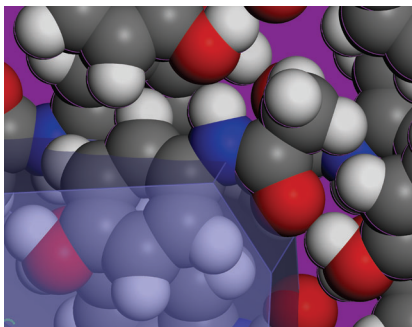


# METAL-NANOTUBE INTERACTIONS-BINDING ENERGIES AND WETTING PROPERTIES



Researchers at the NASA Ames Research Lab and Accelrys used Materials Studio to investigate the interactions of single-walled carbon nanotubes (SWNT) and metals surfaces and clusters.

## Key Product

- DMol<sup>3</sup>

## Industry sectors

- Nanotubes
- Electronics
- Nanotechnology
- Sensors

## Organizations

- NASA Ames Research Lab
- Accelrys, Inc.

Researchers at the NASA Ames Research Lab and Accelrys used the Density Functional Theory (DFT) tool, DMol<sup>3</sup>, to investigate the interactions between single-walled carbon nanotubes (SWNT) and various metal atoms, planes and clusters. The study is expected to provide important insight into application areas such as nanotube-based electronics, catalysts and sensors.

Carbon nanotubes interacting with metal nanoparticles are gaining considerable interest as sensing materials, catalysts, in the synthesis of metallic nanowires, as well as in nanoelectronics applications as Field-Effect-Transistor (FET) devices. A systematic study of electron-beam-evaporation-coating of suspended SWNT with various metals reveals that the nature of the coating can vary significantly depending upon the metal. Thus, Ti (Titanium), Ni (Nickel) and Pd (Palladium) form continuous and quasi-continuous coating, while Au (Gold), Al (Aluminum) and Fe (Iron) form only discrete particles on the SWNT surface. In fact, Pd is a unique metal in that it consistently yields good contacts (i.e. low contact resistance) to both metallic and semiconducting nanotubes. For p-doped semiconductors one expects the contact resistance to go down even

further if a higher work function metal, e.g., Pt (Platinum) is used. Unfortunately, Pt appears to form poor contacts to both metallic and semiconducting SWNTs with lower p-channel conductance than Pd-contacted junctions.

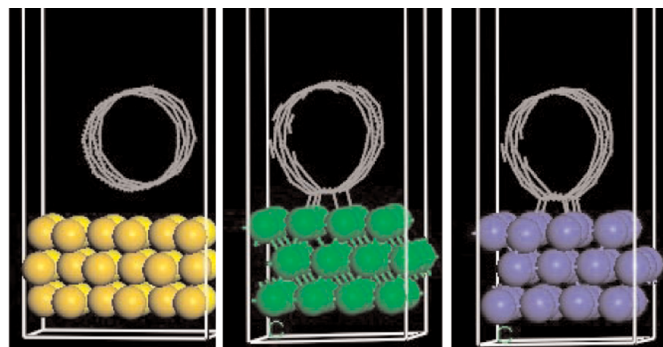
However, the above result is in apparent disagreement with computed interaction energy of a single metal atom on a SWNT, which follows the trend  $E_b(\text{Pt}) > E_b(\text{Pd}) > E_b(\text{Au})$ , where  $E_b$  denotes the binding energy of the metal atom to the SWNT. It does not explain why Pt consistently makes worse contacts than Pd, and why Ti, in spite of its good wetting of a CNT surface, yields good contacts only rarely.

Given the increasing use of metal-coated nanotubes there was an urgent need to find out as much as possible

about these discrepancies. Reporting in the journal 'Chemical Physics Letters', researchers engaged in a preliminary study of the problem.<sup>1</sup> The main contribution of this work was to go beyond single metal atoms, and explore the interaction of metal adlayers, clusters and planes with a SWNT or a sheet of graphite, the latter being representative of wide-diameter SWNTs. Relaxed geometry and binding energies were computed by the DFT-based quantum code DMol<sup>3</sup>, operated within MS Modeling, Materials Studio's modeling and simulation suite, employing periodic boundary conditions, multiple K-points, and accurate basis set and exchange-correlation functionals. The metals chosen were gold, palladium and platinum.

The results were interesting. Isolated atoms performed exactly as previous theory suggested, with binding energy increasing through Au, Pd and Pt. However, for adlayers (i.e. films) the metal-metal binding within the metal film was found to be much stronger than that between the film and graphite. This, coupled, with the fact that Pt has substantially higher cohesive energy, led to the result that binding between Pt layer and graphite is actually smaller than that between Pd film and graphite beyond a film thickness of just two atomic layers. The same trend (i.e. higher binding for Pd to graphite) was also observed for 13-atom metal clusters. Combining the film and the cluster results suggested the existence of a critical cluster size such that metal nanoparticles smaller than such size will efficiently wet the graphite surface, while bigger particles will coalesce into even bigger clusters forming a weaker contact. Such critical cluster size was predicted to be smaller for Pt than for Pd, thereby explaining why Pd is observed to form better contacts.

Further simulations were carried out introducing modelled nanotubes to flat surfaces made of the three metals (See Fig. 1). The results for palladium and platinum showed the formation of direct covalent bonds between the tube and the surface, and a slight deformation of the cross-section of the tube as a result. This effect was stronger on palladium than on platinum - again, reinforcing conclusions from metal film calculations described above.



**Figure 1:** An (8, 0) SWNT on metal surfaces: (a) Au (100); (b) Pd (111); (c) Pt (111). On the Au surface the SWNT is essentially weakly physisorbed. For Pd and Pt surfaces, the metal-adjacent C-atoms undergo  $sp^2 - sp^3$  transition, which significantly deforms the CNT cross-section. Binding on Pd is slightly higher than on Pt.

Another interesting observation from the work was that electron spin plays an important role in determining the equilibrium shape of the 13-atom Pt and Pd clusters, and they could be substantially different from the naively expected spherical shape and icosahedral symmetry. Detailed investigation on this effect is currently underway.

To learn more about Materials Studio by Accelrys, go to [accelrys.com/materials-studio](http://accelrys.com/materials-studio)

## REFERENCES

1. Maiti, A., and Ricca, A., 'Metal-nanotube interactions - binding energies and wetting properties', **2004**, Chemical Physics Letters, 395, 7-11.