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On the possibility of contact-induced spin polarization in interfaces of armchair nanotubes with transition metal substrates

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ABSTRACT

The interaction between armchair carbon and boron nitride nanotubes (NT) with ferromagnetic transition metal (TM) surfaces, namely, Ni(111) and Co(0001), was studied by means of density functional theory. Different configurations of composite compartments mutual arrangement were considered. Partial densities of states and spin density spatial distribution of optimized structures were investigated. Influence of ferromagnetic substrate on nanotubes' electronic properties was discussed. The values of spin polarization magnitude at the Fermi level are also presented and confirm the patterns of spin density spatial distribution.

1. Introduction

The search for new spin filtering materials is one of the acute issues of modern spintronics. Conducting spin-polarized current, these materials may be implemented in magnetoresistive memory elements, hard disk scanning heads, and other devices. Previously it was shown that planar hexagonal nanostructures such as graphene [1–4] and *h*-BN [2,5–7] as well as corresponding zigzag nanotubes [8] have a great potential for utilization in spintronic devices due to the spin polarization induced by the contact with ferromagnetic substrate.

The bonding of *h*-BN with ferromagnetic Co [5,7] and Ni [2,6] surfaces was found to be significantly stronger than that with other metals, such as Cu, Pd and Pt. This result is also confirmed by the theory. It was found that dispersion interaction plays an important role in bonding of *h*-BN with nickel while it is less important for cobalt since *h*-BN is likely to form covalent bonds with cobalt surface [5]. N atoms placed above the topmost metal sites were found to be much more favorable than B atoms. Boron atoms are then located either in *hcp* or *fcc* position. The study of composites' electronic structure reveals the presence of induced magnetic moment on the *h*-BN sheet. Nitrogen atoms possess magnetic moment parallel to that of metal atoms (positive spin polarization) while boron atoms have large magnetic moment being antiparallel to that of Co and Ni (negative spin polarization). Interfaces of graphene with various transition metals are also well-studied by both theoretical and experimental techniques [1–4]. The most stable configuration of mutual arrangement in graphene/Ni(111) composite were determined by means of density functional theory [2,3]. Three different possible positions of carbon atoms were considered (*top, hcp* and *fcc*) but new *bridge* configurations were found during the geometry optimization. The comparison of LDA and GGA-PBE approaches reveals that even though LDA describes such systems better than PBE functional, it tends to overestimate binding energies. Hence, using van-der-Waals correction is necessary here too [3]. Electronic exchange interaction with nickel lead to spin polarization of graphene even in presence of multilayer *h*-BN media [2].

According to previous studies [9–11], interaction between CNTs and metal substrate can vary from physical adsorption [9] to covalent bonding [10] depending on the metal species. It was found that there is a correlation between interaction energy and metal's work function [11]. It also influences charge transfer in these composites. Moreover, the Fermi-level shift of combined system with respect to pristine nanotube can be estimated with reasonable accuracy using phenomenological model developed by Hasegawa and Nishidate [9]. However, 3d metal-based composites (e.g. Fe, Co, Ni) are more complicated due to their prominent

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magnetic and catalytic properties. Interface of (5,0) carbon nanotube with iron nanowire was studied by a combination of density functional theory (DFT) and Non-Equilibrium Green function (NEGF) method [12]. Carbon atoms bonded with iron were found to be slightly spin polarized. Minor spin polarization can be explained in terms of interface structure features. Nanowire is bumped into the tube [12] which leads to much smaller contact area in comparison with the tube lying on the metal slab [8]. Theoretical study of Fe-filled nanotubes deposited on Ni(111) and Cu(111) surfaces shows that the presence of Fe lead to significant change in nanotube's structure in both cases [13]. In fact, it turns to carbon "nanoarch" while metal surface becomes slightly corrugated. Charge density distribution confirms that both Fe and metal substrate affect C–C bonds leading to transformation of the tube. Theoretical investigation of interaction between zigzag carbon and boron nitride nanotubes and ferromagnetic substrates [8] showed that Co-based composites are more perspective in terms of utilization in spintronics. However, though it is known that armchair nanotubes are formed predominately during the synthesis [14], there is still no information about their interaction with ferromagnetic substrates. The present work is to fill this gap and to characterize the interaction of armchair CNTs and BNNTs with Co and Ni and to reveal the features of electronic structure in these nanocomposites.

