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The direct exchange mechanism of induced spin polarization of low-dimensional π-conjugated carbon- and *h*-BN fragments at LSMO(001) MnO-terminated interfaces

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ABSTRACT

Induced spin polarization of π-conjugated carbon and *h*-BN low dimensional fragments at the interfaces formed by deposition of pentacene molecule and narrow zigzag graphene and *h*-BN nanoribbons on MnO_2-terminated LSMO(001) thin film was studied using GGA PBE+U PAW D3-corrected approach. Induced spin polarization of π-conjugated low-dimensional fragments is caused by direct exchange with Mn ions of LSMO(001) MnO-derived surface. Due to direct exchange, the pentacene molecule changes its diamagnetic narrow-band gap semiconducting nature to the ferromagnetic semiconducting state with 0.15 eV energy shift between spin-up and spin-down valence bands and total magnetic moment of 0.11 μ_B. Direct exchange converts graphene nanoribbon to 100% spin-polarized half-metal with large amplitude of spin-up electronic density at the Fermi level. The direct exchange narrows the *h*-BN nanoribbon band gap from 4.04 to 1.72 eV in spin-up channel and converts the *h*-BN ribbon semiconducting diamagnetic nature to a semiconducting magnetic one. The electronic structure calculations demonstrate a possibility to control the spin properties of low-dimensional π-conjugated carbon and *h*-BN fragments by direct exchange with MnO-derived LSMO(001) surface for spin-related applications.

1. Introduction

The roles of indirect and double exchange interactions in manganites was elucidated in several experimental and theoretical publications (see, for example [1,2]). In particular [2], it was found that magnetism of $La_{0.9}Sr_{0.1}Mn_{1-x}Ga_xO_{3+y}$ is caused by Ruderman, Kittel, Kasuya, Yosida (RKKY, [3–5]) mechanism of indirect exchange. Using photoemission and X-ray spectroscopy it was found that in $La_{1-x}Sr_xMnO_3$ ($0.2 \le x \le 0.6$) the oxygen holes are antiferromagnetically bounded with high spin configurations of Mn^{3+} ions [6,7]. The electron-hole excitation leads to charge transfer from O2*p* subband to Mn^{3+} ion with the formation of Mn^{4+} configuration through double exchange mechanism [8]. The LDA electronic structure calculations [9] confirmed the experimental results revealing strong hybridization of Mn*d*- and O2*p* subbands.

In recent years, carbon-based materials attract much attention as promising building blocks for spintronic applications [10–12] because of their extremely high mobility of electrons together with long spin transport length [13,14] caused by weak spin-orbit interactions of carbon atoms. Such remarkable properties allow one to design graphene-based spintronic and spincaloritronic nanodevices.

Many ferromagnetic supports cause strong induced spin polarization of deposited π-conjugated organic media [15,16]. with high magnetoresistance [17,18]. Perovskite manganites are well known as an advantage class of functional with rich variety of magnetic and electric properties, such as half-metallic ferromagnetism, high magnetoresistance, perfect spin polarization and charge/orbital ordering [19–21]. Half-metallic $La_{1-x}Sr_xMnO_3$ (LSMO), which is characterized by colossal magnetoresistance, low-density of charge carriers, high Curie temperature and partial transparency [21,22] is one of the most

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promising materials for magnetic tunnel junctions and effective spin injection in graphene and related π-conjugated organic media. The role of surface magnetization of LSMO was underlined in Refs. [22–24] and it was shown that in the LSMO/Alq_3/Co magnetic tunnel junction, which exhibits magnetoresistance up to 300%, the interfacial spin-dependent metal-organic media hybridization causes an enhancement and even a sign reversal of injected spins. It was also found that the coupling of the electronic states of graphene with Mn ions is very high [25]. The unique magnetic properties of LSMO allow one to develop spin-polarized organic light emitting diodes [26,27] and spin-valve [28,29]. nanodevices. Another example is a spin valve device consisting of carbon nanotube deposited on $La_{0.7}Sr_{0.3}MnO_3$ electrodes [30], which demonstrates a long spin lifetime and high Fermi velocity in the nanotube. Recent photoemission study of the evolution of the electronic structure at C_{60}/LSMO exhibits 0.61 eV interface barrier for the electrons to be injected from LSMO to C_{60}[31].

Due to the long spin lifetime of charge carriers, π-conjugated organic media is considered as promising materials for spintronics nanodevices [32,33] and pentacene molecule $C_{22}H_{14}$ is one of them. This highly conjugated organic molecule exhibits semiconducting electronic properties due to the narrow HOMO-LUMO gap and exciton generation upon absorption of ultra-violet or visible light. It was demonstrated that vertical pentacene-based spintronic devices with $La_{0.7}Sr_{0.3}MnO_3$ and Co electrodes retain magnetoresistive effects up to room temperature [34]. Pentacene binds with Au substrate by weak van der Waals interactions, while Cu and Ag substrates cause chemical interfragment bonding [35]. Recently, spin-dependent molecular symmetries associated with *p–d* hybridization between pentacene and cobalt nanoscale islands deposited on Cu(111) was studied by SP-STM technique [36]. which allows to predict and control induced spin polarization of π-conjugated molecule on magnetic substrates.

