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Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetism of aniline modified graphene-based materials



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ARTICLE INFO

Article history:

Received 15 August 2015

Received in revised form

5 November 2015

Accepted 19 November 2015

Available online 23 November 2015

Keywords:

Graphene

Nanomagnetism

Functionalization

Antiferromagnetism

Nitroaniline

ABSTRACT

The possibility of producing magnetic graphene nanostructures by functionalization with aromatic radicals has been investigated. Functionalization of graphene basal plane was performed with three types of anilines: 4-bromoaniline, 4-nitroaniline and 4-chloroaniline. The samples were examined by composition analysis with energy-dispersive X-ray spectroscopy and magnetic measurements by SQUID magnetometry and electron paramagnetic resonance. Initial graphene was produced by thermal exfoliation. Both pristine and functionalized samples demonstrate strong paramagnetic contribution at low temperatures, which originates from intrinsic defects. Attachment of an organic molecule with the formation of a covalent bond with carbon atom on the basal plane generates a delocalized spin in the graphene π – electron system. Nitroaniline proved to be the most suitable and sufficiently reactive to attach to the basal plane carbon atoms in large amounts. Functionalization of graphene with nitroaniline resulted in appearance both ferromagnetic and antiferromagnetic features with a clear antiferromagnetic transition near 120 K.

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1. Introduction

Graphene is one of the most well-known and discussed material. It is a two-dimensional carbon allotrope modification, in which neighboring atoms in the sp^2 – hybridization form a hexagonal lattice. Interest to this material is caused by its remarkable properties, such as electronic structure, thermal and electrical conductivity, elasticity, strength and many others. Besides the obvious application of graphene in electronic devices and composite materials, its outstanding properties coupled with biocompatibility makes this material very attractive for medicine. For example, due to very high surface area, graphene and graphene-based materials have been widely investigated as a drug and gene carriers [1]. In comparison with metal-based magnetic carriers, which have revolutionized drug delivery, allowing therapeutic agents to be selectively targeted on cell specific level, carbon materials offer a route to non-toxic systems, which minimize exposure of healthy tissue. Other well-known fields of medicine, where graphene is used, are biosensing and bioimaging. Here,

among the applications based on unique electronic properties, the fluorescence quenching ability of graphene [2,3], or the simple usage of graphene as a matrix for detection of molecules [1], very promising is possibility of using magnetic properties of graphene and its derivatives [4,5]. In many theoretical and experimental works, it was shown that due to presence of defects graphene can change its magnetic properties and even a magnetic ordering (ferromagnetism, antiferromagnetism, ferrimagnetism) can appear [6–8]. The main advantage in using magnetic carbon materials in biology/medicine as contrast agents for clinical medical imaging modalities is that they offer a safe alternative to the existing substances [9]. However, in comparison with carbon nanotubes, which have wide applications in biomedical engineering, graphene research is limited, and the studies are mainly directed to graphite oxide, owing to its enriched surface functionalities.

There are two major approaches for creating graphene-based theranostic materials: (i) functionalization of graphene which can provide reaction sites for linking to external species, like biomacromolecules or inorganic nanoparticles and (ii) using intrinsic magnetic properties which appear in defective graphene. In this work we have investigated magnetic properties of some functionalized graphene derivatives. For functionalization nitroaniline, bromoaniline or chloroaniline were used, with isopentyl nitrite and organic solvents.

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2. Synthesis

2.1. Graphene production

The graphene required for further synthesis was produced by thermal exfoliation of graphite oxide. For this, as initial product, pure graphite powder RW-A grade from SGL Carbon was used. The oxidation was carried out by Brodie method [10]. Pure graphite was mixed with potassium chlorate ($KClO_3$) inside a glass flask and placed into an ice bath. The weight ratio of graphite to potassium chlorate was 1:5 respectively. After this, 100% nitric acid (HNO_3) was slowly added by a dropping funnel. It is important to cool down and add nitric acid slowly because occurring reactions are highly exothermic and can lead to explosion. After this the stirring solution was left to reach room temperature. Final stage of oxidation was a thermal treatment at 60 °C for 8 h. During this treatment ClO_2 was removing in a gas form. For filtration, the product was diluted into the water, filtered with paper membrane, washed in 3 M solution of hydrochloric acid (HCl) and was rinsed out until a pH value about six was reached. As final product, green hard sheet of graphite oxide was obtained.

For exfoliation, previously obtained graphite oxide was ground in a mortar to obtain a homogeneous powder. Next, it was placed in a large quartz tube and evacuated below 10^{-4} Torr. For exfoliation process, the volume of quartz tube was disconnected from the pump and inserted into a tube furnace, preheated to 1050 °C. Holder and rubber seals were cooled by water pipe. The system was kept inside furnace for one minute and then was removed and left to slowly cool down to room temperature. At the end of thermal treatment, the tube was evacuated from the gases, which appeared as a result of exfoliation process and was placed into the glove box with inert gas to avoid interaction with oxygen and humidity from environment.

