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Half-Metallicity in Organic Single Porous Sheets

Erjun Kan,*[,†] Wei Hu,[‡] Chuanyun Xiao,[†] Ruifeng Lu,[†] Kaiming Deng,*[,†] Jinlong Yang,*[,‡] and Haibin Su[§]

[†]Department of Applied Physics, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, P. R. China

[‡]Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China

[§]Division of Materials Science, NanYang Technological University, 50 NanYang Avenue, 639798 Singapore

Supporting Information

ABSTRACT: The unprecedented applications of two-dimensional (2D) atomic sheets in spintronics are formidably hindered by the lack of ordered spin structures. Here we present first-principles calculations demonstrating that the recently synthesized dimethylmethylene-bridged triphenylamine (DTPA) porous sheet is a ferromagnetic half-metal and that the size of the band gap in the semiconducting channel is roughly 1 eV, which makes the DTPA sheet an ideal candidate for a spin-selective conductor. In addition, the robust half-metallicity of the 2D DTPA sheet under external strain increases the possibility of applications in nanoelectric devices. In view of the most recent experimental progress on controlled synthesis, organic porous sheets pave a practical way to achieve new spintronics.

Half-metals, which have a metallic nature for electrons in one spin channel and an insulating property in the other spin channel, can provide completely spin-resolved electric current.[1,2] To achieve great promise for use in future nanoelectric devices, half-metals with nanostructures are highly desired. Tremendous effort has been devoted to searching for new half-metallic nanostructures.[3−11] Although two-dimensional (2D) atomic materials such as graphene have been extensively investigated, reported half-metallic 2D sheets are scarce.[12−14] The main obstacle comes from the experimental difficulty in producing structures with an ordered spin arrangement. To solve this problem, the bottom-up approach, in which the atomic sheet would be assembled from small molecules or clusters, has been viewed as the most possible strategy. For example, Abel et al,[15] successfully synthesized a single-layer 2D periodic transition metal (TM)−phthalocyanine (Pc) sheet, and its half-metallicity was discovered in the following theoretical research.[16]

On the other hand, in view of the spin-scattering problem in electron transmission, TM-free half-metals are more important and practical. However, for 2D sheets, such as graphene and BN single layer, the introduction of ordered spin signals is extremely challenging. Up to now, no observation that TM-free 2D sheets can form ordered spin structures has ever been reported. In this sense, the recent progress in organic porous sheets may pave a novel pathway for achieving the long-standing dream of spintronics in 2D atomic sheets through the bottom-up approach.[17−21] For example, Bieri et al.[21] successfully synthesized 2D heterotriangulene polymers. They produced single-layer 2D periodic covalent networks through an on-surface synthesis approach and investigated the samples using scanning tunneling microscopy (STM). For the further development and applications of those porous sheets, a systematic atomic understanding of these sheets would be highly desirable.

In the present work, using first-principles calculations, we systematically studied the magnetic and electronic behaviors of free-standing 2D dimethylmethylene-bridged triphenylamine (DTPA) and similar porous sheets. We found that the isolated DTPA molecules are magnetic, carrying a magnetic moment of 1 μ_B. Further magnetic-coupling calculations showed that the free-standing 2D DTPA covalent network favors ferromagnetic order. Moreover, electronic structure analysis revealed that the 2D DTPA porous sheet is a half-metal and that the half-metallicity is robust under external stress.

Our first-principles calculations were based on spin-polarized density functional theory (DFT) using the generalized gradient approximation (GGA) known as PW91,[22] implemented in the Vienna Ab Initio Simulation Package (VASP) code.[23] The projected augmented wave (PAW) method[24,25] with a plane-wave basis set was used. For the spin-polarized calculations, the Vosko−Wilk−Nusair modification[26] scheme was applied to interpolate the correlation energy. We applied periodic boundary conditions with a vacuum space of 20 Å to avoid interactions between two sheets in nearest-neighbor unit cells. All of the structures were relaxed using the conjugated gradient method without any symmetric constraints. We set the energy cutoff and the convergence criteria for energy and force to be 400 eV, 10^{-4} eV, and 0.01 eV/Å, respectively. During the optimization, 1 × 1 × 1 K point was adopted, while 3 × 3 × 1 was used for total energy calculations.

