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Contact-induced spin polarization in BNNT(CNT)/TM (TM=Co, Ni) nanocomposites

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The interaction between carbon and BN nanotubes (NT) and transition metal Co and Ni supports was studied using electronic structure calculations. Several configurations of interfaces were considered, and the most stable ones were used for electronic structure analysis. All NT/Co interfaces were found to be more energetically favorable than NT/Ni, and conductive carbon nanotubes demonstrate slightly stronger bonding than semiconducting ones. The presence of contact-induced spin polarization was established for all nanocomposites. It was found that the contact-induced polarization of BNNT leads to the appearance of local conductivity in the vicinity of the interface while the rest of the nanotube lattice remains to be insulating. © *2014 AIP Publishing LLC*.
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I. INTRODUCTION

Nanoheterostructures with magnetic tunnel junction (MTJ) are promising composite materials for hard disk scanning heads, magnetoresistive memory elements, and other spintronic devices. In many cases, an insulating layer determines the main physical properties of the nanocomposites. Spin-polarized current is required to get through the interface without change of its projection. Graphene and *h*-BN are promising spin filtering materials.[1–3] We suppose that boron nitride and carbon nanotubes (BNNTs and CNTs) can also be used for this purpose.

Although the contact interaction of carbon and BN nanotubes with ferromagnetic substrates is supposed to be quite similar to that of the corresponding graphene and *h*-BN hexagonal monolayers, which can be considered as nanotubes of extremely large diameter, finite thickness of the tubes can result in significant change of interface properties. This effect is to be investigated in detail.

Interaction of graphene with transition metal surfaces is well studied by both theoretical and experimental methods.[2,4–6] Several configurations, namely, *top:fcc, bridge:top,* and *bridge:fcc* were found to be the most favorable for graphene/Ni(111) system.[4,5] The perfect single-layer *h*-BN has been synthesized by CVD technique using some transition metals as supports.[7] The bonding in *h*-BN/Ni(111) composites is found to be much stronger than in *h*-BN/Pd(111), *h*-BN/Pt(111) and *h*-BN/Cu(111) and can be attributed to hybridization of *h*-BN π-states with 3*d* states of Ni.[4,8] Theoretical results[3,9] confirm the presence of covalent bonding between the *h*-BN and TM fragments in *h*-BN/Co(111) and *h*-BN/Co(0001) nanocomposites.

According to previous studies,[10–13] interaction in CNTs/TM nanocomposites can vary from physical adsorption[10,12] to covalent bonding[11] depending on the nature of substrate. Interfaces of CNTs with 3*d* metals are of a particular interest due to their prominent magnetic and catalytic properties.

The BN nanotubes are significantly more stable in terms of heat and chemical resistance[14] than CNTs. In contrast with CNTs, the BN nanotubes of a different chirality demonstrate the similar electronic structure which can be attributed to a wide band gap. It is reasonable to assume that BNNT's bonding with the metal surfaces may be quite similar to that of *h*-BN. However, the question of the curvature effect is still open, so the interaction between BNNTs and metal surfaces is to be investigated in detail.

The present study is to characterize the interactions of CNTs or BNNTs with ferromagnetic transition metals, namely, Co and Ni, and to reveal the nature of spin polarization of the nanotube fragments caused by interactions with transition metal supports.

II. COMPUTATIONAL METHODS

The first-principles calculations of 3*d* nickel and cobalt interfaces with BN and carbon nanotubes were performed by Local Density Approximation (LDA),[15] plane wave basis set and ultrasoft Vanderbilt-type pseoudopotentials[16,17] using VASP code.[18,19] The energy cut-off was specified as 400 eV in all calculations.

The atomic and electronic structure of metallic (9,0) and semiconducting (10,0) carbon nanotubes as well as (9,0) BN nanotube deposited on transition metal (TM) ferromagnetic Co(0001) and Ni(111) surfaces of hexagonal symmetry was calculated. To reproduce the main features of the electronic structure and spin states of the *NT/TM* composites, 8 layers

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of Co and 9 layers of Ni were chosen to design slab models. To avoid artificial interactions between the slab partners, a vacuum interval along the normal direction to the *NT/TM* interface was equal to 10 Å. Translation vector being parallel to the metal surface and normal to the tube axis was fixed at the values of 17.11 and 19.26 Å for Ni and Co, respectively. The Mönkhorst-Pack[20] *k*-point Brillouin sampling was used. The *k*-point grid contained 6 points along the least translation vector and 1 point along two large translation vectors.

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 *NT/TMslab*, $E_{t(NT)}$ 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 for spin-up and spin-down states, at the Fermi level respectively.

