

Proceedings of the 47th International School and Conference on the Physics of Semiconductors "Jaszowiec 2018"

Solvent Driven Magnetic Order Change in Graphene Decorated with α -Fe₂O₃ Nanoparticles

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We present the studies of the structural and magnetic properties of nanocomposites based on graphene decorated with 25% α -Fe₂O₃ nanoparticles made with the use of either ethanol or acetone. We observed the presence of superparamagnetic blocking of the α -Fe₂O₃ nanoparticles at blocking temperature, $T_B = 46.4$ K or 159 K, for the samples made with the use of either ethanol or acetone, respectively. Our magnetization and magnetic susceptibility data revealed the presence of strong inter-particle interactions in our samples. The magnetic properties of our samples depend strongly on the type of solvent used for the sample preparation.

DOI: [10.12693/APhysPolA.134.954](https://doi.org/10.12693/APhysPolA.134.954)

PACS/topics: gaphene, composites, magnetic properties

1. Introduction

Low-dimensional carbon related nanostructures [1], in particular graphene, became a subject of intense research due to their remarkable properties [2, 3]. Decoration of graphene surface with magnetic nanoparticles is one of the major scientific topics in the recent years due to the high specific surface area of graphene [4] leading to the possibility of introducing new or improving the functional properties of base magnetic material. Nanocomposites based on graphene decorated with magnetic iron oxide nanoparticles show a variety of interesting properties prospective for applications in biomedicine, magnetic fluids, magnetic energy storage, environmental remediation, and catalysis [5, 6]. Graphene decoration with transition metal oxides such as Fe₂O₃ [7] is expected to provide properties important from the point of view of applications due to low toxicity and biocompatibility of this iron oxide.

Our current paper is focused over the studies of structural and magnetic properties of composites prepared from commercial graphene with 25% α -Fe₂O₃ made with the use of either ethanol or acetone solvent. In particular, we wish to study the influence of the solvent type on the magnetic properties of the composite.

2. Sample preparation

For the preparation of composite materials, graphene obtained using the Hummers method and iron nitrate(III) was used. Graphene was first dispersed in ethanol or in acetone. An appropriate quantity of iron nitrate (to reach 25 wt% of Fe₂O₃ in the composite) was

weighted into a beaker and 50 ml of ethanol or acetone was added. Graphene in ethanol or acetone was sonificated for 10 min. A volume of 0.5 ml of the suspension (approximately 0.2 g of graphene) was then transferred to the solution with iron nitrate and stirred for 10 min. Then, ammonia water was added to the slurry to reach pH 11 and to precipitate the iron hydroxide. The reaction mixture was next transferred to a Teflon container and placed in an autoclave. Composite materials were obtained in an autoclave at a temperature of 120 °C kept for 12 h. The obtained composites were rinsed with distilled water and dried at 80 °C for 48 h.

3. Structural characterization

The XRD pattern of prepared samples are presented in Fig. 1. We studied the structural quality using the Epyrean (PANalytical) X-ray diffractometer with the use of Cu K_{α} ($\lambda = 1.54 \text{ \AA}$).

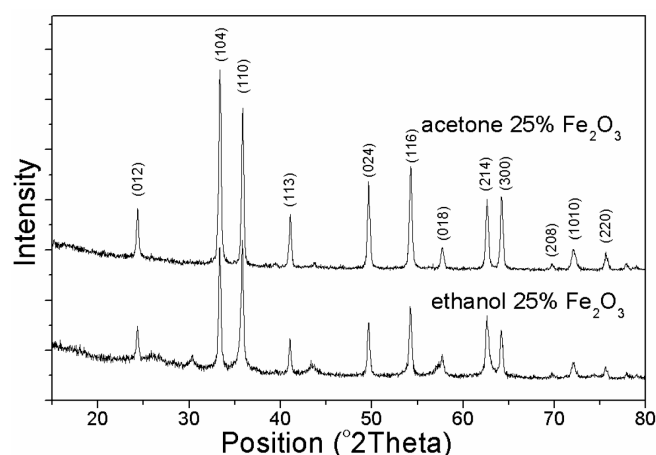


Fig. 1. Diffraction patterns obtained for the graphene + Fe₂O₃ samples prepared with the use of acetone or ethanol.

