Half-metallic ferromagnetism in transition-metal encapsulated boron nitride nanotubes

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Abstract. We have studied zig-zag boron nitride (BN) nanotubes filled with the Ni hexagonal-close-packed nanowire. The Ni/BN nanotube hybrid structures are ferromagnetic metals with substantial magnetism. Some special magnetic properties resulting from the interaction between the Ni nanowire and BN nanotubes are found. The Ni encapsulated BN(9,0) nanotube shows semi-half-metallic behaviour, which can become half-metallic after doping electrons more than 1.4 e per unit cell. The intrinsic half-metallic behaviour can be achieved in two different ways: one is by coating the Ni nanowire with a smaller BN nanotube, i.e., BN(8,0), and the other is using hydrostatic pressure to homogeneously compress the Ni encapsulated BN(9,0) nanotube.

Magnetic nanostructures are a scientifically interesting and technologically important area of research with many current and future applications in permanent magnetism, magnetic recording and spintronics [1]. One of the key properties in magneto-electronics is the so-called half metallicity, i.e., conduction electrons that are 100% spin polarized due to a gap at the Fermi level (\(E_F\)) in one spin channel and a finite density of states (DOS) for the other spin channel. Half-metallic (HM) materials are ideal for spintronic applications, such as tunnelling magnetoresistance and giant magnetoresistance elements.

Encapsulating ferromagnetic structures inside nanotubes has become an active research topic. Carbon nanotubes filled with transition-metal (TM) have been studied extensively both experimentally [2]–[5] and theoretically [6]–[8]. It was found that while TM nanowires

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filled carbon nanotubes can exhibit substantial magnetism, no HM behaviour exists in such systems [7].

Since boron nitride (BN) nanotubes are insulators independent of their chiralities and more chemically inert than carbon nanotubes, they may serve as naturally insulating and/or protective shields for encapsulating conducting metallic clusters, nanowires and nanorods [9, 10]. The magnetic nanostructures isolated by a non-magnetic material, i.e., BN walls, could be efficiently used for high-density data storage, without the drawback of particle agglomeration and magnetic loss due to dipolar relaxation. This kind of protection also prevents the oxidation of the metallic clusters, nanowires and nanorods, which are prone to being oxidized. Recently, BN nanotubes filled with 3d transition metals such as Fe–Ni Invar alloy, Co nanorods, Mo clusters, Ni and NiSi2 nanowires have been successfully synthesized [11]–[14]. However, detailed electronic and magnetic properties of these novel nano-structures are far from well understood. And the question of how the magnetic properties of TM/BN nanotubes differ from those of TM/C nanotubes is open. In this paper, we perform a comprehensive first principles study on the electronic and magnetic properties for these TM/BN nanotube hybrid structures. We show that the electronic and magnetic properties of TM/BN nanotubes differ fundamentally from those of TM/C nanotubes and HM ferromagnetism could be achieved in TM/BN nanotubes under appropriate circumstances.

Our theoretical calculations are performed using the Vienna ab initio simulation package (VASP) [15, 16]. We describe the interaction between ions and electrons using the frozen-core projector augmented wave (PAW) approach [17, 18]. The overall framework is spin-polarized density-functional theory (DFT) [19, 20] in the generalized-gradient approximation (PW91) [21, 22]. The basis set cut-off is 400 eV. In a typical calculation, a one-dimensional (1D) periodic boundary condition is applied along the nanotube axis with Monkhorst–Pack [23] k-point sampling. During structural relaxation, all atoms except the fixed ones are allowed to relax to reach the minimum energies until the Hellmann–Feynman forces acting on them become <0.01 eV Å−1. Since most BN nanotubes are of zig-zag type [24, 25], we choose BN zig-zag nanotubes with a smallest hcp TM nanowire filled inside. Although the most stable bulk phase for Ni is fcc, the stability for Ni nanowires depends not only on the structure but also on the orientation and radius of the nanowires. For example, the smallest hcp Ni nanowire is found to be more stable by about 0.3 eV per Ni than the smallest fcc Ni nanowire in the hcp (111) orientation. The hcp TM nanowire is composed of six TM atoms per unit cell with ABAB staggered triangle packing. BN(8,0), BN(9,0) and BN(10,0) nanotubes filled with the Ni hcp nanowire are studied. Different initial guesses are used for the local magnetic moments including ferromagnetic, antiferromagnetic (alternate up–down spins on A and B TM atoms) and nonmagnetic spin configurations, which are then fully relaxed to obtain the final converged structures and spin alignments. The free-standing hcp Ni nanowire is also studied for comparison with the hybrid structures.