III. RESULTS AND DISCUSSION

In this work, the following possible configurations of *NT/TM* composite slabs were considered: *top:fcc* and *top:hcp* for CNTs (carbon atoms are placed under *top*, *hcp* and *fcc* positions of the TM substrates) and *top(N):fcc(B)*, *top(N):hcp(B)*, hereafter *top:fcc, top:hcp*, for BNNTs (the nitrogen atoms are placed under *top* and boron atoms are placed under *hcp* or *fcc* positions of the substrate, see Figure 1). It was found that *top(B):fcc(N)* and *top(B):hcp(N)* configurations are approximately 1.5 eV higher in energy than *top(N):fcc(B)* and *top(N):hcp(B)* ones, in agreement with the data obtained for *h*-BN monolayer.[2,4,9]

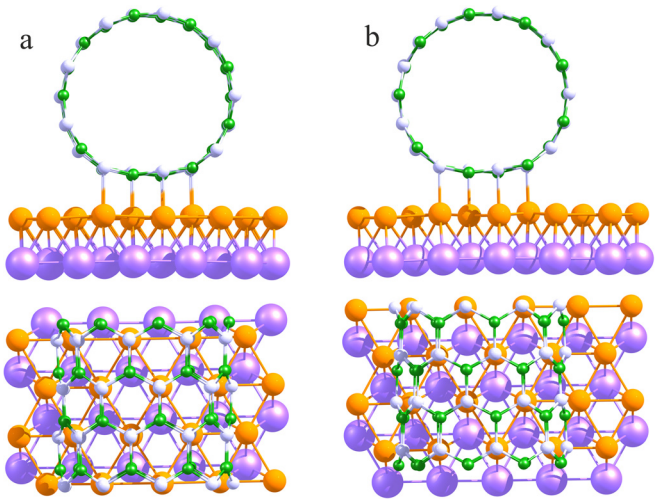

FIG. 1. (a) top(N):hcp(B); (b) top(N):fcc(B) configurations of BNNT/Co nanocomposite. Boron/nitrogen atoms are represented as green and gray balls, respectively. Orange and blue balls correspond to the first and second atomic layers of nickel atoms, respectively.

Table I shows the binding energies of *NT/TM* composites as well as corresponding bond distances. All Co-based nanocomposites were found to be substantially more energetically favorable than Ni ones. The CNT(9,0)(*top:hcp)*/Co, CNT(9,0)(*top:fcc)*/Ni, CNT(10,0)(*top:fcc*)/Co, CNT(10,0)(*top:hcp*)/Ni, BNNT(9,0)(*top:hcp*)/Co and BNNT(9,0)(*top:fcc*)/Ni nanocomposites were found to be the most energetically favorable among all studied structures. The CNT(9,0)/TM interfaces demonstrate slightly stronger bonding than CNT(10,0)/TM ones, which can be attributed to the difference in their conducting properties. Bond distances in *top:fcc* and *top:hcp* configurations remain virtually the same (the difference ≤ 0.01 Å). A slight displacement of the nanotube's atoms from the *top* sites was observed for CNT(9,0)(*top:fcc)*/Co, CNT(9,0)(*top:hcp*)/Co, CNT(9,0)(*top:fcc*)/Ni, CNT(10,0)(*top:hcp*)/Ni and BNNT(9,0)(*top:hcp*)/Ni configurations. The angles between TM-X bonds (X = N, C) and normal to TM surface are in the range of 5–6°. Similar phenomena was also found at graphene monolayer/Ni(111) interface.[5]

To analyze the electronic structure of the composites only the most energetically favorable interface configurations of the composites were considered. Carbon partial density of states (PDOS) of CNT/Ni and CNT/Co nanocomposites for carbon atoms in direct contact with the metal surfaces as well as at the opposite side of the nanotubes are presented in Figures 2(a) and 2(b). The nitrogen and boron PDOSes of BNNT(9,0)/Co composite are presented in Figure 3.

Interfaces of different CNTs with the same type of substrate display very similar state distribution near the Fermi level. In particular, atoms in the direct contact with the metal surfaces demonstrate significant differences between spin-up and spin-down density of states. However, atoms far from the interface are not spin-polarized.

In the case of CNT(10,0)(*top:fcc*)/Co composite, a visible negative spin polarization of the *top* atoms and weak positive spin polarization of atoms far from the interface is detected (Figure 2(c)) with no spin polarization observed at *fcc* carbon atoms. In contrast, for CNT(10,0)(*top:hcp*)/Ni a positive spin polarization of *hcp* atoms (Figure 2(d)) as well as the *top* atoms negative spin polarization was detected.