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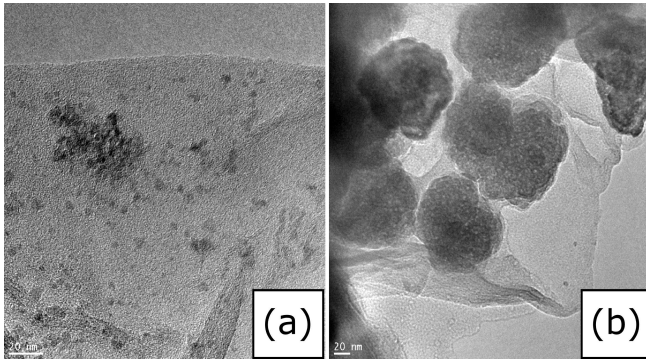


Fig. 2. TEM images of composite obtained in (a) ethanol and (b) acetone.

All peaks on the XRD patterns can be assigned to the rhombohedral Fe₂O₃ phase (ICDD 01-072-0469, space group $R\bar{3}c$, space group number 167, hkl inserted on the graph).

The attached pictures (see Fig. 2) show that the reaction environment affects the morphology of the obtained composites. In the sample obtained in acetone, it can be seen that Fe₂O₃ forms agglomerates with a size above 100 nm. Agglomerates are also observed in the sample obtained in ethanol, but in this case they are smaller. In addition, the size of crystallites in the sample obtained in ethanol is smaller — below 10 nm, and the Fe₂O₃ crystals are more evenly distributed on the surface of graphene in that sample.

4. Magnetic properties

We made detailed measurements of the magnetic properties of two graphene + 25% α -Fe₂O₃ samples made with either ethanol or acetone with the use of the LakeShore 7229 Susceptometer/Magnetometer system. Our studies consisted of the measurements of the dynamic magnetic susceptibility, χ_{AC} , and magnetization, M , done at temperatures from $T = 4.3$ K up to 320 K. The AC magnetic susceptibility measurements were done using mutual inductance method. The static magnetization measurements done using the Weiss extraction technique were made at $B \leq 9$ T and at temperatures from $T = 4.3$ K up to 320 K. Magnetization measurements were also done with the use of the alternating gradient magnetometer (AGM).

The ac magnetic susceptibility was studied as a function of temperature for both samples containing composites made with either ethanol or acetone. The results of the measurements in the form of the temperature dependence of the real part of the magnetic susceptibility, $\text{Re}(\chi_{AC})(T)$, is presented in Fig. 3.

As we can see in Fig. 3, we observe large differences in the $\text{Re}(\chi_{AC})(T)$ dependences between the two studied samples. The $\text{Re}(\chi_{AC})(T)$ dependences for our two samples show values order of magnitude higher than the magnetic susceptibility observed for pure graphene samples, being the reference for us and being the subject

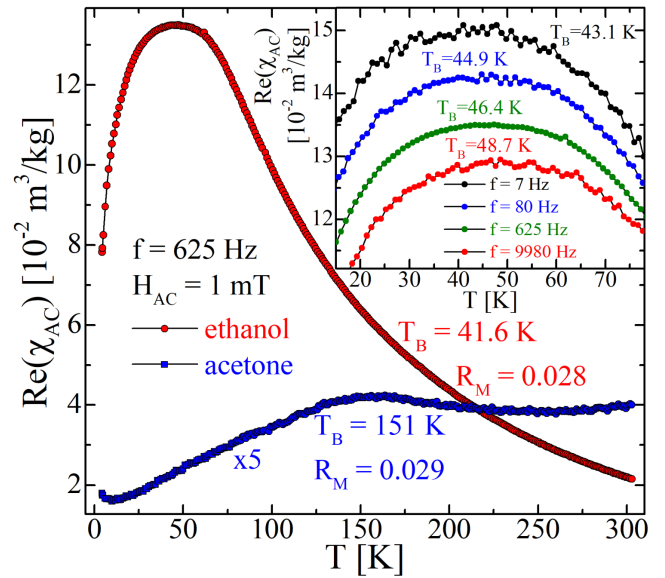


Fig. 3. Temperature dependence of the real part of the magnetic susceptibility obtained for two studied graphene + 25% α -Fe₂O₃ samples. The values of the $\text{Re}(\chi_{AC})(T)$ dependence for the sample made with the use of acetone are multiplied by 5. The inset shows frequency shift of the $\text{Re}(\chi_{AC})(T)$ dependence for the sample made with the use of ethanol.

