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Magnetic Graphite Suspensions with Reversible Thermal Conductivity

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ABSTRACT:

Magnetic graphite nanoflake(GN) suspensions with reversible thermal conductivity(TC) are reported. A process of sulfuric acid intercalation, microwave expansion magnetization, and ultrasonic dispersion is followed to make magnetic GN Poly-Alpha-Olefin(PAO) suspensions. Magnetic field was observed to increase the TC of the suspensions dramatically, up to 325%with 0.8% (w/w) of magnetic GNs. After removing the magnetic field, the TC trends to decrease reversibly. The maximal TC contrast ratio reaches 3 times before and after the effects of magnetic field. Such materials with magnetically reversible TC have great potential in next generation “smart” cooling devices.

Keywords: Magnetic graphite nanoflakes, Suspensions, Thermal conductivity, Reversible, Magnetic field.

1. Introduction:

Environmental response materials with reversible tuning electrical and thermal conductivities have great potential in many applications, such as sensors, smart devices, and thermal storage[1-5]. The tuning

of electrical conductivity could be realized through phase change for specific solid materials[1]. In contrast, due to the little variation of TC during the solid-state phase transitions, tuning of thermal conductivity is difficult for single component materials. Suspensions composed by nanomaterials and base fluid with distinct tunable TC have great potential for fabricating novel "smart" materials. By reversibly building and dismantling the phonon conduct path of nanomaterials in the base fluids, the TC of the suspensions could be regulated effectively. For example, TC of the phase change nanocomposites could be regulated by temperature controlled crystallization process[2,3,6]. The biggest TC contrast ratio around the phase transition point reaches to 3.2 times for GNs/hexadecane composites[2]. And TC of the ferrofluids could be regulated by the effects of magnetic field[7-10]. Due to the dipolar interaction, the magnetic particles tend to align themselves along the direction of the magnetic field, which enhances the TC significantly[8,9,11]. After removing the magnetic field, the TC of the suspensions tends to decrease reversibly. The biggest TC contrast ratio of ferrofluids is reported to be 2.7 with 4.5% (V/V) Fe_3O_4 nanoparticles before and after the effects of magnetic field[7].

The TC of GNs can reach 2000W/mK, which is much higher than that of Fe_3O_4 particles[12]. And the GNs with larger specific surface area are expected to form the phonon conduct paths easier. In this letter, we report a convenient way to magnetic GN suspensions with magnetically reversible TC. The biggest TC enhancement of the suspensions is found to be 325% with 0.8% (w/w) of magnetic GN. The maximal TC contrast ratio before and after the effect of magnetic field reaches 3 times at the weight fraction of 0.6%.