In contrast with CNTs, the electronic structure of the BNNT's atoms distant from the interface is quite similar to that of an isolated nanotube with band gap approximately equal to 3.8 eV. This effect can be explained in terms of strong localization of electrons in BN nanotube, which leads

TABLE I. The binding energies and bond distances for *NT/TMslab*s.

		top:fcc		*top:hcp*	
Nanotube	Metal	E_b, eV	z, Å	E_b, eV	z, Å
CNT(9,0)	Co	−4.646	1.939	−4.720	1.944
	Ni	−2.600	1.922	−2.374	1.929
CNT(10,0)	Co	−4.523	1.944	−4.360	1.949
	Ni	−2.260	1.921	−2.311	1.931
BNNT(9,0)	Co	−3.876	1.993	−3.926	1.990
	Ni	−1.891	1.968	−1.693	1.967

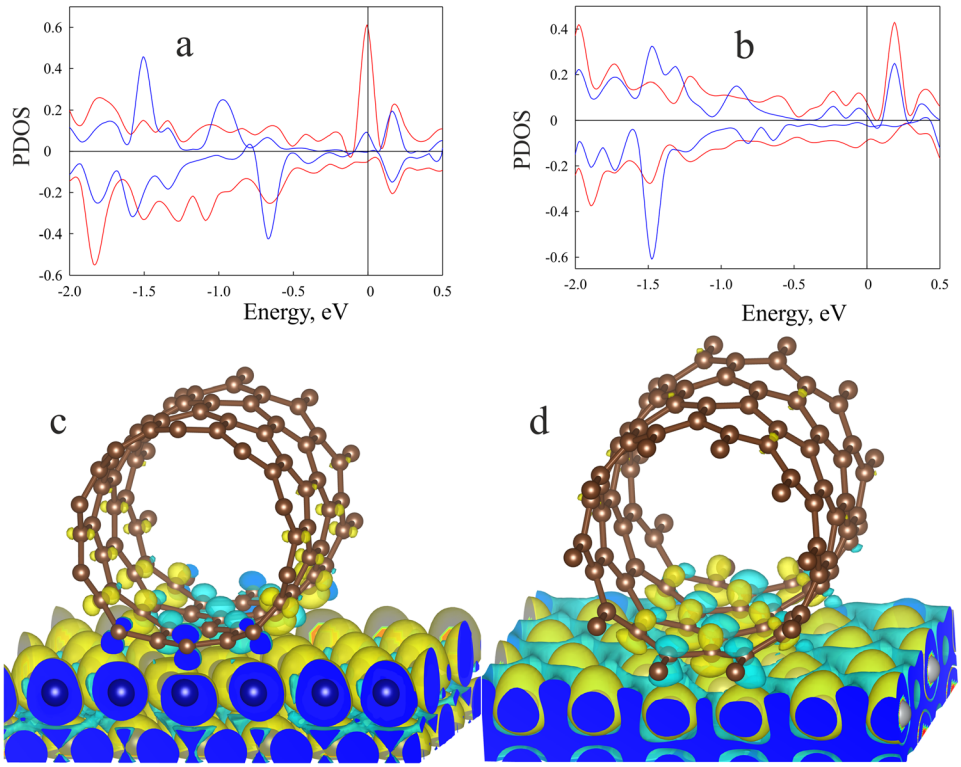

FIG. 2. (a) Partial density of states (PDOS) of CNT(10,0)/Co carbon atoms. (b) Partial density of states of CNT(10,0)/Ni carbon atoms. (c) Spatial distribution of spin density in CNT(10,0)/Co. (d) Spatial distribution of spin density in CNT(10,0)/Ni. Red (blue) line corresponds to the PDOSes of the atoms near to (far from) interfaces (a),(b). Yellow (blue) color corresponds to spin-up (spin-down) electron density (c), (d).