Figure 1 shows the optimized structures for the free standing Ni nanowire and the Ni encapsulated BN nanotubes. In the optimized structures, Ni atoms almost lie in the nitrogen planes of BN nanotubes, as can be seen from the side view for Ni encapsulated BN(9,0) nanotube (figure 1(e)). This relative position along the axis between the BN nanotube and metal nanowire results from the big electronegativity of the nitrogen atom. The comparative calculation for Ni/C(9,0) shows that Ni atoms in Ni/C nanotubes do not lie in any carbon plane but in the middle of two adjacent carbon planes, since all atoms are the same in carbon nanotubes. The symmetry of the Ni nanowire changes little after being coated by BN nanotubes. Generally, after
Figure 1. Relaxed structures of the free-standing Ni nanowire and Ni/BN nanotube hybrid structures. (a) Top view of the free-standing Ni nanowire. (b) Top view of Ni/BN(8,0). (c) Top view of Ni/BN(9,0). (d) Top view of Ni/BN(10,0). (e) Side view of Ni/BN(9,0).

Table 1. The formation energy $E_b$ and total magnetic moment $\mu_{tot}$ for the free standing Ni nanowire and several Ni encapsulated BN nanotubes hybrid structures. See the text for the definitions for the formation energy $E_b$.

| Structure        | $E_b$ (eV) | $\mu_{tot}$ ($\mu_B$/unit cell) |
|------------------|------------|----------------------------------|
| Ni nanowire      | 5.66       |                                  |
| Ni/BN(8,0)       | 0.88       | 4.00                             |
| Ni/BN(9,0)       | −0.04      | 3.49                             |
| Ni/BN(10,0)      | 0.03       | 4.53                             |

being inserted, the Ni nanowire expands a little, e.g., the Ni–Ni distance in a plane (A or B) changes from 2.27 to 2.32 Å in Ni/BN(9,0), and the BN walls expand slightly, 0.01 Å for the BN(9,0) nanotube.

As for the energetics of these hybrid structures, we give the formation energy of the hybrid structures in table 1. The formation energy is defined as $E_b = E(TM/tube) - E(TM) - E(tube)$. And the calculated formation energy for Ni/BN(8,0) is 0.88 eV, which implies the formation of this hybrid structure is endothermic. The absolute value of the formation energy for Ni/BN(9,0) or Ni/BN(10,0) is very small. The slightly more favourable energy for Ni/BN(9,0) than that for Ni/BN(10,0) may result from the symmetry matching between the Ni nanowire and nanotube in Ni/BN(9,0). The positive or small negative formation energy is reasonable, since the insulating BN nanotubes are very stable and inert and there are significant difficulties in wetting a BN graphene-like surface. This also explains that the synthesized BN nanotubes filled with metals are limited and most of these hybrid structures are produced by a two-stage process [11]–[13]: firstly, C nanotubes containing TM nanoparticles at the tube-tips are synthesized; secondly, simultaneous filling of nanotubes with the TM through capillarity and chemical modification of
C tubular shells to form BN nanotubes occur. But once the TM/BN nanotube hybrid structures are formed, they will be stable due to the large inertia of BN nanotubes.

Since Ni/BN(9,0) is the most favourable form among the Ni encapsulated BN nanotubes we studied, we choose it as a typical case for studying the detailed electronic and magnetic properties for Ni/BN nanotube structures. To serve as a reference, the electronic and magnetic properties for the free-standing Ni nanowire are also examined.

The band structures of the free-standing Ni nanowire and Ni/BN(9,0) are shown in figures 2(a1) and (a2), respectively. The free-standing Ni nanowire is ferromagnetic metal, but not HM or semi-HM, as shown in figure 2(a1). Similar results for the Co nanowire were obtained by Yang et al [7]. For the Ni nanowire and Ni/BN(9,0), the DOS around $E_f$ is always dominated by the minority spin part. The analysis of the projected density of states (PDOS) for Ni/BN(9,0) shows that the states around the Fermi level are mainly contributed by Ni 3d orbitals. And almost all the spin density is located at the Ni nanowire. So the electronic or spin transport will occur only in the core metal nanowires. In the spin-resolved band structure of Ni/BN(9,0), there is a gap just above the Fermi level for the spin-up component indicating a semi-HM behaviour, contrasting sharply with the band structure for the free-standing Ni nanowire. It should be emphasized that the semi-HM behaviour is found in the stablest ferromagnetic phase of TM/BN(9,0). Singh et al [26] also found the semi-HM behaviour in an Mn-doped Si hexagonal nanotube, however, in the metastable ferromagnetic phase. The ferromagnetic ground state is helpful for application in spin-polarized transport.

