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Nickel Decorated Single-Wall Carbon Nanotube as CO Sensor

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ABSTRACT

Based on spin-polarized density functional theory (DFT) calculations, the interaction between nickel cluster decorated single-wall carbon nanotube (CNT) and CO molecule has been investigated. DFT calculations are performed with generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) functional. Interaction of CNT and cluster induces spin polarization in the CNT. Nickel decorated CNT has a large magnetic moment of 4.00 μ_B which decreases to 0.10 μ_B when CO molecule is absorbed to it. Such a drastic reduction in magnetization may be detected by SQUID magnetometer. Hence by measuring magnetization change, CNT-cluster system may be used as gas detectors. The charge transfer between the systems has been discussed through Mulliken charge analysis for different orientations of the adsorbed CO molecule. We observed that CNT-cluster system acts as electron donor and CO molecule acts as electron acceptor in this study.

Keywords: Nickel Cluster; Carbon Nanotube; CO Sensor; DFT; Magnetic Moment

1. Introduction

Carbon nanotubes (CNT) can be used in a number of applications such as scanning probes [1], nanoelectronic devices [2], chemical sensors [3] etc. Sensing gas molecules like CO, CO_2, NO, NH_3, O_2, N_2, H_2, CH_4 are vital in a number of fields such as environmental monitoring, agricultural, medical, industrial applications, space missions, control over chemical processes, etc. [3,4]. Nanoscale sensors based on single-wall carbon nanotubes have high sensitivity and fast response time for detecting NO_2 and NH_3 [5]. Understanding the nature of interaction between the adsorbed molecule and CNT is important to fully exploit the potential application of CNT as sensors. Searching for the ways to enhance the adsorption energies is a novel strategy for the gas sensing use of CNT. To create active sites for the adsorption of molecule on the intrinsical inert surface of the CNT, many techniques have been employed, such as, introducing defects on the walls of the CNT [6], embedding or doping foreign atoms [7]. One of the most common methods in sensing technology is the surface adsorption of metal clusters on CNT sidewalls [8]. It is reported that decoration of SWCNT with transition metals exhibits higher sensitivity than the pristine CNTs [8]. The sensitivity of platinum and gold decorated CNTs increases by an order of magnitude for NH_3 and NO_2 detection. In the present study, Ni clusters have been chosen as they are used as catalysts and also exhibit strong adsorption properties to a number of molecules [9]. CO molecule has been considered because of its role as pollutants and toxicants.

2. Calculation Method

Based on generalized gradient approximation (GGA), spin polarized density functional calculations are performed using norm-conserving pseudopotential. The single-zeta basis set has been used and the exchange correlation part of density function is treated with Perdew-Burke-Ernzerhof (PBE) function. All the calculations are performed by using siesta-3.1 package [10]. The full geometry relaxation was performed until the forces on the atoms are less than 0.04 eV/Å and the mesh cut-off value was set at 300 Rydberg. Tetragonal unit cell of 25 × 25 × 12.92 $Å^3$ is employed for the periodic boundary conditions. Semiconducting (5,0) zigzag SWCNT with supercell containing 60 carbon atoms have been used.

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We place Ni_4 cluster of tetrahedron structure at the surface of the nanotube, then, the CO molecule is placed at different sites above and around the Ni_4 decorated CNT. The binding energy (E_b) of CO molecule on the nanotube is calculated as:

$$E_b = E_{(CNT+Cluster+CO)} - E_{(CO)} - E_{(CNT+Cluster)} \quad (1)$$

where $E_{(CNT + Cluster)}$, $E_{(CO)}$ and $E_{(CNT + Cluster + CO)}$ are the total energies of the cluster decorated carbon nanotube, CO molecule and carbon nanotube-cluster-CO system respectively. From the Mulliken population analysis, charge transfer between the adsorbed molecule and system (CNT + Cluster) is analysed.

3. Results and Discussions

The optimized structure of pristine (5,0) SWCNT has a diameter of 4.17 Å. The C-C bond length along the nanotube axis (denoted as $B_{\parallel}$ in **Figure 1**) is 1.42 Å and the other bond aligned partially perpendicular to the nanotube axis ($B_{\perp}$) is 1.47 Å. When the CO molecule is adsorbed on the sidewalls of the pristine (5,0) carbon nanotube, C-C bonds in the hexagonal rings near the adsorbed CO molecule deforms. The $B_{\parallel}$ and $B_{\perp}$ bond in the hexagonal ring close to the adsorbed molecule becomes 1.38 Å and 1.52 Å respectively. As we put Ni_4 cluster on the surface of the CNT, the bond $B_{\parallel}$ near the cluster become 1.46 Å and the bond $B_{\perp}$ near the cluster is 1.52 Å. When we place the CO molecule on the Ni_4 decorated CNT, the tetrahedron structure of the cluster becomes distorted. The most stable geometry has CO molecule near the centre of the cluster with C atom towards the cluster. Change in the C-C bond in the hexagonal ring near the adsorbed molecule is also observed and CO is at a height of 2.62 Å from the CNT. The $B_{\parallel}$ bond close to the adsorbed molecule is 1.44 Å and the $B_{\perp}$ bond is found to be 1.52 Å.