of our studies in Ref. [8]. It is clear signature that the magnetic properties of the graphene + α -Fe₂O₃ composite are dominated by the component related to α -Fe₂O₃ nanoparticles and depend strongly on the solvent used during the sample synthesis. At $T < 20$ K, for the sample made with the use of acetone, we observed a small decrease in the $\text{Re}(\chi_{AC})(T)$ dependence, a feature not observed for the sample made with the use of ethanol, and related to the presence of isolated paramagnetic magnetic moments in this sample. The $\text{Re}(\chi_{AC})(T)$ dependence obtained for our sample made with the use of ethanol shows the presence of a well-defined maximum at temperature of about 45 K. On the other hand, for the sample made with the use of acetone, the observed $\text{Re}(\chi_{AC})(T)$ dependence shows values an order of magnitude lower and the presence of a cusp at temperature of about 150 K followed with an increasing dependence at room temperature. The presence of a symmetric maximum in the $\text{Re}(\chi_{AC})(T)$ curve indicates the presence of a magnetic transition in the system. Identification of the type of the observed transition requires more detailed magnetometric measurements and data analysis.

We made $\text{Re}(\chi_{AC})(T)$ measurements for four different frequencies of the AC magnetic field, $f = 7, 80, 625,$ and 9980 Hz. The results obtained for the selected graphene + 25% α -Fe₂O₃ sample are presented in the inset to Fig. 3. The maxima of the $\text{Re}(\chi_{AC})(T)$ curves obtained at different magnetic field frequencies shift on the temperature scale with an increase of f for both our samples. The position at the temperature scale of the maxima in the $\text{Re}(\chi_{AC})(T)$ dependence defines the spe-

cific blocking temperature, T_B . The $T_B(f)$ dependence can be analyzed using the phenomenological parameter, R_M , proposed by Mydosh [9] defined with the following formula:

$$R_M = \frac{\Delta T_B}{(T_B) \Delta \log(f)}, \quad (1)$$

where $\Delta T_B = T_B(f_i) - T_B(f_j)$, and $\Delta \log(f) = \log(f_i) - \log(f_j)$. For both our samples we obtained similar R_M values about 0.03. The R_M values should be around 0.01 for spin-glasses while $R_M > 0.1$ is known for superparamagnetic systems [9]. The R_M values calculated for our samples are smaller than the values known for the case of the superparamagnetic α -Fe₂O₃ nanoparticles with $R_M > 0.1$. It is a signature of the presence of strong inter-particle interactions between the α -Fe₂O₃ nanoparticles [10] present in our samples causing the system to behave like a spin-glass.

The experimental $T_B(f)$ dependences allowed us to estimate the values of the static true superparamagnetic blocking temperature, T_B . We approximated the $T_B(f)$ dependence to $f \rightarrow 0$ Hz to estimate T_B values of our samples. The estimated T_B values for our samples are gathered in Fig. 3. The temperature of superparamagnetic blocking of the α -Fe₂O₃ nanoparticles changes with the average nanoparticle size and the type of the host matrix. Literature data shows that T_B values changes from 19 K for 4 nm diameter nanoparticles in the silica matrix [11], $T_B \approx 22$ K for 5 nm diameter nanoparticles embedded in the polymer matrix [12] up to $T_B \approx 120$ K for the 3 nm diameter nanoparticles embedded in the alumina matrix [13]. The differences in T_B observed for our samples are related to the change of the average diameter of the nanoparticles between the samples made with the use of either ethanol or acetone.

For the sample made with the use of acetone we observed signatures of the presence of another magnetic transition at $T > 320$ K, outside of the measurement range. It is probable that this transition will be the Morin transition in this sample, a feature observed for the α -Fe₂O₃ systems [14].

We made the magnetization measurements as a function of the applied static magnetic field $B \leq 9$ T at several stabilized temperatures lower than $T = 200$ K. The selected $M(B)$ curves obtained for our samples are presented in Fig. 4.

