

Synthesis, characterization, and magnetic properties of room-temperature nanofluid ferromagnetic graphite

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We report the chemical synthesis route, structural characterization, and physical properties of nanofluid magnetic graphite (NFMG) obtained from the previously synthesized bulk organic magnetic graphite (MG) by stabilizing the aqueous ferrofluid suspension with an addition of active cationic surfactant. The measured magnetization-field hysteresis curves along with the temperature dependence of magnetization confirmed room-temperature ferromagnetism in both MG and NFMG samples. © 2009 American Institute of Physics. [doi:10.1063/1.3265945]

Nanofluids can be defined as fluids containing suspended solid particles with sizes in the nanometers scale. In recent years, substantial progress has been made in developing technologies in the field of magnetic microspheres, nanospheres, and nanofluids.¹⁻⁴ A most recognizable class of magnetically controllable nanofluids (simultaneously exhibiting both *fluid* and *magnetic* properties) are suspended colloids of nanosized iron oxide particles (Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$). At the same time, the important for applications biocompatible ferrofluids normally use water as a vehicle. In order to prevent agglomeration, the magnetic nanoparticles have to be stabilized by ionic interaction using some kind of bioagent (such as, e.g., fatty, aspartic, and glutamic acids or peptides). Alternatively, the coprecipitation of ferrous/ferric ions can be performed in the presence of the appropriate biopolymer (such as polyvinyl alcohol or polyethylen glycol). Several clinically important enzymes and proteins (including, among others, bovine serum albumin, streptokinase, chymotrypsin, and glucose oxidase) have been immobilized based on this method. On the other hand, carbon materials constitute one of the most fascinating classes of structures, exhibiting a wide variety of forms and properties. They have been increasingly attracting the attention of the scientific community mainly because of their potential applications in *high-technology* devices. For these reasons, the availability of macroscopic quantities of bulk room-temperature magnetic carbonlike graphite is of utter importance not only for a wide number of natural sciences, but also for technological applications of this material in engineering (as well as in medicine and biology).⁵⁻¹⁰ We have already reported the method to obtain macroscopic quantities of pure *bulk* ferromagnetic graphite.¹¹⁻¹⁴ The as-obtained modified graphite has a strong magnetic response even at room temperature (which manifests itself through a visible attraction by a commercial magnet).¹²

In this letter, we present the chemical route for synthesizing nanofluid magnetic graphite (NFMG) as well as its

structural and magnetic properties. We emphasize that this NFMG constitutes a unique material at the nanoscale level which is both magnetic and 100% organic. Both characteristics together give the NFMG an enormous plethora of potential uses, ranging from applications in biomedicine (such as imaging, magnetic drug targeting, delivering, hyperthermia, etc.) to applications in paints and inks.

The chemically modified magnetic graphite (MG) reported here was produced by a vapor phase redox reaction in closed nitrogen atmosphere (N_2 , 1 atm.) with copper oxide using synthetic graphite powder (Fluka, granularity <0.1 mm). After obtaining the MG, we have prepared the nanofluid suspension (NFMG) by dissolving graphite in acetone, adding a cetyltrimethylammonium bromide (CTAB) cationic surfactant, and bringing it to an ultrasonic edge. The resulting homogeneous solution was separated in a centrifuge at 6000 rpm. After five consecutive washes with acetone (to remove an excessive surfactant), de-ionized water was added and the solid sample was brought back to an ultrasonic edge for 1 min. The above procedure provided the necessary homogeneity and stability of the obtained solution. The adsorption of active agents on the surface of the graphite results from the favorable interaction between the surface and species of the solid adsorbents. Various interactions (such as electrostatic attraction, covalent binding, hydrogen binding, nonpolar interactions, and lateral interactions between adsorbed species) can contribute to the adsorption processes, facilitating the aqueous suspension of graphite. Recently, this field of research has been renewed by studies with fluid carbon nanotubes, among other forms.¹⁵⁻¹⁷ To assess the presence of CTAB molecules on the surface of NFMG, we performed micro Raman analysis with samples of graphite dried in vacuum at a temperature of 60 °C for 6 h.

