Experimental and theoretical study of Tetrakis(dimethylamino)ethylene induced magnetism in otherwise nonmagnetic graphene derivatives

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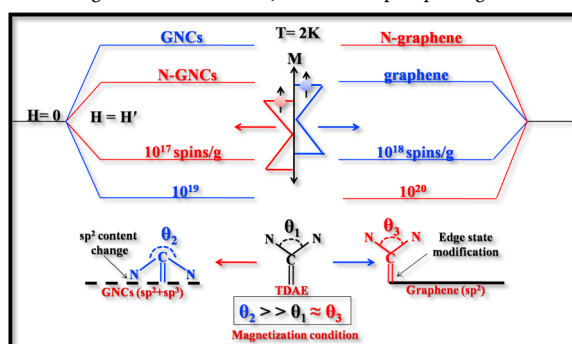
HIGHLIGHTS

- Modification in magnetization in graphene and graphene like nanocarbons with nitrogen loading.
- Pauli-enhanced anti-ferromagnetic interactions in graphene.
- Variations in radical state.
- Edge state modifications in both the systems by nitrogen.
- Modification in spin density of states.

GRAPHICAL ABSTRACT

Under magnetization condition, scenario of spin splitting and Dirac cone is shown vis-à-vis, at 2K for the systems.

ABSTRACT

Magnetic nanocarbon offers unique opportunities for future molecular spintronic applications. In such nanocarbons, emergence of magnetization mainly comes from vacancy and adatom. Present work deals with comparison of magnetic interactions in Graphene-like nanocarbons (GNCs) and graphene by adding, tetrakis (dimethyl amino) ethylene (TDAE, $(CH_3)_2N_2C = CN_2(CH_3)_2$), an organic ferromagnet. Initially, synthesized nanocarbon compounds were functionalized by ~ 10 at % of TDAE. Magnetic analysis, by SQUID, showed decrease in saturation level spin density and moments/nm^2 in N-doped graphene like nanocarbons (N-GNCs), while enhancement in N-doped graphene (N-graphene). The FC-ZFC study showed significant irreversibility in magnetic anisotropy that obeys anti-ferromagnetic order up to ~ 20 K in graphene. Moreover, it exhibits modifications in magnetic environment of molecular carbon due to alteration in centro-symmetry and skewness of central $N_2C{=}CN_2$ molecule, as revealed by electron spectroscopy by chemical analysis. The tendency of donor nitrogen to transfer charge is disproportionate and results in acquiring different radical states by N-GNCs (-1) and N-graphene (-2). Computational studies have been carried out for pristine graphene nanoribbons (GNRs), both armchair and zigzag and GNR with monovacancy with and without passivation. Unpassivated zigzag GNR exhibits magnetic moments at the edges but the magnetic moment is quenched at the edge atoms on adsorption of the molecule.

1. Introduction

Graphene has been shown to be a material appropriate for spintronics applications through introduction of magnetic ordering [1]. As a 2D electronic system, due to the delocalized π bonding network, ideal graphene is intrinsically nonmagnetic [2]. The magnetic moments in graphene are generated as a result of defect, localization of electrons in or around defects (vacancies, edges and covalently bonded dopants) and graphene nanoribbons with certain edge geometry [3,4]. A promising approach to imprint magnetic ordering isdoping/functionalization of graphene lattice with non-carbon atoms such as nitrogen, sulphur [5] or fluorine [6], different transition metal atoms and ferromagnetic insulators such as magnetic oxides EuO, EuS, high Curie-temperature materials Yttrium Iron Garnet (YIG), NiO, CoFe$_2$O$_4$ [7]. Among all dopants, nitrogen (N) is the most popular and is well studied for graphene due to similarity in its atomic size with carbon atom [8–10]. With one additional electron as compared to a carbon atom, nitrogen acts as an n-type (electron-donating) dopant. Nitrogen doping therefore affects the electric conductivity and the electronic density of states; moreover, graphitic nitrogen is able to provide π electrons close to the Fermi level of graphene. Various doping methods have been used to form nitrogen doped graphene such as gas mixture of nitrogen, liquid organic precursors (acetonitrile, pyridine and aniline) [11,12]. It has been proposed theoretically as well as experimentally that depending on the concentration and packing geometry of doped N-atoms, it is possible to induce a magnetic response in graphene [13]. The nature of dopant plays crucial role in predicting the magnetic properties.

In our previous communication, we have discussed room temperature magnetic interactions in graphene like nanocarbon (GNC) [14]. In continuation, we have now studied magnetic interactions using SQUID magnetometer at temperatures from 2K to 300K. In order to induce magnetic interactions, we have selectively chosen tetrakis (dimethyl amino) ethylene (TDAE); a high temperature organic ferromagnet [15] and a strong spin polarized donor to functionalize graphene and GNCs. The effective interactions are increased in TDAE incorporated graphene compared to GNCs. The focus of the current work is to reveal variations in magnetic behavior of graphene and GNCs incorporated with TDAE to explore their prospects in spintronics applications.