2. Computational methods

The first-principles density functional theory calculations of nickel and cobalt interfaces with BN and carbon armchair (5,5) nanotubes were performed using VASP code [15–18]. GGA PBE potential [19,20] and projector augmented wave [21,22] method (PAW) and D3 Grimme's correction [23] of weak dispersion interaction were implemented.

First, unit cells of bulk Co and Ni were optimized. Then we cut them normal to [001] and [111] crystallographic directions in order to obtain corresponding surfaces. Next, metal slabs were simulated by constructing supercells containing 7 surface unit cells along one of the directions. The length of slabs (16.85 Å for Co and 16.90 for Ni) was sufficient for tubes in neighboring images could be placed distant from each other in order to simulate isolated nanotubes on metal surface. Artificial interactions in periodic boundary conditions were avoided by setting the vacuum interval of approximately 10 Å in direction normal to the interface. As well as in previous study of interfaces with zigzag tubes [8], Co(0001) and Ni(111) slabs consisted of 8 and 9 atomic layers, respectively. Then, CNT(5,5) and BNNT(5,5) optimized structures were deposited on metal surfaces in the way ensuring the best commensuration between slab's and tube's translation vectors.

The Mönkhorst-Pack [24] *k*-point Brilloin sampling was used. The *k*-point grid contained 12 points along the least translation vector and 1 point along the largest translation vector. Hexagonal symmetry of Co(0001) supercell was taken into account by specifying number of *k*-points in larger lateral direction as 2. This is reasonable because a vector there is defined not only by the first coordinate but has also a small contribution of the second one. For Ni(111), orthorhombic supercell was used, so 1*k*-point was enough in this case. The energy cut-off was specified as 400 eV in all calculations. All abovementioned values were carefully tested on either these systems or the similar ones containing zigzag nanotubes [8] and were found to be sufficient in describing such interfaces.

Table 1
The binding energies and bond distances for *NT/TM slabs*.

Nanotube	Metal	*top:fcc*		*top:hcp*		*bond*	
		E_b, eV	*z*, Å	E_b, eV	z, Å	E_b, eV	*z*, Å
CNT (5,5)	Co	–	–	−1.534	2.040	−1.515	2.044
	Ni	−1.918	2.030	–	–	−2.074	2.033
BNNT (5,5)	Co	−1.097	2.097	−1.150	2.099	–	–
	Ni	−1.675	2.055	−1.680	2.063	–	–

To reveal the stability of interfaces, the binding energy was estimated using following equation:

$$E_b = E_{t(NT/TM\ slab)} - E_{t(NT)} - E_{t(TM\ slab)}, \quad (1)$$

where E_b is binding energy of a nanotube with metal slab surface, $E_{t(NT/TMslab)}$ is the total energy of hybrid structure, $E_{t(NT)}$ is nanotube's total energy, and $E_{t(TMslab)}$ is the total energy of a metal slab. The magnitude of spin polarization was calculated as

$$\xi = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}, \quad (2)$$

where $n_\uparrow$ and $n_\downarrow$ are electron densities at the Fermi level for spin-up and spin-down states, respectively.

3. Results and discussion

In this study the following possible configurations of *NT/TM* composites were considered: *top:fcc* and *top:hcp* for CNT and *top(N):fcc(B)*, *top(N):hcp(B)*, hereafter *top:fcc*, *top:hcp*, for BNNT (Fig. 1). *Top(B):fcc(N)* and *top(B):hcp(N)* configurations were found to be much higher in energy than *top(N):fcc(B)* and *top(N):hcp(B)* ones, in agreement with the data obtained for *h*-BN monolayer [1,2,7] and zigzag tubes [8]. The *top:fcc* configuration of CNT(5,5)/Co and *top:hcp* configuration of CNT(5,5)/Ni relaxed into the *bond* configuration (carbon bond is placed above the TM atom) during the optimization (Fig. 1). The deformation of the tube was observed in these cases (see Fig. 3). This new configuration may be referred to the *bridge* configurations found in graphene/Ni(111)