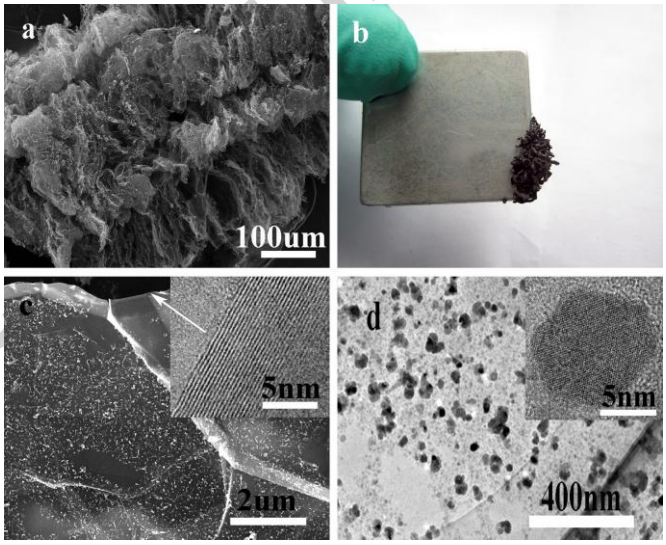
2. Experiments

Expandable graphite was prepared from natural graphite (Asbury Carbons) by a chemical intercalation method. For the intercalation process, 2.2g of natural graphite was reacted with 100ml of the oxidative agent(mixture of H_2SO_4 and H_2O_2 with mole ratio of 10:1) at room temperature for 60 min. Then the slurries were rinsed with distilled water, followed by filtering and baking on a hotplate at 100°C for 24 h. Fe_3O_4 decorated graphite worms were obtained by thermal expansion of the mixture of expandable graphite and ferric-acetylacetonate(1:1 in weight) in a 750W commercial microwave oven (HAIER) for 120s. The magnetic graphite worms were then dispersed in PAO by using a high-intensity ultrasonic probe (JY98-IIIDN, 400W, NingBoXinZhi) to create a 0.8% weight fraction of magnetic GN suspensions. The obtained uniform suspension was then dispersed in PAO and further ultrasonication was performed to obtain 0.2, 0.4, and 0.6% suspensions. The dispersions become stable suspensions after they cool to room temperature.

The morphologies of magnetic graphite worms and nanoflakes were observed by a scanning electron microscopy (SEM, S-4800, HITACHI). The microstructures of magnetic GNs were examined using a transmission electron microscopy (TEM, H600, HITACHI). The phase structure of magnetic GNs was analyzed by XRD(X' Pert PRO MPD, Cu target). Magnetic property of the suspensions was characterized by a vibration sample magnetometer (VSM, LakeShore7307). A transient hot-wire instrument was used to measure the TC of the magnetic GN suspensions at 25°C. The uniform magnetic field to the suspensions was generated by a solenoid, with the field tuned by a programmable current source.

3. Results and discussion

The morphologies and structures of the samples are showed in Fig.1. After microwave expansion magnetization, expandable graphite transforms to graphite worm, which show expanded layer structures with attached nanoparticles (Fig.1(a)). Fig.1(b) shows the graphite worms are magnetically activated by the decoration of magnetite (Fe_3O_4). The SEM image shows many nanoparticles (with size of tens nm) attached to the surface of the GN. However, the density, size and distribution of the nanoparticles on the GN are not uniform due to the scrolling induced curvature of GN(Fig.1(c)). The size of the GNs is about several microns, the thickness of the nanoflake is around 8 nm with about 20 single layer structures (insert image of Fig.1(c)). Distribution of the nanoparticles attached is further characterized by TEM. In Fig.1(d), we can see substantial small nanoparticles(around 10 nm, insert image) are attached on the surface of GNs. Meanwhile, there are some big nanoparticles with diameter around 30-50nm among the tiny nanoparticles.



The phase of the magnetic GNs is examined by XRD and the pattern of the sample is shown in Fig. 2. The reflection peaks at 26.5° and 54.7° are from GNs. The peaks of 30.1°, 35.5°, 43.0°, 53.5°, 57.2°, and 62.7° in the patterns can be indexed to the facecenter cubic phase of magnetite(Fe_3O_4) with lattice

parameter of a=8.374 A˚, which are in agreement with the standard values(JCPDSfileno.01–1111). As no impurity is observed, the XRD pattern confirms that the components of magnetic GNs are graphite and Fe_3O_4.