2. Methodology

2.1. Experimental

2.1.1. Preparation of GNCs, graphene and TDAE doped graphene and GNCs

GNCs are synthesized according to protocol reported in ref. [16] and graphene by chemical vapor deposition method [17]. To incorporate TDAE, a suspension of 0.5 g GNCs/graphene was prepared in 25 ml of tetra hydro furan (THF) in which 0.1 ml TDAE (1 wt %) solution is added with subsequent sonication (30 min), stirring (300K, 8–10 h), settlement (5 h) and filtration. As prepared TDAE treated GNC samples are termed as N–GNCs and TDAE treated graphene is termed as N–graphene. The dried powder obtained is used for further investigations.

2.1.2. Material characterization

Electron spectroscopy for chemical analysis (ESCA) measurements are performed on both the systems using an Omricron ESCA probe (Omricron nanotechnology). The FTIR measurements are carried out over 400-4000 cm^{-1} and Raman experiments over 200-3500 cm^{-1}; at photo-excitations 532 nm. ESR measurements are performed on powder specimen at 9.4 GHz (X band) with microwave input 950 mW. Scanning electron microscopy imaging (SEM) is carried out with S-4700 microscope and transmission electron microscopy (TEM) imaging with a JEOL-2100F microscope. Magnetic measurements are carried out on a Quantum Design MPMS-XL-1 SQUID magnetometer with a 1T magnet

over 2–300 K with sensitivity better than 5×10^{-8} emu. For thermo-magnetic measurements, both field cooled (FC) and zero field cooled (ZFC) curves are obtained at 100 Oe over 2–300K. The susceptibility, χ, measurements are performed at 1T magnetic field at 2 and 300K. Prior to analysis, the diamagnetic corrections are performed on the collected data.

2.2. Computational

Theoretical studies have been carried out for pristine graphene nanoribbons (GNR) and GNR with monovacancy defect. Both arm-chair (AGNR) and zigzag GNR (ZGNR) have been considered. The calculations have been performed using the Quantumwise Virtual Nanolab (VNL) package [18]. A supercell approach has been used for calculating the minimum energy geometry and subsequently the electronic structure. In this cell the nanoribbon is placed along the z-direction. We have considered 10 × 10 atom cell for armchair and 14 × 7 atom cell for zigzag nanoribbons so that the number of atoms is comparable in the two cases. We have considered vacuum of 15 Å on each side in the y-direction and 10 Å in the x-direction to prevent interaction between the periodic images of the system. Two positions −CN$_2$ molecule at the middle and at the edge of the AGNR have been considered. The binding energy is calculated using the Slater-Koster tight-binding method [19] as implemented in the software [20]. The preferred position for the molecule on the AGNR has been accordingly decided to be at the edge. This observation also agrees with the inputs given from the experiments. For the ZGNR, we have accordingly considered only the edge position. The preferred geometries are then relaxed without any constraints using spin-polarized density functional theory (DFT) [21–23]. The Fritz-Haber Institute (FHI) pseudopotential [24] with the Perdew–Burke-Ernzerhof (PBE) exchange-correlation energy functional [25] has been used in the calculation. The basis set used is double zeta polarized (DZP) [26]. Optimization is performed till all the force components are reduced to less than 0.01 eV/Å. A 1 × 1 × 17 Monkhorst-Pack **k**-point mesh is used in the calculations as per the underlying geometry of the graphene nanoribbon and for convergence of the total energy. Calculations have also been carried out for GNRs passivated with hydrogen atoms. The binding energy (BE) is calculated using the following formula:

BE = (Energy of the molecule adsorbed GNR) – (Energy of GNR + energy of molecule).

Larger negative values of the BE indicate a more stable configuration.

3. Results and discussion

3.1. Chemical analysis using electron spectroscopy

For ESCA analysis, spectral convolutions in terms of background corrections, total least squared fitting for Lorentzian-Gaussian life time broadening, etc., have been carried out as per standard protocols. All binding energy values are referenced to the C-1s peak at 284.80eV. Fig. 1 shows ESCA spectra of C-1s recorded for (a) GNCs, (b) N–GNCs (c) graphene and (d) N-graphene. The binding energy (in eV), assigned chemical moieties, and their atomic % are indicated in the figure. The observed change in FWHM, intensity, and binding energy shift reconfirms successful doping of nitrogen in GNCs and graphene [17].

In Fig. 1(a), C–1s at 285.33 eV is shifted to 284.66 eV, indicating lower binding energy in N-GNCs. In Fig. 1(b), the peak at 284.60 eV is sp^3 bonded amine based moiety (C−NH$_2$) [27]. The other two peaks are assigned to C−O−C and C−C, having characteristic similar to the peaks in GNCs. The % decrease in oxygen content, in GNCs, is indicative that, reaction takes place at O═C−OH (carboxyl) and −C−O−C (epoxy) sites with emergence of amine in the sp^2 network [28]. However, no appreciable change in C content has been observed, after doping TDAE in