FIRST-PRINCIPLES STUDY OF THE INTERACTION BETWEEN ATOMS, SMALL MOLECULES AND CARBON NANOTUBES: ELECTRONIC AND CATALYTIC PROPERTIES

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An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: PHYSICS

The original of the complete thesis is on file
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Troy, New York

April 2008
(For Graduation May 2008)

ABSTRACT

Carbon nanotubes have attracted much attention ever since their first discovery by Iijima in 1991. Being quasi-one-dimensional structures, carbon nanotubes have unique physical properties such as high stability, strength and stiffness, low density and elastic deformability. Their local symmetry on honeycomb structure, together with the size of the nanotube, provide them with fascinating electronic structures. While the geometric structure of carbon nanotubes are very stable, the electronic structure of carbon nanotubes is, on the other hand, quite sensitive to charge transfer caused by small dopants such as atoms and/or small molecules. This provides us a way of tailoring and controlling their electronic properties. The idea of such tailoring and controlling comes from the fact that the sp^2 σ bonds which form the zigzag skeleton of carbon nanotubes are energetically more stable than the sp^2 π bonds which are responsible for the electronic structure of the carbon nanotubes. In other words, we can easily change the electronic structure of carbon nanotubes without losing to much their structural advantages. There are many applications for pristine carbon nanotubes such as field emission electrodes, transistors, etc. And there are even more applications for the "modified carbon nanotube" in different areas, such as hydrogen storage materials, bio/chemical sensors, Schottky diode, etc. The tailored electronic properties of the resulting nanotube-based complexes may have influences on their transport and catalytic phenomena.

The first principles density functional method is a powerful scheme to study nano-scale systems. It provides information including the structure, energy and various electronic properties of the interested systems. It provides insights of a problem, often in a more detailed and systematic manner. DFT, together with Landauer-Büttiker electron transport theory, allows us to determine the I-V characteristics of a molecule and provide the insights to such behavior simultaneously.

In this thesis, we will show several studies done via density functional theory simulations on how atoms and small molecules interact with different carbon nanotubes. We will study the detailed geometric and electronic structures of these

systems and how these doping may control and/or affect the electronic and catalytic properties of carbon nanotubes at a microscopic level. In particular, we will study how the interaction of H_2 with CNTs could be improved on metal coated CNTs. We will show how metal coated CNTs, serving as a cathode, can improve the oxygen reduction reaction, as compared to traditional Pt electrodes. We will also study the effect of metal coating on the transport behavior of carbon nanotubes. We will also present several transport studies of metal coated CNTs and study both charge and spin associated transport behavior through CNTs.

Chapter 1 gives a brief introduction on the CNT electronic properties and some background information about this report. In chapter 2, a brief description is given about the First Principles "Density Functional Theory" (DFT). Chapter 3 gives a short description of the transport formalism that we have used in our calculation. In chapter 4, 5, 6 and 7, we will give examples of our first principles density functional study on the electronic and catalytic properties of the carbon nanotubes and how the interaction of atoms and small molecules may affect these properties. Finally, a brief summary and future work is presented in chapter 8.