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Magnetic properties of graphite oxide and reduced graphene oxide

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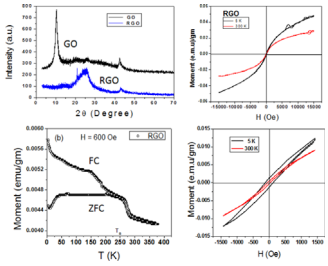
HIGHLIGHTS

- GO and reduced—GO have been synthesized by standard chemical method.
- Both the oxides exhibit hysteresis and weak superparamagnetic behaviours at RT.
- Superparamagnetism in these oxides is attributed to the presence of single domains.
- Hysteresis is due to defect induced moments coupled by ferromagnetic interaction.

GRAPHICAL ABSTRACT

XRD, Magnetic moment Vs Field and FC and ZFC cures for RGO.



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ABSTRACT

Graphite oxide (GO) and reduced graphene oxide (RGO) have been prepared using standard chemical methods. The formations of the oxides are characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) studies. Both the oxides exhibit weak superparamagnetism and hysteresis for the first time at room temperature. Magnetic moment for RGO is comparatively smaller than that of GO sample. The superparamagnetism in these oxides is attributed to the presence of single domains, each domain being cluster of defect induced magnetic moments coupled by ferromagnetic interaction. Apart from these single domain clusters there are other defect induced moments coupled by ferromagnetic interaction which show ferromagnetism and hysteresis.

1. Introduction

Reduction of graphite oxide (GO) is a common method for the production of graphene [1]. GO is synthesized from graphite by one of the three methods due to Brodie [2], Staudenmaier [3], and Hummers and Offeman [4] or some modification of these methods. The dispersion of GO in water is ultrasonicated to exfoliate its single layers called graphene oxides. Then this dispersion of graphene oxide is reduced by a chemical like hydrazine, sodium borohydride, alkalis, ascorbic acid, hydroquinone etc. GO can also be directly reduced by thermal or electrochemical methods. Sometimes a combination of chemical and thermal methods is applied for efficient reduction of GO. On reduction GO is changed to reduced graphene oxide (RGO). RGO is not the same as pristine graphene because a significant amount of oxygen still remains in RGO [1].

In this paper an experimental study about the magnetic properties of GO and RGO powder samples is presented. McIntosh et al. [5] have studied the electronic and magnetic properties of graphene oxide and RGO films.

Like graphite, GO has a layered structure with greater interlayer separation as revealed by the X-ray diffraction (XRD) studies. The FTIR spectrum of GO shows that there are four oxygen functional

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groups in GO—epoxide (–O–), hydroxyl (–OH), carbonyl (–C=O) and carboxyl (–COOH). The most popular structural model for GO is that due to Lerf and Klinowski [6]. A GO layer has two types of regions—oxidized regions and non-oxidized regions. They are randomly distributed and their relative size depends on the degree of oxidation. The oxidized regions contain the oxygen functional groups where the sp^2 carbon network is completely changed. In the non-oxidized regions the original sp^2 carbon network is preserved. The epoxide and hydroxyl groups are bonded on both sides of the layer while the other two groups occur at the edges of the layer. The GO layer is also wrinkled. On reduction the functional groups are partially removed and the sp^2 carbon network is partially restored. In RGO some residual functional groups still remain. GO is an electrical insulator due to the strong disruption of the sp^2 carbon network. RGO is a conductor due to the partial restoration of the sp^2 network. But its conductivity is less than that of graphene because of the residual functional groups and disorder present in RGO [5].

Yazyev [7] has reviewed the subject of magnetism in graphene materials and nanostructures. Rao at al. [8] have reviewed the works on the magnetic properties of graphene and related materials. Many theoretical works [9–19] have predicted the magnetic behaviours of graphene due to the existence of various defects in it. The defects may be topological defects (pentagons, heptagons or their combinations), point defects like vacancies, adatoms etc., and extended defects like edges, cracks, voids etc. Also graphene has defects like wrinkles, ripples, corrugations etc. on its surface.

Vozmediano et al. [9] have shown that due to the lattice defects in graphene, like cracks or voids, local magnetic moments are developed and the RKYY interaction between these moments is ferromagnetic due to the semimetallic properties of graphene. Yazyev et al. [10] have shown that due to vacancy defect or hydrogen chemisorption defect a magnetic moment of about one Bohr magneton is developed and the coupling between the magnetic moments is either ferromagnetic or antiferromagnetic. For the case of disordered graphene and irradiated graphite [11], Yazyev [12] has shown that only single-atom defects can induce ferromagnetism in them. Vacancies, substitutional atoms and adatoms can produce magnetism in graphene [13,14]. Li et al. [15] have shown that addition of monovalent and divalent adatom on graphene can also induce magnetic moments. Some studies shows that zig-zag edges can produce magnetism in graphene [16–18]. The presence of von Hove singularities can also produce magnetism [19].