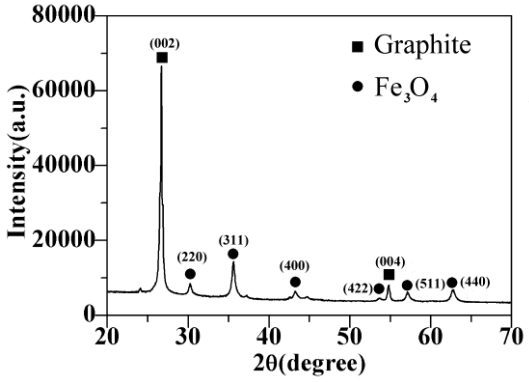


Fig. 3 shows magnetization curves of the magnetic suspensions with different amount of GNs at room-temperature. The saturation magnetization of the suspensions enhances with the increase of magnetic GNs weight fractions, within the range of 0.094emu/g (0.2%w/w) to 0.826emu/g (0.8%w/w). The suspensions with the weight fraction of 0.2%, 0.4% and 0.6% show super-paramagentic behavior, while the sample with 0.8% exhibits small magnetic hysteresis. Such results indicate that the tiny Fe_3O_4 nanoparticles with single magnetic domain dominate the super-paramagentic properties of the suspensions. The small magnetic hysteresis in the high weight fraction should be caused by the big Fe_3O_4 nanoparticles with multi magnetic domain. The super-paramagentic properties are beneficial for the reversible control of the GNs conduct path by magnetic field.

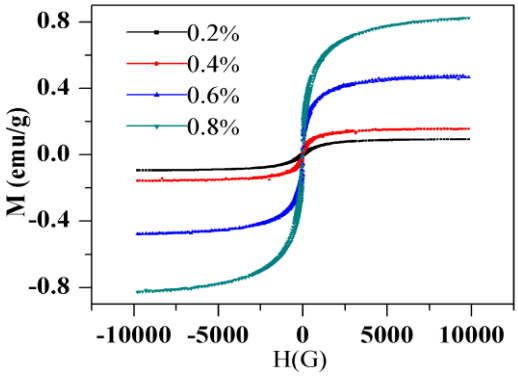
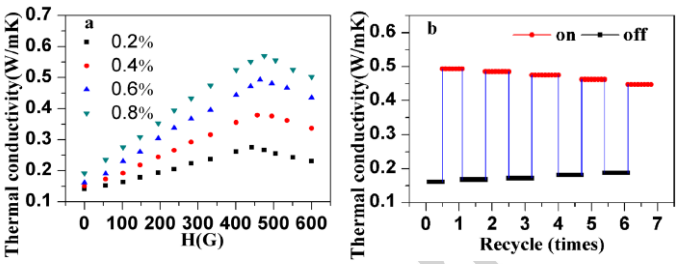


Fig.4a shows the TC variation of the magnetic suspensions with different GN weight fraction as a function of magnetic field. It reveals that the TC increases with the magnetic field at the beginning, reaches the maximal values, then tends to decline. The biggest TC enhancement is 325% at the weight fraction of 0.8%(w/w), the corresponding magnetic field is 475G. Similar to the ferrofluids, phonon conduct paths could be formed by magnetic GNs under the effects of the dipole-dipole interaction in appropriate magnetic field. The increase of the conduct paths could explain the enhancement of TC. As the magnetic field is increased continually, the magnetic GN aggregations becomes bigger and bigger. The growing GN clusters induce inhomogeneous of the suspensions, the local concentration of GNs around hot-wire could be reduced, which makes the measured TC lower[10].

After reaching the maximum TC, the reversible decline of TC is observed as we remove the magnetic field. The re-dispersion of GNs which is caused by liquid convection and brownian motion should be responsible for the observation[3]. The biggest TC contrast ratio before and after the effects of magnetic field is 3 times for the suspensions with 0.6% (w/w) GNs. The repeatability of TC variation of the suspensions (0.6%w/w) with magnetic field is shown in Fig.4b. Along with the first five cycles, the biggest TC with magnetic field decreases from 0.493W/mK to 0.448W/mK. The TC without magnetic field increases from 0.162W/mK to 0.187W/mK. The corresponding TC contrast ratio decreases from

3.04 to 2.40. The TC variation during the repeatability test should be caused by the growing magnetic GN clusters under the repeated regulation of magnetic field. The growing clusters are beneficial for the TC in the original state because of the local percolation behavior. In contrast, the small clusters are easier to form the conduct paths in base fluid under the effects of magnetic field[2, 3]. Therefore, the biggest TC with the effects of magnetic field decreases with the increasing cycles. Our result shows the TC switching of the suspensions are repeatable, the stability of the switching may be improved by appropriate functionalization of the GN[2,3].