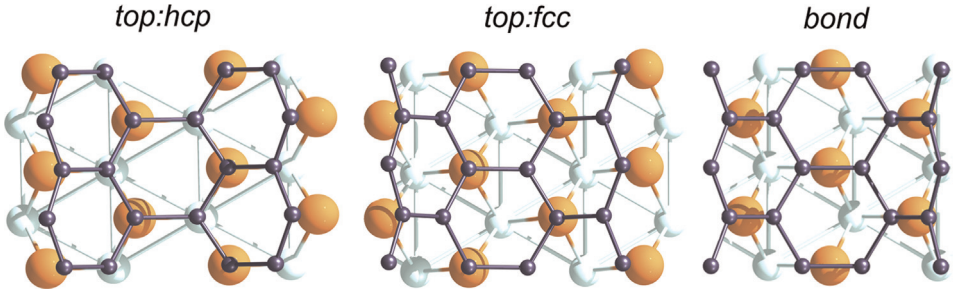

Fig. 1. Configurations of nanotubes' location on the metal substrate. Carbon atoms presented as small dark balls; big orange and smaller light green balls correspond to metal atoms of first and second layer, respectively. Upper part of the tube is not presented for the sake of better representation. (2 columns fitting). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

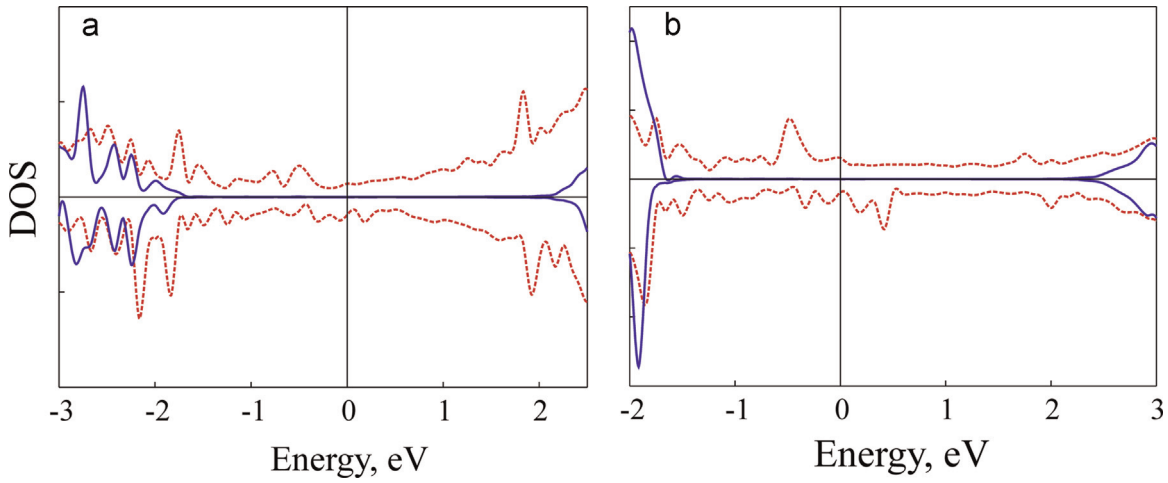

Fig. 2. Boron (a) and nitrogen (b) PDOSes of BNNT(5,5)/Ni composite. Red (blue) line corresponds to atoms near to (far from) the interface. (2 columns fitting). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