Several experimental works about the magnetic properties of graphene samples, prepared by different methods, have been reported. Wang et al. [20] have observed room temperature ferromagnetism in graphene samples produced by reducing GO by hydrazine followed by thermal treatment. Matte et al. [21] have found the presence of both ferromagnetic and antiferromagnetic features in three kinds of graphene samples prepared by different methods. Sepioni et al. [22] have studied magnetization of graphene nanocrystals obtained by ultrasonic exfoliation of graphite. No ferromagnetism has been detected by them at any temperature down to 2 K. Their graphene sample is diamagnetic like graphite and exhibits only a weak paramagnetic contribution noticeable below 50 K. In the above reported works [20–22], graphene samples show different kinds of magnetic behaviours such as paramagnetism, ferromagnetism and antiferromagnetism. All the theoretical studies show that due to various kinds of defects, local magnetic moments are developed. If their concentration is relatively small, the moments will be well separated from one another and they will not be coupled. So paramagnetism will be observed. In the work of Sepioni et al. [22] the graphene sample is produced by sonic exfoliation of graphite in organic solvents. Such a sample contains small concentration of defects. So, the sample shows weak paramagnetic behaviour [22]. On the other hand, if the concentration of defects is high, the defect induced magnetic moments (spin units) may be coupled by RKYY or exchange interactions. Then ferromagnetism (ferrimagnetism) and/or antiferromagnetism will appear. In the works [20,21] the concentrations of defects being high such behaviours are observed. Xie et al. [23] have observed room temperature ferromagnetism in partially hydrogenated epitaxial graphene.

In the special case a cluster of defect induced moments (spin units) coupled by ferromagnetic interaction may form a single domain. Such single domains are expected to show superparamagnetism [24]. It is not yet observed in pristine graphene. Hong et al. [25] have found superparamagnetism and hysteresis in nitrophenyl—functionalized epitaxial graphene. This is attributed to the effect of the functionalization of the top layer of the graphene sheet which consists of a mixture of ferromagnetic (ferrimagnetic), superparamagnetic and antiferromagnetic regions.

Now let us consider the magnetic behaviour of GO. In GO all kinds of defects as in graphene can exist. Also the binding of O-atoms to the carbon network can give rise to magnetic moments [15]. The O-atom in the epoxide group is bonded to two C-atoms of the two different sub-lattices of the graphene network. So by Lieb's theorem [26] the epoxide group cannot induce magnetic moment. But the O-atom in the hydroxyl group is bonded to only one C-atom of either sub-lattice and hence by Lieb's theorem can induce local magnetic moment. In a theoretical work, Wang et al. [27] have shown that for a certain structure of a hexagonal graphene ring bonded to two hydroxyl groups a magnetic moment of $1.2\mu_B$ is developed, where μ_B is the Bohr magneton. Hence such moments developed due to hydroxyl groups are to be considered along with the moments developed due to the defects as in graphene. If the moments are not coupled, weak paramagnetism will be observed in GO. If they are coupled by interactions, ferromagnetic, antiferromagnetic or superparamagnetic behaviours will be observed in GO.

In RGO the oxygen functionalities are removed partially and the sp^2 carbon network is restored partially. So in RGO the same types of defects occur as in GO. We expect same kinds of magnetic behaviour as in GO—ferromagnetism, antiferromagnetism, superparamagnetism or paramagnetism.

2. Experimental

2.1. Synthesis of GO and RGO and their structural characterization

GO is synthesized from graphite by the modified Hummers and Offeman method. It is characterized by the XRD (PANalytical X'Pert PRO 3560) diffractometer using Cu$K\alpha$ radiation ($\lambda=0.15405$ nm). The diffraction patterns are given in Fig. 1. The main peak at $2\theta=10.28^\circ$ gives an interlayer separation of 0.8615 nm. RGO is produced by the reduction of GO with sodium borohydride $NaBH_4$ following standard procedure. The XRD pattern of RGO is also included in Fig. 1. It shows that the main peak of GO has disappeared completely. The main peak of RGO occurs at $2\theta=25.60^\circ$ giving the separation between the RGO layers in the RGO crystallites as 0.3450 nm. This is significantly larger than the interlayer separation of 0.3340 nm in graphite indicating that the RGO layers have not combined to form graphite. They remain as RGO sheets.

2.2. Characterization of GO and RGO by FTIR spectroscopy

Fig. 2 shows comparative FTIR spectra (Perkin Elmer Spectra Two) of GO and RGO. While no significant peak is found in graphite, the presence of different types of oxygen functionality in graphite oxide has been confirmed at 3400 cm^{-1} (O–H stretching vibrations), at 1726 cm^{-1} (stretching vibrations from C=O), at