So why does the band structure for Ni/BN(9,0) differ so much from that for the free standing Ni nanowire since BN nanotubes are generally inert? As the semi-HM energy gap arises in the majority spin part, we focus only on the majority spin part. There are two states crossing the Fermi level in the spin majority part in the Ni nanowire, namely a non-degenerate state $\alpha$ and a double-degenerate state $\beta$, as can be seen from figure 2(a1). Partial charge analysis shows that the $\alpha$ state mainly distributes in the middle of planes A and B, while the $\beta$ state almost locates at planes A and B. After the Ni nanowire is inserted into BN nanotubes, the $\alpha$ state near $\Gamma$ is shifted to lower energy; in contrast, the $\beta$ state near $\Gamma$ is shifted to higher energy. To see what causes the change of the $\alpha$ and $\beta$ states on coated by BN nanotubes, we plot the partial charges of the $\alpha$ and $\beta$ states for the free-standing Ni nanowire and Ni/BN(9,0) in figures 2(b) and (c). We can see that the $\alpha$ state becomes more delocalized but the $\beta$ state becomes more localized after the Ni nanowire is inserted into BN nanotubes. The different charge distributions between $\alpha$ and $\beta$ states and the fact that the energy of $\alpha$ state is lower than that of $\beta$ state in Ni/BN(9,0), suggest the $\alpha$ state is a bonding orbital and the $\beta$ state is an anti-bonding orbital. The bonding and anti-bonding interactions are responsible for the different energy shifts for the $\alpha$ and $\beta$ states, respectively.

Since low-dimensional HM materials are ideal for spintronic applications, can Ni encapsulated BN nanotubes become HM? Theoretically, by doping electrons more than 1.4 $e$ per unit cell to lift the Fermi level upward by about 0.1 eV using some techniques, such as applying gate voltage in a MOSFET-like system, Ni/BN(9,0) could become HM. Even a metal to semiconductor transition could occur by doping 4.0 $e$ per unit cell to lift the Fermi level upward more than 0.25 eV. On the other hand, seeking intrinsic HM in nanostructures is a more elegant solution to this question. Since the semi-HM in Ni/BN(9,0) results from the hybridization between the Ni nanowire and BN nanotube, the HM behaviour is expected to occur in Ni encapsulated BN nanotubes with an increased hybridization effect. Two different means are considered to increase the hybridization. Firstly, we study the hcp
Figure 2. Spin-resolved band structures and partial charges of the $\alpha$ and $\beta$ states for the free-standing Ni nanowire and Ni/BN(9,0). (a1) and (a2) are the band structures for the free-standing Ni nanowire and Ni/BN(9,0). The left panel is for the majority spin and the right panel is for the minority spin. (b1) and (b2) are the partial charges for the $\alpha$ state of the free-standing Ni nanowire and Ni/BN(9,0), respectively. (c1) and (c2) are the partial charges for the $\beta$ state of the free-standing Ni nanowire and Ni/BN(9,0), respectively. The $\alpha$ and $\beta$ states refer to those marked in (a1) and (a2).
Figure 3. Spin-resolved band structures for Ni/BN(8,0) and two radial homogeneously shrunken Ni encapsulated BN(9,0) nanotube hybrid structures: (a) Ni/BN(8,0), (b) 5% radial shrinkage, and (c) 10% radial shrinkage. The left panel is for the majority spin and the right panel is for the minority spin.