The results (shown in Fig. 1) revealed the presence of the peak at 1650 cm^{-1} corresponding to NFMG, in addition to the peak at 1350 cm^{-1} (known as the “disordered” D band) in the MG sample. For further comparison, Fig. 1 also depicts the Raman spectrum showing characteristic bands of the surfactant used in the suspension (CTAB). Observe that, as expected, the CTAB functional groups, the hydrophobic

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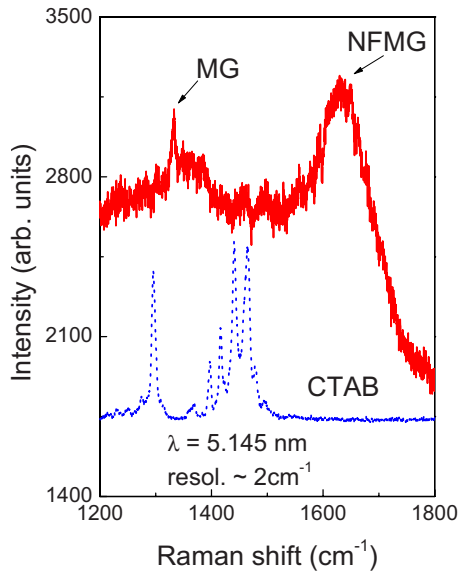


FIG. 1. (Color online) Raman spectra for chemically modified MG, surfactant used in the suspension (CTAB), and the aqueous suspension of the NFMG.

(carbonic chain) and hydrophilic (cationic-active tensions with positive charge) parts of the surfactant correlate with the band structure of the graphite. Since the hydrophilic part tends to bind with the water molecules, its action results in stabilization of the nanofluid suspension. The structural characterization of NFMG was performed by transmission electron microscopy (TEM) using Philips CM-120 microscope. TEM analysis (see Fig. 2) reveals a flakelike morphology of NFMG. Relating the size of the scale in Fig. 2 with the size of the particle in the nanofluid, the latter is estimated to be of the order of 10 nm. To test the magnetic properties of both MG and NFMG samples, we performed the standard zero field cooled (ZFC) measurements using a MPMS-5T superconducting quantum interference device magnetometer from Quantum Design. Figure 3 presents the effective ZFC curves for MG and NFMG samples (taken under the applied magnetic field of 1 kOe) after subtraction of the paramagnetic contributions. Notice that both MG and NFMG samples exhibit magnetization curves typical for ferromagnetic materials with the onset Curie temperatures around 300 K. Thus, we can conclude that the aqueous suspension of graphite (NFMG) does not affect the room-temperature magnetization of the MG sample. Given an average value of 10 nm for particle sizes in both MG and NFMG (deduced from TEM images), the low-temperature anomalies seen in Fig. 3 for both samples are most likely related to the finite size effects.

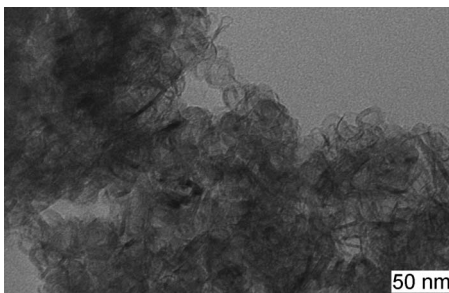


FIG. 2. TEM image of NFMG sample showing a flakelike structure with an average size of the particle of the order of 10 nm.

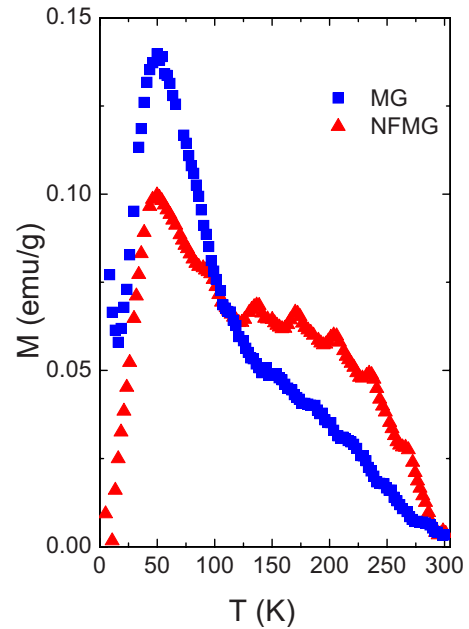


FIG. 3. (Color online) The temperature dependence of the effective ZFC magnetization for MG and NFMG samples (after subtracting the paramagnetic contributions).

Besides, according to Fig. 4 (which shows M-H curves at 2 and 300 K), the hysteresis does not disappear with increasing the temperature and manifests itself in nonzero values of remnant magnetization and coercive magnetic field (H_C). Consequently, we can conclude that, even though the material has a relatively small value of H_C , it does exhibit a true ferromagnetic behavior up to 300 K.