Before studying the 2D DTPA porous sheet, we first investigated the geometric and electronic properties of the isolated molecules constituting the 2D sheet. For comparison with the DTPA molecules, similar molecules consisting of boron-doped and pure graphene nanoflakes (GFs) were also studied in our research, as shown in Figure 1a,b. Similar to pristine graphene, no buckling was found after structural relaxation in these molecules. Moreover, we found that all three molecules favor spin-polarized ground states, and the calculated magnetic moments were 1 μ_B for B-doped GF and DTPA and 2

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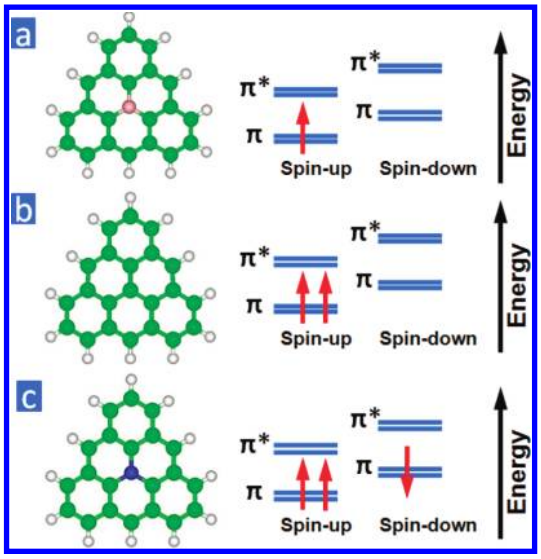

Figure 1. Geometric structures of molecules and schematic diagrams of spin-resolved orbital energy levels for isolated molecules of (a) B-doped graphene nanoflakes, (b) graphene nanoflakes, and (c) DTPA, in which all of the functional groups have been substituted with H atoms. The blue, green, pink, and white balls denote N, C, B, and H atoms, respectively.

μ_B for GF. For the GF molecule, the fully occupied spin-up π orbital produces a net magnetic moment of 2 μ_B, as shown in Figure 1. For B-doped GF and DTPA, one hole or electron is introduced into the double-generated π orbital, resulting in a magnetic moment of 1 μ_B.

Magnetic order. Since the isolated molecules are magnetic, it is of interest to study the preferred magnetic coupling when they are connected into porous sheets. From the calculated results for the isolated molecules, it is reasonable to speculate that a 2D porous sheet constructed from GF molecules would favor antiferromagnetic (AFM) coupling, while B-doped GF and DTPA molecules would prefer ferromagnetic (FM) interactions. As we know, the spin-up π orbital of the GF molecule is fully occupied. Therefore, virtual hopping is allowed only in the AFM arrangement, as shown in Figure 2. For B-doped GF and DPTA, however, the situation is quite different. Because the π orbital is only half-occupied, virtual hopping is allowed for FM configurations, leading to a lower energy in the FM states.

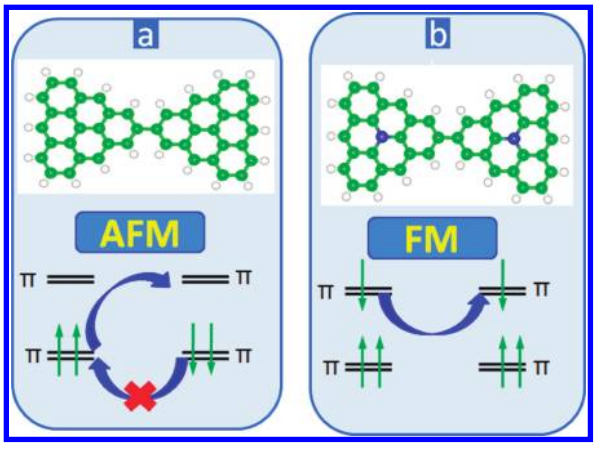

Figure 2. Schematic diagrams of the exchange mechanisms. (a) For a GF-based 2D porous sheet, virtual hopping leads to an AFM arrangement. (b) For a DTPA-based porous sheet, the FM configuration is favored by the same mechanism. The blue, green, and white balls denote N, C, and H atoms, respectively.

To confirm the above deduction, we carefully studied the magnetic interaction through DFT calculations. For the GF-based 2D sheet, we found that the AFM arrangement is more stable than the FM one by 168 meV/unit cell. In contrast, for the B-doped GF and DTPA sheets, there is no stable solution with the AFM configuration, and the FM state is the ground state. The nonmagnetic state is higher in energy by 50 and 70 meV/unit cell for the B-doped and DTPA sheets, respectively. Furthermore, we also calculated the magnetic interactions of a GF-based sheet doped with electrons. The calculated results show that the FM state is favored for doping of one electron per molecule, as revealed for the DTPA sheet.

The long-range magnetic interactions found in these porous sheets is very interesting and important. For the doped TM atoms in semiconductors, the magnetic atoms can interact only in neighborhood because of the strong localization of d and f electrons. However, in these porous sheets, the spin-polarized electrons are much more extended (see Figure 1S in the Supporting Information), and the extended tails of the spin wave functions ensure the long-range magnetic order, endowing them with great potential in spintronics.

