



Magnetic properties of sulfur-doped graphene



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ABSTRACT

While studying magnetism of *d*- and *f*-electron systems has been consistently an active research area in physics, chemistry, and biology, there is an increasing interest in the novel magnetism of *p*-electron systems, especially in graphene and graphene-derived nanostructures. Bulk graphite is diamagnetic in nature, however, graphene is known to exhibit either a paramagnetic response or weak ferromagnetic ordering. Although many groups have attributed this magnetism in graphene to defects or unintentional magnetic impurities, there is a lack of compelling evidence to pinpoint its origin. To resolve this issue, we systematically studied the influence of entropically necessary intrinsic defects (e.g., vacancies, edges) and extrinsic dopants (e.g., S-dopants) on the magnetic properties of graphene. We found that the saturation magnetization of graphene decreased upon sulfur doping suggesting that S-dopants demagnetize vacancies and edges. Our density functional theory calculations provide evidence for: (i) intrinsic defect demagnetization by the formation of covalent bonds between S-dopant and edges/vacancies concurring with the experimental results, and (ii) a net magnetization from only zig-zag edges, suggesting that the possible contradictory results on graphene magnetism in the literature could stem from different defect-types. Interestingly, we observed peculiar local maxima in the temperature dependent magnetizations that suggest the coexistence of different magnetic phases within the same graphene samples.

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1. Introduction

Carbon nanomaterials are regarded as one of the best-suited platforms for spintronics due to their low density, inherently low spin-orbit coupling, and large spin-flip scattering lengths [1,2]. Ideally, any sp^2 carbon system is expected to exhibit diamagnetic behavior due to the existence of π -electron orbital magnetism [3]. However, the origin of anomalous ferromagnetic ordering and paramagnetic response in sp^2 carbon systems has puzzled researchers for many decades [4–6]. This unexpected presence of magnetic ordering in nanocarbons is a major impediment for realizing long spin-flip scattering lengths required for spintronic applications. Although there have been many efforts to understand the presence of magnetism in pure carbon-based nanomaterials

[7–11], many of them have been either controversial or irreproducible. This is likely due to the presence of unintentional magnetic impurities (e.g., residual Fe catalyst particles in carbon nanotubes), poorly characterized defects, and intrinsic topology (e.g., curvature in C_{60} and nanotubes). Graphene, a two-dimensional atom-thick layer of sp^2 carbon, is well suited for elucidating the origin of magnetism due to its fairly simple honeycomb lattice with unique electronic and optical properties [12,13]. Furthermore, the properties of many carbon nanomaterials (e.g., fullerenes, carbon nanotubes, graphite, and some polycyclic aromatic molecules) are often theoretically derived from their underlying graphene lattice.

Many theoretical studies have predicted that point defects in graphene exhibit a non-zero magnetic moment, which can possibly interact with each other resulting in a long-range ferromagnetic ordering [7,8,14–18]. Nair et al. reported a purely paramagnetic behavior in highly defective fluorinated and ion-irradiated graphene, implying the absence of any defect-defect interactions leading to ferromagnetic (FM) ordering [19,20]. On the

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contrary, others have observed signatures of FM in defected graphene indicating possible interactions between defect-induced magnetic moments [21–23]. Collectively, both intrinsic defects (e.g., vacancies and edges) and extrinsic dopants (e.g., fluorine dopants, ion-irradiation induced pores, and unintentional magnetic impurities) have been proposed to increase paramagnetic response of graphene, and in some cases even cause FM ordering through defect-defect interactions. As we and others have previously shown, the nature of defects plays a critical role in an unexpected magnetic ordering in many nanostructured materials (particularly, nanograined oxides) derived from non-magnetic bulk, for example ZnO [24–27]. Accordingly in this study, we controllably doped graphene nanoplatelets (GnPs) with sulfur (an extrinsic defect) to tune different magnetic interactions between intrinsic (e.g., between vacancies) and extrinsic defects (e.g., vacancy and S-dopant). Our X-ray photoelectron spectroscopy (XPS) studies and density functional theory (DFT) clearly evince the formation of covalent bonds between S dopants and intrinsic defects. While we observed that pristine GnPs prepared using the chemical exfoliation method exhibited a weak FM ordering due to the presence of intrinsic defects, we found that the FM ordering systematically decreased with increasing S dopants suggesting that the interactions between S-dopants and intrinsic defects demagnetize GnPs.

2. Experimental procedure

Grade M GnPs (xGnP-M-5, 99.95 at% carbon and 0.05 at% sulfur) were purchased from XG Sciences, Inc. (Michigan, USA). Pristine GnPs consist of short stacks of graphene sheets with an average thickness of approximately 6–8 nm and average size of 5 μm (see Fig. S1). In the chemical exfoliation process, as-received GnPs (5 g) were exfoliated in 100 ml of N-Methylpyrrolidone (NMP) for 2 h using a 1/8" tip sonicator at 120 W, and then vacuum filtered using a 0.45 μm nylon membrane. Subsequently, the collected "cake" was re-sonicated using a fresh portion of NMP for 6 h and vacuum filtered. Finally, the vacuum filtered GnPs were washed in water thrice and oven dried at 130 $^{\circ}\text{C}$ for 24 hours.

