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Zero-Dimensional Graphene and Its Behavior under Mechanochemical Activation with Zinc Ferrite Nanoparticles

Monica Sorescu[1], Matthew Knauss[1], Alice Perrin[2] and Michael McHenry[2]

[1]*Duquesne University, Department of Physics, Fisher Hall, Pittsburgh, PA 15282*

[2]*Carnegie Mellon University, Department of Materials Science and Engineering, Roberts Hall, Pittsburgh, PA 15213*

ABSTRACT

Equimolar mixtures of zero-dimensional graphene (SkySpring Nanomaterials, 1-5 nm particle size) and zinc ferrite nanoparticles (Alfa Aesar, 50 nm particle size) were exposed to mechanochemical activation by high-energy ball milling for time intervals of 0-12 hours. Their structural and magnetic properties were analyzed by Mössbauer spectroscopy and magnetic measurements. The spectra of zinc ferrite milled without graphene were fitted with one quadrupole-split doublet (quadrupole splitting 0.5 mm/s, isomer shift 0.23 mm/s) and indicated that zinc ferrite was superparamagnetic. The line width of the doublet increased from 0.41 to 0.64 mm/s, which correlates with a reduction in particle size as effect of the ball milling processing performed. When graphene was added to the milling powders, the Mössbauer spectra showed the appearance of another quadrupole doublet, with a quadrupole splitting of 0.84 mm/s and an isomer shift of -0.38 mm/s. Its abundance to the spectrum remained constant to 4.48% while the milling time was increased. This second doublet could be related to carbon atoms occupying neighborhoods in the proximity of iron atoms. Hysteresis loops were recorded in an applied magnetic field of 5 T at a temperature of 5 K. A change in the approach to saturation of the loop was observed, with saturation being achieved for the sample milled for 12 hours with graphene. Zero-field-cooling-field-cooling (ZFC-FC) was performed on all samples between 5-300 K with an applied magnetic field of 200 Oe. Graphene was found to stabilize the magnetic properties of the milled system of powders to a blocking temperature of about 90 K.

INTRODUCTION

Graphene (also encountered as reduced graphene oxide, rGO) is a two-dimensional one-atom-thick carbon material composed of sp^2 hybridized carbon atoms, exhibiting excellent electrical, mechanical and thermal properties, which have been widely used in many fields, such as electronics, sensors, batteries and supercapacitors [1-8]. Both theoretical and experimental studies have demonstrated that the intentional incorporation of heteroatoms into the graphene structure could effectively modify its electronic and chemical properties. On the other hand, the competing incorporation of carbon atoms into the ferrites structure during milling represents the central hypothesis of the present study.

If two-dimensional graphene-based materials have been the subject of many investigations, zero-dimensional graphene (graphene nanoparticles) leaves room for future contributions. In particular, the behavior of graphene nanoparticles during mechanochemical activation with other magnetic nanoparticles deserves researchers' attention. Indeed, nanoparticles possessing magnetic properties introduced in a non-magnetic graphene host combine both the benefits of the unique properties of graphenes and magnetization. When these magnetic particles are inserted in a graphitic matrix, the carbon layers isolate the particles magnetically from each other, providing protection against oxidation. Alternatively, the incorporation of carbon in ferrite nanoparticles lattice may give rise to nanocomposite and new hybrid materials, which can open up new prospects in bioengineering and energy applications, such as controlled drug delivery, magnetic recording media, magnetic toners, magnetic resonance imaging, ferrofluids, as well as in electrochemical energy storage and supply.

In this study, the graphene-ferrite nanocomposite systems were synthesized by high-energy ball milling of zinc ferrite and graphene and characterized by Mössbauer spectroscopy and magnetic measurements. The hyperfine and magnetic parameters were detailed as function of ball milling time and other processing parameters.

