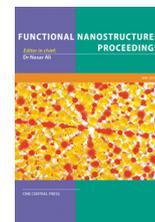


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Proximity Induced magnetism in Graphene for Energy Storage Application

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ABSTRACT

Evidence of significant induced ferromagnetism in multilayer graphene coated with ferrimagnetic nanoparticles (NPs) is observed. Evidence of induced ferromagnetism at room temperature in bulk samples of MLG, coated with ferrimagnetic magnetite (Fe_3O_4) Nps through a facile one-step ultrasonic treatment in a surfactant. This observation of proximity induced ferromagnetism in bulk samples of commercial MLG may open up several applications including energy storage. Magnetization versus magnetic field shows that the saturation magnetization $M_s = 58.6$ emu/gm for pristine Fe_3O_4 increased to $M_s = 158.4$ emu/gm for a 1:1 composite of Fe_3O_4 to MLG. These results lead to induced $M_s = 253$ emu/gm in MLG resulting from its proximity to Fe_3O_4 . The as-prepared materials with low coercivity and high saturation magnetization find broad applications in energy storage applications with large supercapacitance value for use in supercapacitors and superior rechargeable stability to be used as an anode material in lithium ion batteries.

I. INTRODUCTION

Low-dimensional Fe_3O_4 nanoparticles, with properties rather different from those of bulk magnetite, are particularly promising for applications in energy storage applications with large supercapacitance value for use in supercapacitors [1] and rechargeable lithium ion batteries [2]. For viable applications, it is desirable to have magnetic nanoparticles with controllable size, uniform morphology, good crystallinity, and high dispersibility [3, 4]. However, magnetic nanoparticles tend to aggregate easily into larger clusters owing to their intrinsic attraction and are susceptible to losing dispersibility over time. Therefore, a large number of studies are aimed on stabilizing magnetic nanoparticles by modifying them with surfactants, polymers, organic, and inorganic chemicals [5-10].

In this paper, we report a facile approach to coat graphene nanosheets with Fe_3O_4 nanoparticles. The mechanisms for attachment of Fe_3O_4 nanoparticles onto graphene and their magnetic properties are discussed.

II. EXPERIMENTAL PROCEDURE

Commercially available graphene from Cheap Tubes Inc. was used without further purification. The surfactant sodium dodecyl benzene sulfonate (SDBS) and Fe_3O_4 nanoparticles from Sigma-Aldrich were used as received. Graphene used in this experiment, was synthesized from acid exfoliation and is around 12-15 layers thick with specific surface area of 600-750 m^2/g . Initially, 4.0 g surfactant was dispersed in deionized water of resistivity 18 $\text{M}\Omega\text{-cm}$ using ultrasonication for 15 minutes until a clear solution formed. Then, 0.4 g graphene was added to the solution and sonicated for an additional 15 minutes. For the optimum dispersion of graphene, the ratio of graphitic precursor to surfactant has been reported to be 1: 10 [11]. A ratio was regarded optimum if graphene remained dispersed and did not reaggregate after sonication. As a final step, 0.4 g Fe_3O_4 nanoparticles were added to the mixture and sonicated for 30 minutes. After the ultrasonic treatment, the solution was heated inside a vacuum oven at 75 $^\circ\text{C}$ for 12 hours at a pressure of 15 inches of mercury.

III. RESULTS AND DISCUSSION

VSM measurements were carried at maximum field of 2500 Oe, in steps of 5 Oe, at room temperature in plane and out of plane configurations. For comparison purposes, magnetic properties of pristine Fe_3O_4 nanoparticles were also measured. As expected, Fe_3O_4 nanoparticles exhibit lower saturation magnetization (M_s) than bulk samples due to surface disorder and modified cationic distributions associated with nanoparticles. Pristine graphene exhibits a weak diamagnetic response while Fe_3O_4 nanoparticles show a ferrimagnetic behavior during magnetic measurements. The composite graphene coated with Fe_3O_4 nanoparticles attained coercivity of 2.1 Oe. This decrease in the coercivity of samples coated with Fe_3O_4 can be attributed to the presence of surfactant which inhibits any significant interparticle interaction. Similar, decrease of coercivity has been observed in oleic acid-coated NiO nanoparticles [12]. In addition, there are reports of samples with larger magnetic softness depending upon the volume fraction of iron oxide [13]. The saturation and remanent magnetizations (M_r) for graphene coated with Fe_3O_4 nanoparticles measured at a maximum applied field of 2500 Oe are 158.4 and 7.02 emu/g, respectively. The significant increase in M_s and M_r values of graphene coated with Fe_3O_4 nanoparticles is possible due to their coupling. In addition, the saturation magnetization of graphene coated with Fe_3O_4 nanoparticles is more than double the corresponding magnetizations of graphene or carbon nanotubes coated with Fe_2O_3 nanoparticles reported earlier [14]. A detailed characterization and analysis of graphene coated with Fe_2O_3 nanoparticles is presented in our earlier reports [15, 16]. To the best of the authors' knowledge, this is the first report of the preparation of Fe_3O_4 coated graphene using a simple ultrasonic treatment [17]. Magnetic force microscopy of the nanocomposite compared with that of pristine Fe_3O_4 shows that nanocomposites of graphene / Fe_3O_4 , depicts magnetic domains of Fe_3O_4 nanoparticles conglomerates with a random direction. The magnetic domains show a repulsive force of domains randomly distributed in a background of an attractive force domain.

IV. CONCLUSIONS

In summary, we presented a simple approach to coat Fe_3O_4 nanoparticles onto graphene using a one step ultrasonic treatment. Various characterization tools were used to confirm the structural integrity and uniform dispersion of Fe_3O_4 nanoparticles onto graphene sheets. STEM and TEM observations provide clear information regarding the distribution of Fe_3O_4 nanoparticles on carbon matrix. The surfactant prevents the agglomeration of graphene and facilitates dense coating with Fe_3O_4 nanoparticles. Chemical methods of coating Fe_3O_4 nanoparticles on graphene sheets allow higher loading and uniform distribution of these nanoparticles, giving rise to magnetic composites that possess interesting magnetic properties. XRD measurements and Raman spectroscopy suggests formation of electrostatic forces between graphene with Fe_3O_4 nanoparticles that enable a firm adherence of nanoparticles on the surface. Graphene coated with Fe_3O_4 nanoparticles demonstrated the highest enhancement of magnetic properties and achieved a saturation magnetization of 158.4 emu/g. Graphene coated with Fe_3O_4 nanoparticles demonstrated nominal coercivity corresponding to ideal magnetic soft material. These results could facilitate approaches to synthesize graphene based composites with enhanced magnetic properties toward applications in energy storage applications with large supercapacitance value for use in supercapacitors as well as for anode material in Li-ion battery.

V. ACKNOWLEDGMENTS

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