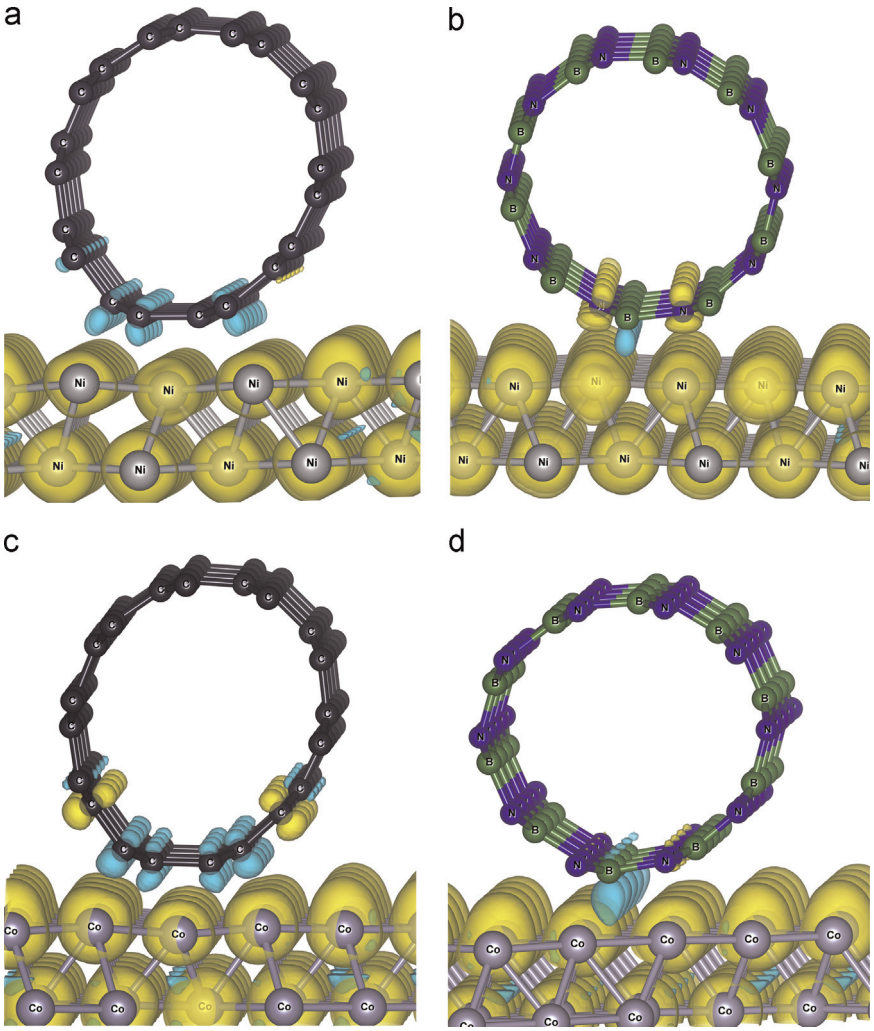

Fig. 3. Spatial distribution of spin density in (a)CNT(5,5)/Ni; (b) BNNT(5,5)/Ni; (c) CNT(5,5)/Co; (d) BNNT(5,5)/Co. Yellow (blue) color corresponds to spin-up (spin-down) electron density (2 columns fitting). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

composite [3]. It should be noticed that only a slight displacement of the tube's atoms from *top* sites was observed in interfaces of Co and Ni with zigzag nanotubes [8]. However, *bond* configuration is not stable for BN nanotubes, initial structure relaxing into one of the favorable configurations. For both Ni and Co-based composites the energy difference between configurations is negligible (see Table 1), the biggest one observed in CNT(5,5)/Ni system (~0.15 eV) is still too small to separate them in synthesis condition. In general, bonding of TM slab with carbon nanotubes is stronger than that with BNNTs, in agreement with previous

Table 2
Magnitude of spin polarization of nanotube's atoms at the Fermi level.