MATERIALS AND METHODS

The zinc ferrite powders were purchased from Alfa Aesar (99% metal basis, average particle size of about 50 nm). Graphene powders were purchased from SkySpring Nanomaterials (average particle size 1-5 nm). Powders of zinc ferrites and graphene were ball-milled in a hardened steel vial with 12 stainless-steel balls (type 440; eight of 0.25 inches diameter and four of 0.5 inches diameter) in the SPEX 8000 mixer mill for time periods ranging from 0 to 12 h. The ball/powder mass ratio was 5:1. The powders were manually ground in air to obtain a homogeneous mixture prior to their insertion in the mechanochemical device.

A constant acceleration spectrometer (SeeCo) with a 25 mCi ^{57}Co source diffused in Rh matrix was used to record the room temperature ^{57}Fe transmission Mössbauer spectra. The WINORMOS package of programs was used for the least-squares fittings of the Mössbauer spectra. Magnetic measurements were performed with a SQUID magnetometer at 5 T. The hysteresis loops were recorded at 5 K and the zero-field cooling data were collected with an applied magnetic field of 200 Oe.

RESULTS AND DISCUSSION

Equimolar mixtures of zero-dimensional graphene and zinc ferrite nanoparticles were exposed to mechanochemical activation by high-energy ball milling for time intervals of 0-12 hours. Their structural and magnetic properties were analyzed by Mössbauer spectroscopy and magnetic measurements. The spectra of zinc ferrite milled without graphene (Fig. 1) were fitted with one quadrupole-split doublet (quadrupole splitting 0.5 mm/s, isomer shift 0.23 mm/s) and indicated that zinc ferrite was superparamagnetic. The line width of the doublet increased from 0.41 to 0.64 mm/s, which correlates with a reduction in particle size as effect of the ball milling processing performed. When graphene was added to the milling powders, the Mössbauer spectra (Fig. 2) showed the appearance of another quadrupole doublet, with a quadrupole splitting of 0.84 mm/s and an isomer shift of -0.38 mm/s. Its abundance to the spectrum remained constant to 4.48% while the milling time was increased. This second doublet could be related to carbon atoms occupying neighborhoods in the proximity of iron atoms in the ferrite lattice.

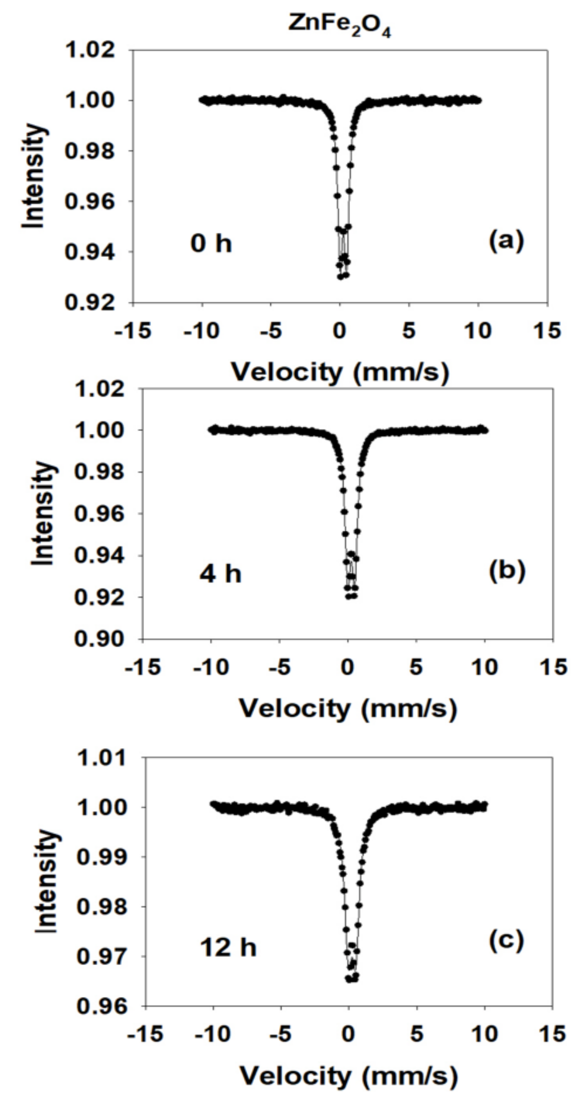

Figure 1: Mössbauer spectra of zinc ferrite ball milled for (a) 0 hours; (b) 4 hours and (c) 12 hours.