Zigzag *h*-BN (ZBNNRs) [37,38] and graphene nanoribbons (ZGNRs) are other examples of the key π-conjugated media to promote spin injection through tunneling junctions, chemical passivation and create insulating layers. It was shown that ZGNRs are antiferromagnetic semiconductors [39] with ferromagnetic spin ordering at each edge [40–42]. Zigzag graphene nanoribbons can be used in spintronics as spin-FET [43] spin logic gates and spin filtering devices [42]. A new highly efficient spin caloritronics MR devices can be fabricated using ZGNR with heterojunctions consisting of single (or double) hydrogen-terminated ZGNR [44]. It is worth to note that ZGNRs demonstrate single-channel room temperature ballistic conductivity on a length scale equal to ten micrometers, which is greater the theoretically predicted value for perfect graphene [45,46]. The unique properties of graphene nanoribbons open unique possibility to create novel LSMO-based heterostructures with induced half-metallic ferromagnetic nature for promising spintronics and spin caloritronics applications.

In this paper, the mechanism of induced spin polarization of pentacene, narrow zigzag graphene and *h*-BN nanoribbons at the interfaces through the direct exchange with MnO_2-terminated LSMO(001) thin film was studied by electronic structure calculations. The surface induces asymmetry causes formation of 2D electron gas localized at the interfaces and lift of spin degeneracy of low-dimensional fragments. The types of coordination of the fragments, the nature of bonding, the degrees of spin polarization of low-dimensional π-conjugated carbon and *h*-BN fragments are predicted and theoretically studied. It was found that weak dispersion forces determine the nature and energy of bonding between the fragments and LSMO(001) substrate.

2. Computational methods

To run all electronic structure calculations of pentacene, graphene- and *h*-BN zigzag nanoribbons deposited on MnO_2-terminated LSMO(001) surface, *ab initio* Density Functional Theory (DFT) within the projector augmented wave (PAW) [47] method and GGA+*U* [48,49] exchange-correlation functional proposed by Perdew, Burke and Ernzerhof (PBE) [50] were used. The empirical D3 Grimme corrections [51] and periodic boundary conditions (PBC) was employed. The U=2 and J=0.7 eV parameters and cutoff energy E_{cutoff}=450 eV were adopted from earlier LSMO calculations [52–54]. For unit cell calculation the Brillouin zone reciprocal space was sampled by 12×12×12 *k*-points using Monkhorst-Pack scheme [55]. To perform all electronic structure calculations, VASP code was used [56,57]. The electronic structure calculations of bulk $La_{0.67}Sr_{0.33}MnO_3$ reveal a translation vector equal to 3.886 Å which is in a good agreement with experimental data (a=3.876 Å [58] and a=3.87 Å [59]) and previous theoretical calculations (a=3.89 Å [52]).

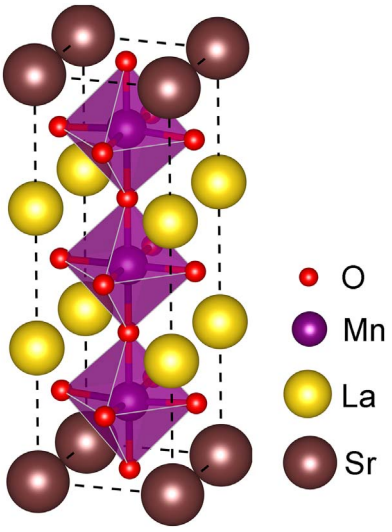

Fig. 1. Atomic structure of $La_{0.67}Sr_{0.33}MnO_3$. The oxygen, manganese, lanthanum and strontium atoms are presented in red, purple, yellow and grey-pink respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The atomic structure of $La_{0.67}Sr_{0.33}MnO_3$ is presented in Fig. 1. Following the experimental data [60–65], the MnO_2 terminal layer could be employed to design the slab model of LSMO(001) thin film to introduce direct exchange mechanism for induced spin polarization of low-dimensional π-conjugated nanofragments. The structure of LSMO(001) contains six layers: one SrO layer formed by tetrahedrally coordinated Sr ions on the bottom of the plate, two MnO layers formed by octahedrally coordinated Mn ions, one top surface MnO layer formed by MnO_5 pyramids and two LaO layers formed by tetrahedral La ions. The La and Sr ions occupy the centers of the cubes formed by Mn ions.

To simulate the LSMO(001)-based heterostructures zigzag graphene and *h*-BN nanoribbons were used as well as highly conjugated pentacene molecule ($C_{22}H_{14}$, five linearly-fused benzene rings). The supercells of narrow zigzag graphene and *h*-BN nanoribbons consist of three C_6 or B_3N_3 hexagons in width and three hexagons in length ($C_{24}H_6$ and $B_{12}N_{12}H_6$ supercells) with standard notations 4-ZGNR and 4-ZBNNR, respectively. Since the Mn ions make dominant contribution to the magnetic properties of LSMO and provide a high degree of induced spin polarization of low-dimensional π-conjugated fragments, the MnO-terminated LSMO(001) surface was used to design low-dimensional heterostructures, namely pentacene/LSMO(001), 4-ZGNR/LSMO(001) and 4-ZBNNR/LSMO(001). The 5×2×1 ($La_{20}Sr_{10}Mn_{30}O_{90}$) and 8×2×1 ($La_{32}Sr_{16}Mn_{48}O_{144}$) supercells were used to simulate the pentacene/LSMO(001) and 4-ZGNR/LSMO(001) and 4-ZBNNR/LSMO(001) heterostructures, respectively. To avoid artificial interactions between the supercell images, the vacuum interval of 17 Å along *c* direction was used. 2×6×1 and 1×6×1 Γ-centered Monkhorst-Pack *k*-point Brillouin zone sampling