Nanocomposite	ξ, %
BNNT(5,5)/Co *(top:fcc)*	1.5
BNNT(5,5)/Co *(top:hcp)*	15.2
BNNT(5,5)/Ni *(top:fcc)*	11.7
BNNT(5,5)/Ni *(top:hcp)*	24.8
CNT(5,5)/Co *(bond)*	13.0
CNT(5,5)/Co *(top:hcp)*	8.8
CNT(5,5)/Ni *(bond)*	3.9
CNT(5,5)/Ni *(top:fcc)*	17.4

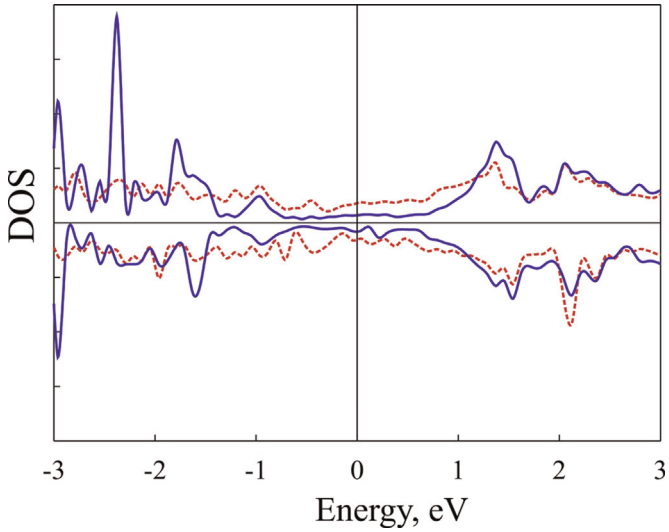

Fig. 4. Partial density of states of CNT(5,5)/Ni carbon atoms. Red (blue) line corresponds to atoms near to (far from) the interface. (1 column fitting). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

studies [8]. In contrast to planar structures and zigzag nanotubes, Ni-based composites are more energetically favorable than Co-based ones.

Then, the electronic structure of composites was analyzed. Minor energy discrepancy between configurations makes it reasonable to analyze all of them.

According to the partial densities of states plotted for the atoms being in direct contact with metal surface and for the atoms on the opposite side of the tube (Fig. 2), BN (5,5) nanotube demonstrates local contact-induced conductivity while the rest of the tube remains to be an insulator, as well as the (9,0) one [8]. The positive spin polarization was observed for the nitrogen atoms while the boron atoms are negatively spin-polarized (Fig. 3b and d). Spin density distribution is quite similar for all 4 BNNT-based nanocomposites. However, their magnitude of spin polarization differs significantly (see Table 2). This can be attributed to the larger distance between boron and metal atoms in *top:fcc* configuration which weakens the effect of its polarization. Indeed, we can see that polarization of nanotube BNNT(5,5)/Co (*top:hcp*) system is mainly caused by negative polarization of boron atom while it is almost fully compensated by positively polarized nitrogen atoms (see Fig. 3) in BNNT(5,5)/Co (*top:fcc*). The same tendency, though less pronounced, can be observed in BNNT(5,5)/Ni composites (see Table 2). These results are in good agreement with those for planar *h*-BN sheet [5] and (9,0) BN nanotubes [8].

Electronic structure of carbon atoms being distant from interface is also quite similar to that of an isolated nanotube, while the vanishing of the gap is observed for atoms in direct contact with metal slab (Fig. 4). These atoms are visibly negative spin-polarized (Fig. 3a and c). There is also a positive polarization of the next atoms in CNT(5,5)/Co (*bond*). However, we can see again that both for Co and Ni-based interfaces ξ depends strongly on the configuration (Table 2) while energy difference between them is very small. This means that the yield of both configurations in synthesis would be almost the same which, in turn, makes their utilization in spintronic devices much less perspective even though some of them show significant values of spin polarization.

4. Conclusion

The interfaces of armchair carbon and boron nitride nanotubes with ferromagnetic Co(0001) and Ni(111) surfaces was investigated by first-principles calculations. In general, all composites are negatively spin-polarized. However, we found that the value of spin polarization differs significantly from one possible configuration of composite to another. Unfortunately, for all considered systems there is almost no difference in energy among the variants of nanotube and metal substrate mutual arrangement. This makes their utilization in spintronics unreasonable, in contrast with previously studied zigzag nanotubes [8]. However, contact-induced local conductivity in boron nitride nanotubes still can be used somewhere in nanoelectronic devices. Particularly, their high thermal conductivity along with abovementioned unique electronic properties allows using them in thermoelectric coolers based on the Peltier effect.

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