In summary, we have reported the synthesis, structural characterization, and magnetic properties of NFMG. The structural analysis of NFMG confirmed its stability in aqueous solution. By measuring the magnetization as a function of temperature and applied magnetic field in both MG and NFMG samples, we observed the typical ferromagnetic behavior. The comparative study unambiguously demonstrated that, after the chemical treatment, both MG and all its suspensions (prepared with acetone, CTAB, and water) exhibit a stable net magnetization at room temperature.

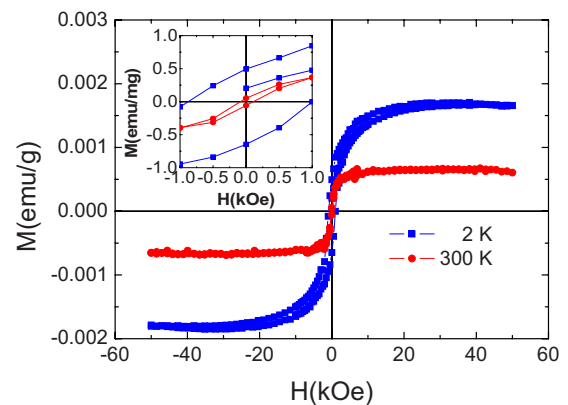


FIG. 4. (Color online) The hysteresis curves for NFMG sample for two temperatures (2 and 300 K) showing a ferromagneticlike behavior of the sample. Inset: low-field M-H curves.

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- ¹J. Philip, P. D. Shima, and B. Raj, *Appl. Phys. Lett.* **92**, 043108 (2008).
- ²D. Wu, H. Zhu, L. Wang, and L. Liu, *Curr. Nanosci.* **5**, 103 (2009).
- ³E. Tombacz, D. Bica, A. Hajdu, E. Illes, A. Majzik, and L. Vekas, and *J. Phys.: Condens. Matter* **20**, 204103 (2008).
- ⁴*Magnetism: Molecules to Materials III*, edited by J. S. Miller and M. Drillon (Wiley, Weinheim, 2002).
- ⁵T.L. Makarova, *Semiconductors* **38**, 615 (2004), and references therein.
- ⁶Y. Kopelevich, P. Esquinazi, J. H. S. Torres, and S. Moehlecke, *J. Low Temp. Phys.* **119**, 691 (2000).
- ⁷P. Esquinazi, A. Setzer, R. Höhne, C. Semmelhack, Y. Kopelevich, D. Spemann, T. Butz, B. Kohlstrunk, and M. Losche, *Phys. Rev. B* **66**, 024429 (2002).
- ⁸P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K. H. Han, and T. Butz, *Phys. Rev. Lett.* **91**, 227201 (2003).
- ⁹A. V. Rode, E. G. Gamaly, A. G. Christy, J. G. Fitz Gerald, S. T. Hyde, R. G. Elliman, B. Luther-Davies, A. I. Veinger, J. Androulakis, and J. Giapintzakis, *Phys. Rev. B* **70**, 054407 (2004).
- ¹⁰P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama, and M. Kinoshita, *Chem. Phys. Lett.* **180**, 327 (1991).
- ¹¹F. M. Araújo-Moreira, H. Pardo, and A. W. Mombrú, Patent No. WO/2005/123580 (December 29, 2005).
- ¹²A. W. Mombrú, H. Pardo, R. Faccio, O. F. de Lima, A. J. C. Lanfredi, C. A. Cardoso, E. R. Leite, G. Zanelatto, and F. M. Araújo-Moreira, *Phys. Rev. B* **71**, 100404 (2005), and references therein.
- ¹³R. Faccio, H. Pardo, P. A. Denis, R. Yoshikawa Oeiras, F. M. Araújo-Moreira, M. Veríssimo-Alves, and A. W. Mombrú, *Phys. Rev. B* **77**, 035416 (2008).
- ¹⁴H. Pardo, R. Faccio, A. W. Mombrú, F. M. Araújo-Moreira, and O. F. de Lima, *Carbon* **44**, 565 (2006).
- ¹⁵H. Zhu, C. Zhang, Y. Tang, J. Wang, B. Ren, and Y. Yin, *Carbon* **45**, 226 (2007).
- ¹⁶O. E. Andersson, B. L. V. Prasad, H. Sato, T. Enoki, Y. Hishiyama, Y. Kaburagi, M. Yoshikawa, and S. Bandow, *Phys. Rev. B* **58**, 16387 (1998).
- ¹⁷Y. Yang, E. Grulke, G. Zhang, and W. Gefei, *J. Nanosci. Nanotechnol.* **5**, 571 (2005).