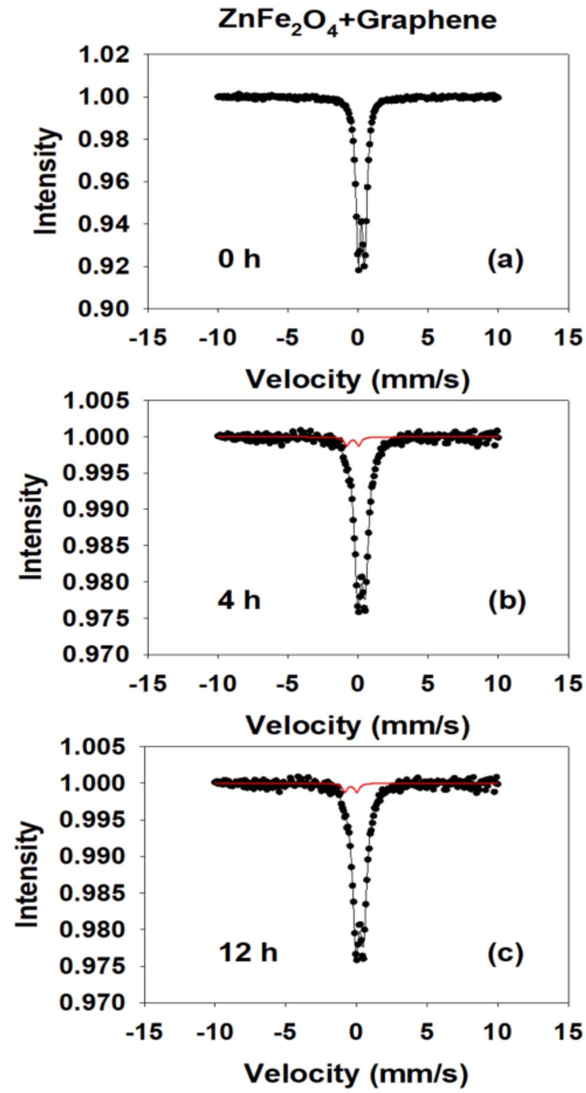

Figure 2: Zinc ferrite with graphene nanoparticles ball milled for (a) 0 hours, (b) 4 hours and (c) 12 hours, respectively.

Hysteresis loops were recorded in an applied magnetic field of 5 T at a temperature of 5 K. A change in the approach to saturation of the loop was observed (Fig. 3), with saturation being achieved for the sample milled for 12 hours with graphene. Zero-field-cooling-field-cooling (ZFC-FC) was performed on all samples between 5-300 K with an applied magnetic field of 200 Oe (Fig. 4). The blocking temperature of the superparamagnetic zinc ferrite powder was determined from the ZFC curves and found equal to 55 K (Fig. 4(a)). Graphene was found to stabilize the magnetic properties of the milled system of powders to a blocking temperature of about 90 K (Fig. 4(c)). Since the blocking temperature increases with C dissolution in the ferrite, this would imply that is contributing to an increased magnetic anisotropy [9].