Half-metallicity. To understand the electronic properties of these sheets, we performed spin-polarized band structure calculations. For the DTPA-based porous sheet, the half-metallic behavior is clearly presented in Figure 3. In addition,

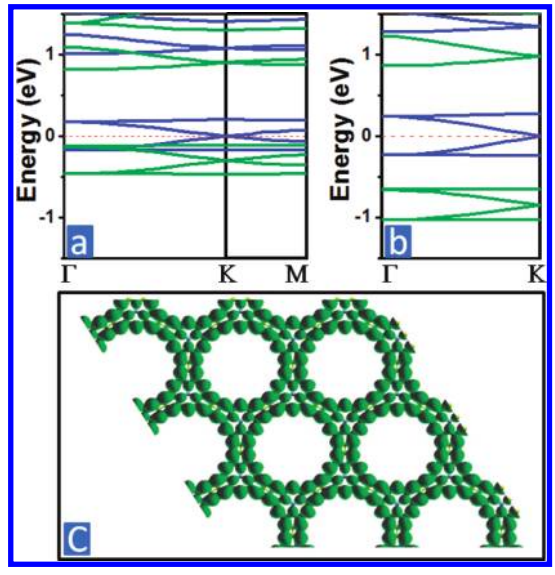

Figure 3. (a, b) Spin-polarized band structures of the DTPA-based porous sheet obtained from (a) GGA and (b) HSE calculations. Green lines are spin-up channels, and blue ones are spin-down channels. (c) Partial band charge density plot at the Fermi level.

the size of the band gap in the semiconducting channel is roughly 1 eV, which makes the DTPA sheet an ideal spin-selective conductor. To confirm the robustness of the half-metallicity, we also performed HSE[27] hybrid functional calculations. Because of computational limitations for these huge systems, we calculated only the band structure of the FM DTPA-based porous sheet. Qualitatively similar to the GGA calculations, the HSE results predict that the FM DTPA-based porous sheet is a half-metal. Moreover, from the plotted HSE

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band structure, we found that the band curve is almost same as the GGA one. Therefore, the results of the GGA and HSE calculations are qualitatively consistent.

On the other hand, it was important to make sure that the metallic character in the spin-down channel is not a kind of localized state. In Figure 3c, we show a plot of the partial charge density at the Fermi level in the DTPA-based sheet, which indicates that those states have delocalized π character. Therefore, the half-metallicity discovered in the DTPA-based sheet is solid. The B-doped GF porous sheet shows a similar half-metallic property, with the only difference being that the metallicity appears in the spin-up channel. However, the GF-based porous sheet does not demonstrate the amazing half-metallicity. By doping electrons, we found that at the level of 1 electron per GF molecule, the porous sheet is changed into a half-metallic FM sheet, as found for the DTPA-based sheet. In light of the development of the experimental setup, our results demonstrate the possibility of manipulating the electronic behaviors of these porous sheets by applying a gate voltage on substrate−porous sheet devices.

As we know, the reported porous sheets were synthesized on a metal surface. External stress inevitably modifies the geometric structure of the porous sheets through sheet−substrate interactions, thereby affecting the electronic properties of these porous sheets. Therefore, a critical issue determining the practical applications is whether the half-metallicity can be preserved under external stress. To answer this question, we carefully studied the electronic behaviors of the DTPA-based porous sheet under an external strain ε, defined as $\varepsilon = (a_1 - a_0)/a_0$, where a_0 is the optimized unit cell parameter of the sheet and a_1 is the unit cell parameter adopted in our calculations. As shown in Figure 4, we found that the

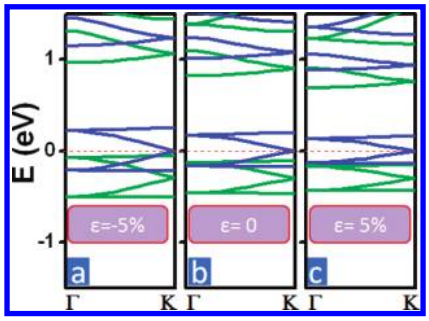

Figure 4. Spin-polarized band structures of a DTPA-based porous sheet under external strain. Green lines are spin-up channels, and blue ones are spin-down channels.

half-metallicity in the DTPA-based porous sheet is robust and can survive under external strain at a high level of 5%, which is much higher than that caused by sheet−substrate interactions. Moreover, the width of the bands crossing the Fermi level becomes narrower with increasing unit cell parameter, which is reasonable because the covalent bonding is weakened by stretching.

In summary, using DFT calculations, we have systematically studied the electronic and magnetic properties of 2D organic porous sheets. Our results reveal that the DTPA-based sheet favors FM coupling and displays the half-metallicity that is robust under external strain beyond the effect of a substrate. In addition, the size of the band gap in the semiconducting spin channel is roughly 1 eV, which makes the DTPA sheet promising as an ideal spin-selective conductor. In comparison with other TM-doped half-metallic 2D atomic sheets, the studied 2D sheets constructed with organic molecules, which have been successfully synthesized, are privileged for spintronics because of the weak spin scattering. In view of the most recent experimental progress on controlled synthesis, our results pave a practical way to achieve new spintronics based on 2D porous atomic crystals.

■ ASSOCIATED CONTENT

Supporting Information

Calculated atomic positions, spin density, band structures, and projected density of states. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

ekan@mail.njust.edu.cn; kmdeng@mail.njust.edu.cn; jlyang@ustc.edu.cn.

Notes

The authors declare no competing financial interest.

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