구두발표 II-1

Magnetism of Fe clusters encapsulated in carbon nanotube

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1. Introduction

Recently there has been much interest in obtaining transition metal (TM) nanoparticles or nanoclusters in a manufacturing process of carbon nanotubes (CNTs) and understanding their chemical and physical properties for the potential applications in many fields [1-4]. The CNTs protect the TM nanoclusters from surface oxidization and reduce the inter-cluster dipolar interaction by nonmagnetic separation [2, 3]. The TM nanoclusters in CNTs are expected as a potential candidate for high-density magnetic recording media [4].

There are systems of Fe nanoclusters have been coated with CNTs [3], trapped at the tip of aligned CNTs [2], and encapsulated in carbon nanohorn [5] as well as CNTs [6]. The Fe clusters coated with single-wall carbon nanotubes (SWNTs) have the diameter of 2-10 nm. The average size of Fe clusters trapped at the tip of CNTs is about 70 nm, which is much larger than the critical size (20 nm) of single domain particles with bcc α-Fe structure. Yueh *et. al.* have synthesized Fe clusters with the size of 30, 150, and 300 Å in the center of CNTs [6]. They found that there is a strong hybridization between C 2*p* and Fe 3*d* orbitals, and the degree of delocalization for Fe 3*d* orbitals increases with the size of Fe cluster. Motivated by the Yueh *et. al.*'s experiment, we investigate the electronic structure and magnetic properties of Fe clusters encapsulated in CNTs.

2. Model and computational method

We have used small Fe_6 bipyramid, Fe_{13} icosahedral clusters, and zigzag (11,0) SWNT. The Fe clusters are inserted into the (11,0) SWNT and the geometries are optimized by *ab initio* spin-polarized total energy calculations [7]. We have used the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof 1996 for the exchange-correlation energy. We solved the self-consistent Kohn-Sham equations by direct diagonalization of the Hamiltonian in atomic orbitals basis set consisting of finite-range numerical pseudoatomic wave functions. Norm conserving Troullier-Martins pseudopotentials factorized in the Kleinman-Bylander form were used to consider core electrons. The Γ-point is considered for the convenience of calculations. The geometry is optimized until the atomic force is less than 0.04 eV/Å using the conjugate gradient method.

We used a supercell of (11,0) SWNT with three primitive cell in order to ignore interaction between Fe clusters. For calculational convenience the lattice parameters of the supercell in xy-plane are set to 20 Å. We obtained bond length, binding energy, the amount of charge transfer, magnetic moment, and spin polarization.

3. Results and discussion

Figure 1(a) shows that Fe_6 bipyramid cluster and (11,0) SWNT, where the calculated average Fe-Fe bond length of Fe_6 cluster is 2.46 Å. The top view of Fe_6@(11,0) SWNT is displayed in Fig. 1(b), where Fe-C distances are in the range of 2.56 - 3.69 Å. The average Fe-Fe bond length for Fe_6 cluster in Fe_6@(11,0) SWNT do not vary much compared with that of freestanding Fe_6 cluster, as shown in Table 1. The average Fe-Fe bond length of 2.56 Å for Fe_{13} cluster in Fe_{13}@(11,0) SWNT is slightly larger than that of freestanding Fe_{13} cluster. The average Fe-C bond length of 2.26 Å for Fe_{13}@(11,0) SWNT is close to that of 2.06 Å in Fe_3C bulk cementite structures.

The binding energies of Fe_6@(11,0) and Fe_{13}@(11,0) SWNT are 1.68 eV and 5.40 eV, respectively. For Fe_{13}@(11,0) SWNT, there are strong interactions between Fe and C atoms. According to Mulliken population analysis for Fe_6@(11,0) SWNT, the electronic charge of Fe atoms with Fe-C distance less than 3.2 Å is depleted, whereas the Fe atoms with much longer Fe-C distance receive the electronic charge. The overall charge transfer occurs from Fe cluster to CNT with the amount of 0.13 *e*.

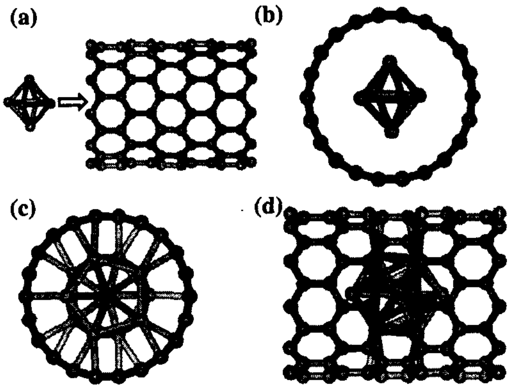

Fig. 1. (a) Fe_6 cluster and (11,0) SWNT (b) top view of Fe_6@(11,0) SWNT (c) top view of Fe_{13}@(11,0) SWNT (d) side view of Fe_{13}@(11,0) SWNT.

The magnetic moment of 3.46 μ_B/Fe for Fe_6@(11,0) SWNT is slightly larger than that of freestanding Fe_6 cluster, and the magnetic moment of Fe_{13}@(11,0) SWNT is 0.58 μ_B/Fe smaller than that for freestanding Fe_{13} cluster. The spin polarization of Fe cluster for the encapsulated system is obtained from the difference of partial density of states (PDOS) for majority and minority spin at Fermi level. The spin polarization of Fe_{13} cluster in Fe_{13}@(11,0) SWNT increases compared with that of freestanding Fe_{13} cluster due to depletion of majority spin electron near the Fermi level.

	Fe-Fe bond length (Å)	**μ (μ_B/Fe atom)**	**SP (%)**
Fe_6	2.46	3.33	97
Fe_{13}	2.54	3.53	25
Fe_6@(11,0) SWNT	2.46	3.46	66
Fe_{13}@(11,0) SWNT	2.56	2.95	77

Table 1. Fe-Fe bond length, magnetic moment (μ), and spin polarization (SP) of Fe_6, Fe_{13}, Fe_6@(11,0), and Fe_{13}@(11,0) SWNT.

In conclusion, when Fe cluster and SWNT strongly interact, overall charge transfer occurs from Fe cluster to SWNT. The magnetic moment of Fe cluster encapsulated in CNT decrease by 16 %, but the spin polarization increase by 68 %. The results indicate Fe cluster encapsulated in CNT can be expected as candidate for spin-dependent nanodevices.

4. Reference

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