4. Conclusion

We developed a convenient way to fabricate magnetic graphite suspensions with high TC enhancement under the effects of magnetic field. The biggest enhancement of the TC is 325% with 0.8% (w/w) of magnetic GN. The TC trends to decrease reversibly after removing the magnetic field. The maximal TC contrast ratio before and after the effects of magnetic field reaches 3 times at the weight fraction of 0.6%. GN suspensions with magnetic field tunable TC have great potential for the “smart” cooling application in nano and microelectromechanical systems (NEMS and MEMS).

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Reference:

[1] Imada M, Fujimori A, Tokura Y. Metal-insulator transitions. Reviews of Modern Physics. 1998;70:1039.
[2] Zheng R, Gao J, Wang J, Chen G. Reversible temperature regulation of electrical and thermal conductivity using liquid–solid phase transitions. Nature Communications. 2011;2:289.
[3] Sun P, Wu Y, Gao J, Cheng G, Chen G, Zheng R. Room Temperature Electrical and Thermal Switching CNT/Hexadecane Composites. Advanced Materials. 2013;25:4938-43.
[4] Feng W, Qin M, Lv P, Li J, Feng Y. A three-dimensional nanostructure of graphite intercalated by carbon nanotubes with high cross-plane thermal conductivity and bending strength. Carbon. 2014;77:1054-64.
[5] Feng W, Li J, Feng Y, Qin M. Enhanced cross-plane thermal conductivity and high resilience of three-dimensional hierarchical carbon nanocoil-graphite nanocomposites. RSC Advances. 2014;4:10090-6.
[6] Schiffres SN, Harish S, Maruyama S, Shiomi J, Malen JA. Tunable Electrical and Thermal Transport in Ice-Templated Multilayer Graphene Nanocomposites through Freezing Rate Control. ACS nano. 2013;7:11183-9.
[7] Philip J, Shima P, Raj B. Nanofluid with tunable thermal properties. Applied Physics Letters. 2008;92:043108--3.
[8] Shima P, Philip J, Raj B. Magnetically controllable nanofluid with tunable thermal conductivity and viscosity. Applied Physics Letters. 2009;95:133112--3.
[9] Li Q, Xuan Y, Wang J. Experimental investigations on transport properties of magnetic fluids. Experimental Thermal and Fluid Science. 2005;30:109-16.
[10] Philip J, Shima PD, Raj B. Enhancement of thermal conductivity in magnetite based nanofluid due to chainlike structures. Applied Physics Letters. 2007;91:203108-3.
[11] Wright B, Thomas D, Hong H, Groven L, Puszynski J, Duke E, et al. Magnetic field enhanced thermal conductivity in heat transfer nanofluids containing Ni coated single wall carbon nanotubes. Applied Physics Letters. 2007;91:173116.
[12] Balandin AA. Thermal properties of graphene and nanostructured carbon materials. Nature materials. 2011;10:569-81.

Figure Captions:

Fig.1. (a) SEM image of magnetic graphite worm, (b) photograph of magnetic active graphite worms, (c) SEM image of GN with Fe_3O_4 nanoparticles(insert picture is HRTEM image of GN edge),(d) TEM image of GN with Fe_3O_4 nanoparticles(insert picture is HRTEM image of the small nanoparticle).

Fig.2. XRD patterns of magnetic graphite worms.

Fig.3. Magnetization of magnetic suspensions with different GN weight fractions.

Fig.4. (a) TC variation of magnetic suspensions with different weight fraction of GNs as a function of magnetic field, (b) repeatability of TC variation of the suspensions with 0.6%(w/w) GNs, circles and squares indicate the biggest TC with magnetic field and lowest TC without magnetic field during the different cycles, respectively.

Research highlights:

1. Magnetic graphite suspensions are fabricated based on microwave expansion magnetization.
2. The biggest TC enhancement of the suspensions under the magnetic field is 325%.
3. TC of the suspensions is regulated reversible by magnetic field.
4. The maximal TC contrast ratio before and after the effects of magnetic field reaches 3 times.