The $M(B)$ curve obtained for our graphene + 25% α -Fe₂O₃ samples varies between the samples. Both magnetization curves presented in Fig. 4 shows lack of saturation even at $B = 9$ T. It is a signature of a strong magnetic frustration in the system, most probably related to the presence of strong inter-particle interactions in our samples. We observe large differences in the magnetization values observed for both our samples. This result, in agreement with the magnetic susceptibility data, indicates the significance of the preparation procedure in the effective magnetic moment of the graphene + α -Fe₂O₃ nanocomposites.

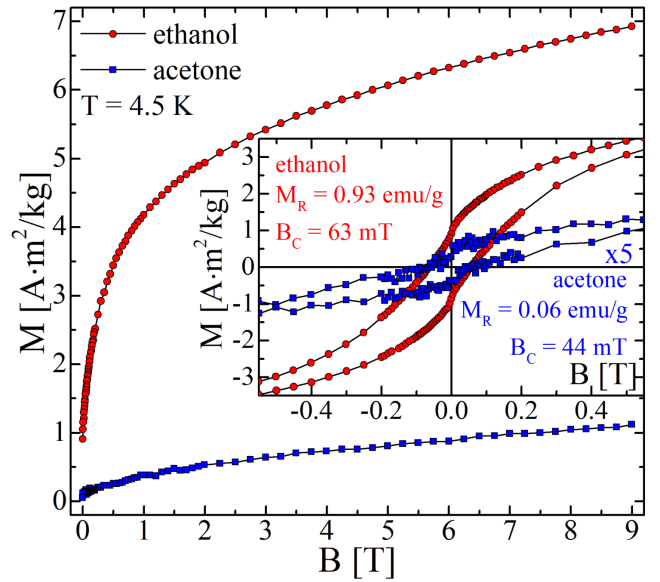


Fig. 4. Magnetic field dependence of the magnetization obtained for the graphene + 25% α -Fe₂O₃ composite samples made with the use of either ethanol or acetone. In the inset, the values of the $M(B)$ dependence for the sample made with the use of acetone are multiplied by 5.

We also performed the $M(B)$ hysteresis curves measurements at $T < 300$ K for both our samples. The obtained $M(B)$ hysteresis curves obtained at $T \approx 4.5$ K for our samples are presented in the inset to Fig. 4. The irreversible $M(B)$ curves behavior is present for all our graphene + 25% α -Fe₂O₃ samples. Inspection of data in the inset to Fig. 4 shows difference in the $M(B)$ hysteresis curves between the samples made with the use of either acetone or ethanol. Both $M(B)$ hysteresis curves have elliptical shape indicating the existence of distribution of magnetic domain structure of the α -Fe₂O₃ nanoclusters.

We calculated two parameters describing the shape of the $M(B)$ hysteresis curves for our samples, e.g., the remanent magnetization and coercive field, M_R and B_C , respectively. Both the $M_R(T)$ and the $B_C(T)$ dependences for our samples decrease as a function of temperature and at $T > T_B$ our samples does not show magnetic irreversibility. Both M_R and B_C values are higher for the sample made with the use of ethanol than the values obtained for the sample made with the use of acetone (see labels to the inset to Fig. 4). It is therefore possible to tune the magnetic properties of the nanocomposite via preparation procedure.

5. Summary

Summarizing, we report the experimental studies of the magnetic properties of two graphene + 25% α -Fe₂O₃ nanocomposites made with the use of either ethanol or acetone. The magnetic properties of the studied composites strongly depend on the type of the solvent used

during the sample synthesis. For both our samples we observe the presence of superparamagnetic blocking at temperatures $T_B \approx 50$ K and 150 K for the sample made with the use of ethanol or acetone, respectively. The superparamagnetic blocking, however, is suppressed by the presence of strong inter-particle interactions. The change of the synthesis solvent plays major role in the magnetic behavior of our samples resulting in much higher magnetization for the sample made with the use of ethanol. Both the shape and the parameters characterizing the magnetization hysteresis loops depend strongly on the change of the preparation method. We clearly show the possibilities to control the magnetic properties of graphene + Fe₂O₃ nanocomposite over a wide range of values.

Acknowledgments

This work was supported by project: LIDER/496/L-6/14/NCBR/2015 financed by The National Centre for Research and Development.

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