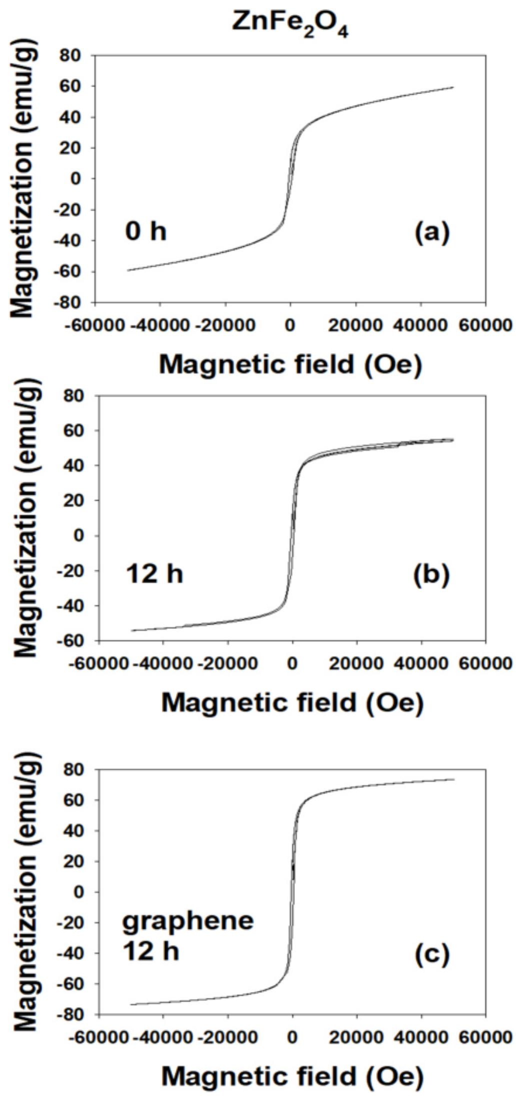

Figure 3: Hysteresis loops recorded at 5 T and 5 K for zinc ferrite at milling time of (a) 0 hours (b) 12 hours and (c) 12 hours with graphene

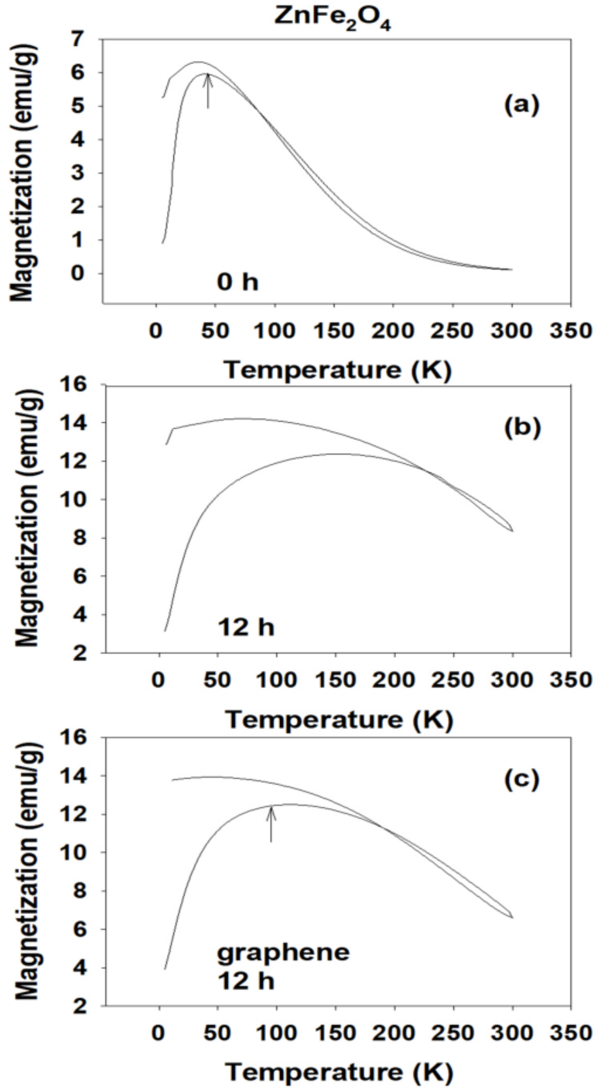

Figure 4: ZFC-FC magnetic measurements at 200 Oe and 5-300 K for zinc ferrite and zinc ferrite milled with zero-dimensional graphene nanoparticles at (a) 0 hours of milling, (b) 12 hours and (c) 12 hours with graphene.

CONCLUSIONS

We successfully performed the mechanochemical activation of graphene nanoparticles with zinc ferrite nanoparticles using high energy ball milling. The main results obtained are: (i) carbon atoms enter the lattice of the ferrite; (ii) the approach to saturation of the hysteresis loops is modified as effect of milling and introduction of graphene; and (iii) the blocking temperature of the superparamagnetic nanoparticles is changed as effect of graphene introduction.

ACKNOWLEDGMENT

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