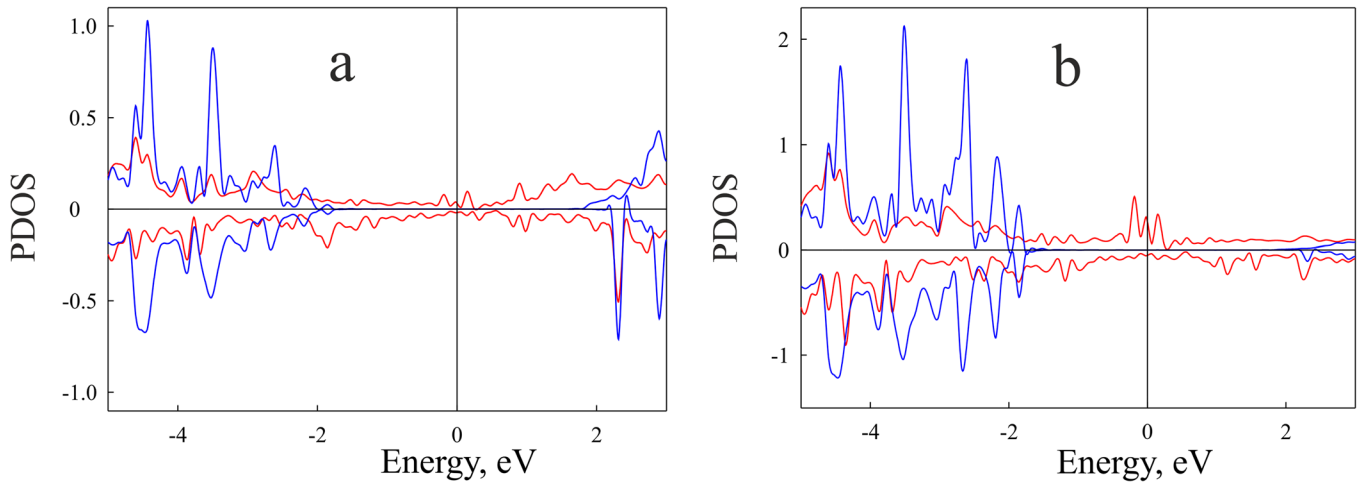

FIG. 3. Boron (a) and nitrogen (b) PDOSes of BNNT(9,0)/Co composite. Red (blue) line corresponds to atoms near to (far from) the interface.

to the difficulties in spin polarization spreading along the tube's diameter. However, contact-induced polarization leads to the filling of the unoccupied states and vanishing of the band gap. It causes an appearance of local conductivity in BNNT(9,0)/Ni and BNNT(9,0)/Co composites. According to the spin density spatial distribution (Figure 4), the nitrogen atoms of BNNT/Ni are positively spin polarized, while only weak negative polarization is observed at boron atoms. In contrast, significantly stronger negative polarization on B is observed in the case of BNNT/Co due to the much shorter distance between boron and cobalt atoms in *top:hcp* configuration than between B and Ni in *top:fcc* (3.749 and 5.761 Å, respectively).

The magnitude of nanotubes' total spin polarization is presented in Table II. The NTs deposited on Co surface are

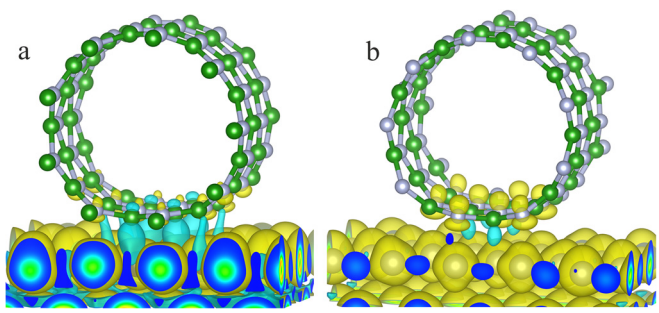

FIG. 4. Spin density spatial distribution of BNNT(9,0)/Co (a) and BNNT(9,0)/Ni (b). Yellow (blue) color corresponds to spin-up (spin-down) electron density. Boron (nitrogen) atoms are represented as green (gray) balls.

TABLE II. Magnitude of spin polarization of nanotube's atoms for the most energetically favorable *NT*/*TM* configurations.

	ξ, %	
Nanotube	Co	Ni
CNT(9,0)	35	14
CNT(10,0)	87	17
BNNT(9,0)	55	13

significantly more spin polarized than those on Ni slabs. This can be attributed to the different number of electrons for these ferromagnetic metals. Conducting nature of CNT(9,0) results in spreading of both spin-up and spin-down density along the tube's diameter and decreasing of spin polarization value.

IV. CONCLUSIONS

Different configurations of carbon and boron nitride nanotube interfaces with cobalt (0001) and nickel (111) supports were studied using DFT-LDA method. The electronic structure analysis of the most stable configurations reveals the presence of contact-induced spin polarization in all composites. It was found that NT/Co composites are approximately twice as low in energy as NT/Ni ones and spin polarization in these systems is also much stronger. Lower energy of CNT(9,0)/TM in comparison with CNT(10,0)/TM can be attributed to the difference in their conducting properties. Conducting nature of CNT(9,0) also causes a weaker spin polarization in comparison with other tubes. In addition, BNNTs demonstrate a local contact-induced conductivity while the fragments distant from interface remain to be insulating.

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