all cases, metallic catalysts are necessary for their formation: The metals used are pure transition metals such as Ni, Co, Fe, Pd or rare earth metals (REM) such as Y, Ce or a mixture of these different metals. We will examine the role of this catalyst in the formation process of C-SWNTs, which can be deduced from careful high resolution transmission electron microscopy studies, combined with quantum molecular mechanics simulations.

The structure of single-wall carbon nanotubes has been investigated in samples synthesized from different techniques. In all cases, the nanotubes are self-assembled in crystalline ropes attached at one end to metallic particles. These similarities suggest a common growth mechanism based on a vapor-liquid-solid model. In this model, formation of the nanotubes proceeds via solvation of carbon vapor into metal clusters, followed by precipitation of carbon excess in the form of nanotubes when the temperature falls down to the solidification temperature of the metallic droplet. Such a process implies a root growth mechanism which has been studied by quantum molecular dynamics simulations. It has been shown that carbon atoms can be added at the root of a growing tube by a diffusion-segregation process occurring at the surface of the catalytic particle.

We will then focus more particularly on the nucleation and growth of SWNTs where carbon atoms precipitate from particles larger than the tube diameter. The structure of the particles has been studied in detail for different Ni-REM mixtures (REM = Y, Ce, La) by combining high-resolution transmission electron microscopy, energy loss spectroscopy and energy filtered chemical mapping. The results show that the particles attached to long SWNT ropes always have a REM composition lower than 10 atthat REM atoms are located at the surface of the particles in the form of thin precipitates extended over 2–3 atomic planes and having the REM_2C structure. These results reveal that Ni and REM play distinct and complementary catalytic activities in the formation of SWNT which will be discussed in detail.