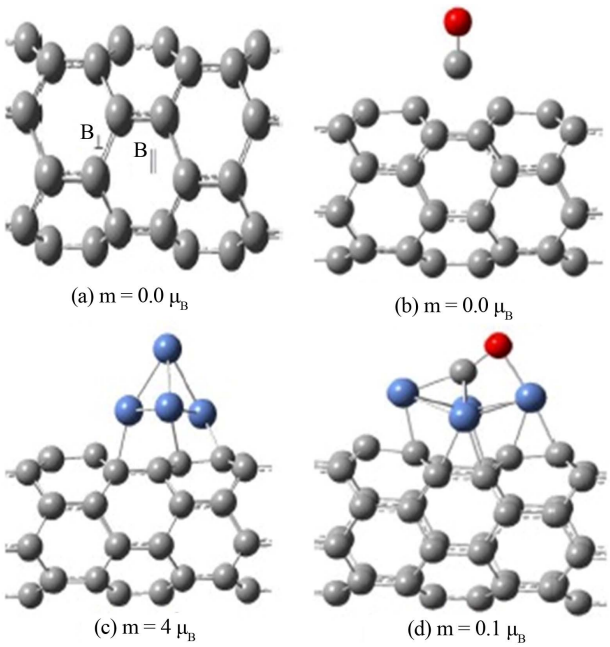

Figure 1. Structure and observed magnetic moments, m of (a) pristine (5,0) SWCNT (b) CO adsorbed on (5,0) SWCNT (c) Ni_4 decorated (5,0) SWCNT (d) CO adsorbed on the Ni_4 decorated (5,0) SWCNT.

The binding energy of Ni_4 cluster on the (5,0) CNT is −7.97 eV. The –ve value indicates the stability of the cluster decorated CNT, which is required for using them as sensor. The binding energy of the CO molecule on the pristine CNT is −11.70 eV and the binding energy on the Ni_4 decorated CNTs is −16.44 eV. We observed that the binding energy of CO is enhanced when the CNT is decorated with Ni_4 cluster, a favorable feature for sensors. CO molecule is an electron attracting molecule with a net positive charge at the oxygen end and an electron affinity of 1.33 eV [11]. Hence, CO withdraws electrons from the CNT-cluster system. The Mulliken population analysis also reveals that electrons are transferred from the CNT-cluster system to the CO molecule. The charges on the C and O atoms of the CO molecule are −0.57 e and −0.29 e respectively and a total charge of −0.84 e is transferred to the CO molecule from the CNT-cluster system. The magnetic moments of the structures are presented in **Figure 1**. The bare Ni_4 cluster has a magnetic moment of 6.00 μ_B. The pristine CNT and CO adsorbed CNT have zero magnetic moment. On placing the Ni_4 at the surface of the non-magnetic CNT, the structure has a net magnetic moment of 4.00 μ_B. This magnetic moment is contributed by the Nickel cluster. When CO is adsorbed on the cluster decorated CNT, we observed that the net magnetic moment suddenly decreases to 0.10 μ_B. This sudden drop in the magnetic moment is due to the transfer and rearrangements of electrons between the adsorbed CO and CNT-cluster system.

4. Conclusion

Based on first principle calculations, the possibility of using Nickel cluster decorated single-wall carbon nanotube as CO sensor has been investigated. DFT calculations are performed with generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) function. Mulliken charge analysis shows that the adsorbed CO molecule acquires electronic charge from the cluster decorated SWCNT. Because of strong CNT-cluster interaction, spin polarization is induced in the CNT. Nickel decorated CNT has a large magnetic moment of 4.00 μ_B, which changes abruptly to 0.10 μ_B when CO is attached to it. So adsorption of CO molecule diminished the magnetic property of the system (Ni_4 decorated SWCNT). This abrupt change in magnetization on CO adsorption may be detected, hence suggesting the possibility of using CNT-cluster as gas detectors.

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