Ni nanowire coated with a smaller BN nanotube, i.e., BN(8,0) nanotube. The spin-resolved band structure for Ni/BN(8,0) shown in figure 3(a) obviously indicates a HM behaviour. Although the formation of Ni/BN(8,0) is endothermic, Ni/BN(8,0) or other similar hybrid structures could be synthesized at high temperature with some subtle experimental methods, such as mechanic techniques and/or two-stage process. Secondly, we investigate the Ni encapsulated BN(9,0) nanotube upon hydrostatic pressure. We simulate the pressure by fixing a homogeneous radial shrunken BN(9,0) nanotube and then fully relaxing the Ni nanowire. Radial shrinkages to two different levels, 5 and 10%, induced by homogeneous external pressures 2.6 and 6.7 GPa, respectively, are examined. Here, we assume that these external pressures would not cause Ni/BN(9,0) to transform to the oval shape. This is reasonable since the estimated transition pressure is 5.7 GPa for BN(9,0) if we use the 1/R³ relationship between the transition pressure and the radius of the nanotube, and the fact that BN nanotubes have similar mechanical properties as carbon nanotubes, and the transition pressure for C(6,6) (about 4.0 GPa) [27]; moreover, the transition pressure for Ni/BN(9,0) should be larger than this value due to the presence of the core Ni nanowire. The band structures of the Ni-encapsulated shrunken BN(9,0) nanotubes are shown in figures 3(b) and (c). We can clearly see that an energy gap is induced in the spin majority band of the hybrid structure after a small radial shrinking. Moreover, we find that the HM energy gap increases along with the increase in the shrinkage, as seen from figure 3 that the HM band gap for 10% shrunken Ni/BN(9,0) is larger than that for 5% shrunken Ni/BN(9,0). The radial shrinkage smaller than 5% would not induce such a semi-HM to HM transition. In the two cases, both with a decrease in the radius of the nanotube and therefore increased hybridization, the bonding and anti-bonding interactions become stronger. Once the interactions are strong enough, the HM can arise in these hybrid systems. Additionally, we find that the oval deformation could not induce the transition from semi-HM to HM. For the oval deformation, the hybridization between the Ni nanowire and BN nanotubes is not thorough since the oval deformation only increases the interaction between some Ni atoms and nanotube, but the interaction between other Ni atoms and nanotube is weakened.
The results about the total magnetic moment for the free-standing Ni nanowire and hybrid Ni/BN nanotubes are listed in table 1. As we can see, the total magnetic moment are decreased after forming a hybrid Ni/BN nanotube. This is typically due to the hybridization of the metal 3d states with the 2s and 2p states of boron and nitrogen. Interestingly, the reduction amount does not have a simple relationship with the radius of the BN nanotubes. When the radius is large enough, the reduction amount decreases with the increase in the nanotube radius, which can be explained by the weak hybridization effect.

Although only Ni encapsulated BN nanotubes are analysed in detail in our discussion, the main results for Ni encapsulated BN nanotubes apply equally to other TM, such as Fe, and Co-encapsulated BN nanotubes. All these three TM/BN(8,0) are HM. The hydrostatic pressure can induce the transition from non-HM to HM for TM/BN nanotube hybrid systems. By performing a calculation on the Ni nanowire coated by a double-walled BN nanotube, called BN(8,0)@BN(16,0), we find a HM behaviour in such a system, indicating that the speical magnetic properties for TM encapsulated multi-walled BN nanotubes are mainly dependent on the innermost BN wall. Detailed discussions will appear elsewhere [28]. It is noteworthy that the special magnetic properties are unique for TM/BN nanotube hybrid structures and are not found in previous studies on TM/C nanotube hybrid structures [7]. Recently, ferromagnetism in the systems consisting of B, N and C atoms is also reported [29, 30]. Although the metal-free ferromagnetism is attractive, the energy difference between the ferromagnetic state and the nonmagnetic state is small [30], thus the proposed systems might have low Curie temperature. In contrast, the ferromagnetism in TM/BN nanotube hybrid structures is due to the strong ferromagnetic metals, and these hybrid structures is expected to have high Curie temperature.

In conclusion, we have performed an extensively first principles study on BN nanotubes encapsulated with the Ni hcp nanowire. All Ni/BN are ferromagnetic metals. The hybridization between the Ni nanowire and BN nanotubes leads to semi-HM or HM ferromagnetism in Ni/BN nanotubes. Ni/BN(9,0) is the most favourable form among the Ni-encapsulated BN nanotubes we studied and shows semi-HM behaviour, which could be turned into HM behaviour by doping electrons more than 1.4 e per unit cell. Moreover, HM ferromagnetism could be achieved by coating the Ni nanowire with a small radius BN nanotube, i.e., BN(8,0). Interestingly, for Ni encapsulated BN nanotubes the HM behaviour could also be accomplished by the homogeneous shrinkage of BN nanotubes induced by hydrostatic pressure. And the HM band gap could be tuned by the applied pressure. Importantly, the interesting magnetic properties are not particular to Ni/BN nanotubes, but prevalent characters for Fe, Co and Ni-encapsulated BN nanotubes. Almost all spin density and transport electrons locate in the core TM nanowire in TM/BN, differently from TM/C, in which electron and spin are more delocalized. All these special properties of TM/BN are very useful for spintronics and spin-polarized transport.

Acknowledgments

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