2.2. Functionalization

Functionalization was performed by covalently bonded phenyl groups with different radicals (4-bromoaniline, 4-chloroaniline and 4-nitroaniline). For this was used the wet chemistry way. The procedure of functionalization was adapted from [11]. All the preparations with air-sensitive substances were performed inside a glove box with an argon atmosphere (< 1 ppm O_2 , H_2O). The reactions with anilines were carried out outside of the glove box under nitrogen atmosphere. In order to prevent the evaporation of reagents during the synthesis, a reflux condenser with water

cooling was used. During reaction, teflon-coated magnetic stirrer was used for mixing. Heating was provided by a heated oil bath. The procedure of functionalization was carried out as follows: previously produced graphene was mixed with N-Methyl-2-pyrrolidone (NMP) and chosen aniline under the nitrogen environment; mixture was heated to 60 °C after that was added isopentyl nitrite and it was left for a night. All the reagents were from “Sigma-Aldrich” company and used as received. For filtration, the reaction mixture was diluted in dimethylformamide (DMF) and filtered through the cellulose membrane filter (RC 58 with pore size 0.2 μm) under reduced pressure. After this, the powder was washed with acetone and dried with a rotary evaporator connected to mechanical pump. The pressure and temperature were approximately 30 Torr and 90 °C.

3. Characterization

Magnetic measurements were carried out on a Quantum Design MPMS-XL-1 SQUID magnetometer with a 1 T magnet and working temperatures range of 1.8–400 K. For the measurements, powder samples were placed into gelatin capsules and were fixed inside plastic straws. For thermomagnetic measurements, both field cooled (FC) and zero field cooled (ZFC) curves were obtained with typical applied field of 100 Oe and in the temperature range from 2 to 300 K. The diamagnetic contribution of the gelatin capsule was assumed to be negligible and overall magnetization to be determined by the sample. Electron paramagnetic resonance was measured on a E-112 VARIAN spectrometer with a cryostat ESR-910 from Oxford Instruments. Compositional analysis was done by EDS (Energy-dispersive X-ray spectroscopy) technique on a JEOL JEM-2200FS microscope with a Schottky gun working at 200 kV (point resolution 0.19 nm) at IMEM-CNR and equipped with an in-column energy filter (Ω -type), a CCD high resolution camera, STEM detectors, and an EDS detector.

4. Results and discussions

4.1. Structural characterization and composition analysis

In Fig. 1a, the (002) peak at $2\theta \approx 26.5^\circ$ for pristine graphite indicates an interlayer spacing of 0.335 nm. The (002) peak of graphene oxide (GO) is shifted to $2\theta \approx 15.2^\circ$, indicating that the interlayer spacing increases to 0.6 nm after oxidization. The

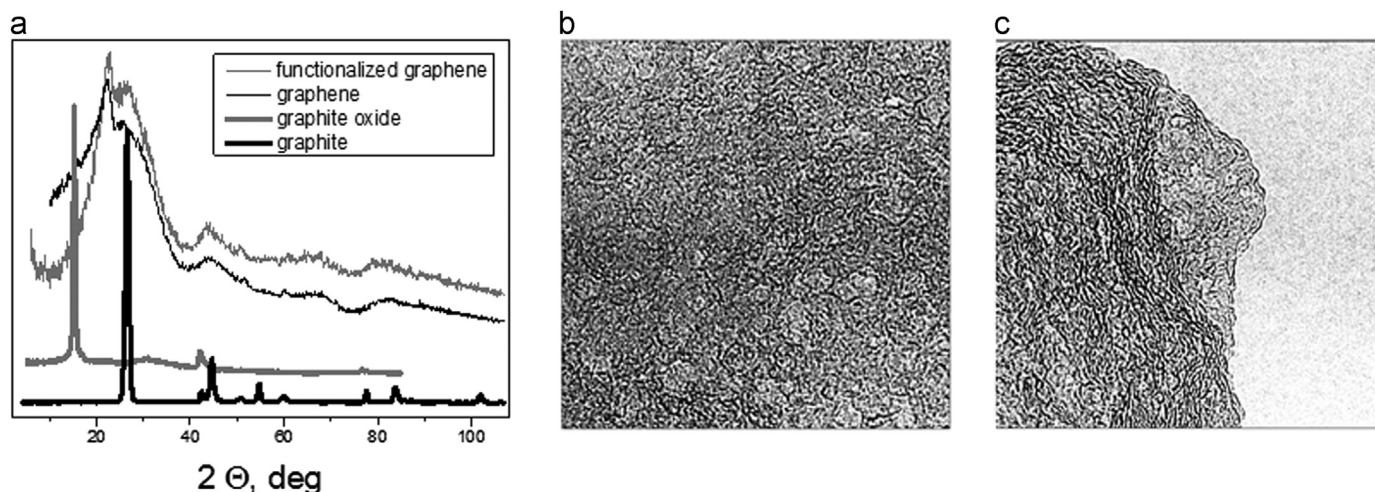


Fig. 1. Structure and morphology of modified graphenes. a: X-ray diffractograms of starting graphite, graphite oxide, graphene and graphene functionalized with nitroaniline. b,c: HRTEM images of graphene functionalized with nitroaniline 36×36 nm² (b) and 46×46 nm² (c).

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