In the sulfur doping experiment, three 100 mg samples of the exfoliated GnP powders were mixed with 99.5% elemental sulfur, (100 mesh, Alfa Aesar) at nominal concentrations of 1, 1.5 and 3 wt% of S using a mortar and pestle (labeled as pristine GnP, 1 wt% S GnP, 1.5 wt% S GnP and 3 wt% S GnP). The mixed GnP-S samples were vacuum-sealed in quartz tubes (1/4" diameter and 6" in length) and annealed in a furnace at 1000 $^{\circ}\text{C}$ for 24 h. After cooling down to room temperature, the quartz tubes containing the samples were gently shaken by hand for homogenizing the sample, and then reheated again at 1000 $^{\circ}\text{C}$ for another 24 h. Subsequently, the furnace was cooled to 440 $^{\circ}\text{C}$ for 2 h and the sealed quartz tubes were partially pulled out of the furnace to facilitate condensation of any unreacted sulfur at the opposite cold end of the sealed tubes.

The magnetic properties of samples used in this study were measured using a Quantum Design[®] vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID) magnetometer. The DC temperature dependent magnetic susceptibility was measured both in zero-field-cooled (ZFC) and field-cooled (FC) conditions with temperature ranging from 3 to 150 K. A Dilor XY triple grating monochromator was used for collecting the micro-Raman spectra of all samples with the 514.5 nm excitation from an Ar⁺ ion laser. XPS studies were performed in a Phi spectrometer equipped with a monochromatic Al K _{α} source (1486.6 eV), which has an overall resolution of 0.5 eV.

The samples were tested for magnetic impurities such as Fe through inductively coupled plasma mass spectrometry (ICP-MS)

measurements (X series II, Thermo Scientific) using an internal standard containing Li, Y, and In with a detection limit of 0.05 ppb (corrected for sample dilution). For the measurements, 10 mg of sample was dissolved in 10 ml of 70% nitric acid for 24 h under constant stirring. Subsequently, HNO₃ containing graphene was centrifuged, and the supernatant was removed and diluted into 2% HNO₃ for evaluating the presence of Fe impurities.

The calculations are performed using the projected augmented wave formalism [28,29] of DFT as implemented in the Vienna *ab initio* simulation package [30,31]. The exchange correlation potential is approximated by a generalized gradient approximation using the Perdew–Burke–Ernzerhof functional [32]. The DFT orbitals are expanded in plane wave basis with a relatively high energy cutoff of 600 eV. The vacancies and vacancy clusters are modeled in 10 \times 10 \times 1 supercells of the two atom unit-cell of graphene (lattice constant: 2.468 Å), with a 15 Å vacuum in the vertical direction. We used a relatively large supercell to reduce the undesired interaction between vacancies and their images arising from periodic boundary conditions. The reciprocal space is sampled with 5 \times 5 \times 1 *k*-point mesh equivalent to the 50 \times 50 \times 1 *k*-point mesh for the two-atom unit cell. The same density of *k*-points is used for simulated nano-ribbons with zig-zag- and armchair-edges modeled in 160- and 168-atom computational cells, respectively. All the atomic configurations are optimized with spin-polarized DFT.

3. Results and discussion

As shown in Fig. 1, finite areas of hysteresis loops provide a clear evidence for FM in both pristine and doped GnP samples at 300 and 5 K, with saturation values (M_s) \sim 0.06 (pristine), 0.017 (1.5 wt% S GnP), and 0.043 emu/g (3 wt% S GnP). The FM is embedded in a large diamagnetic (DM) background (see insets in Fig. 1a and b), which arises from the underlying graphene lattice. Although graphite/graphene is diamagnetic, the presence of defects (as it will be discussed later) induce weak FM, similar to nanograined oxides [24–27]. The observed saturation of FM at relatively low fields (\sim 1.2 kOe at 300 K) for both pristine and doped samples indicates: (i) the presence of moderately large spin-clusters, and (ii) that the average size of spin-clusters was not affected by doping. The magnetic coercivity (H_c) increased significantly for all samples at 5 K (see Table 1) implying that room temperature thermal activation energy \sim 25 meV is sufficient to induce spin-flip in all GnP samples. Interestingly, the percent increase in H_c at 5 K (relative to H_c at 300 K) is highest for pristine samples (\sim 250%) and considerably small in doped samples (\sim 20%). Such observations, when juxtaposed with our DFT calculations, could be attributed to dopant-induced passivation of thermal spin fluctuations in unsaturated edge-states of GnPs. Lastly, we observed a non-monotonic decrease of M_s in S-doped samples (see Table 1) confirming that the S-dopants demagnetized GnP samples. Our detailed ICP-MS analysis (Table 2) confirmed that the magnetic response (shown in Fig. 1) is not from magnetic impurities such as Fe, which were found to be $<$ 20 ppb in both pristine and doped samples.

All samples exhibited an excellent crystallinity as evidenced from C 1s peak in the XPS spectra (Fig. 2a). The S-dopant concentration was quantified from the relative photoemission cross-sections for the C 1s and the corresponding S 2p peaks. We inferred that pristine, 1 wt% S, 1.5 wt% S and 3 wt% S nominal S-doped GnPs contained 0.05, 0.07, 0.18 and 0.25 at% substituted sulfur, respectively. We limited our magnetization studies to pristine, 1.5, and 3 wt% samples because the S concentration in the pristine and 1 wt% S samples was not significantly different (see Table S1). Furthermore, our XPS results suggest that S is

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