

Multiscale Simulations of Carbon Nanotube Nucleation and Growth: Electronic Structure Calculations.*

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As part of Oak Ridge National Laboratory's (ORNL) multiscale simulations to understand fundamental aspects of the nucleation and growth of carbon nanotubes, several different types of first principles surface and bulk electronic structure calculations have been carried out.

In the surface-related work, Ni was chosen as the catalytic particle. A 38 atom Ni cluster and several low-index Ni surfaces have been studied. The computational methods are based on density-functional theory (DFT) using a plane-wave formalism with ultrasoft pseudo potentials. The binding energies of a C atom on various Ni surfaces and the corresponding facets on the Ni cluster have been obtained. In spite of the apparently large differences of these two types of substrate, the energetic ordering of the sites for C atom adsorption is the same. In other words, the small clusters yield essentially the same results as larger clusters and extended surfaces. The Ni(100) facet is favored for C adsorption over the Ni(110) and Ni(111) surfaces. The diffusion barriers for C atom on these surfaces have also been obtained; the highest mobility is on the Ni(111) surface. Other results and the future directions of this research will be discussed.

In the work related to bulk processes, extensive calculations have been carried out on clusters of carbon atoms to which various transition metal atoms are attached. Although the calculations are generally based on DFT, most of them use Gaussian orbital basis sets rather than pseudo potentials and plane wave expansions as in the surface work. After some trial and error, a C cluster in the form of a flake containing fourteen atoms with an armchair type termination was chosen. This represents a segment of an "unrolled" carbon nanotube. The binding energies of C, Ni, Co, Fe, Cu, and Au atoms to this flake were then calculated in an effort to gain insight into the mechanism for the high catalytic activity of Ni, Co, and Fe and the lack of it in Cu and Au. In a suggested nucleation scenario, the role of the transition metal ions is to complete the dangling bonds of the flake and so counteract the strain energy introduced by deforming the flake into the nanotube caps. The calculations indicate that the binding energies of Cu and Au to the C flake are about an eV less than those of the three catalytic elements, the unfilled d shells clearly playing a role in this regard. Details of the calculations will be given and possible implications for the role of the catalytic particles discussed. The connection between the electronic structure results and mesoscopic continuum calculations of CNT growth will be sketched.

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