Preparation and Thermal Conductivity of Alumina/Reduced Graphene Oxide Composite Dispersed Aqueous Nanofluids

Guoqiang Yang¹, Xiaofeng Yu¹, Qibai Wu¹,*, Haiyan Zhang¹,2,*, Wenwu Li¹ and Yannan Qian¹,2

¹School of Materials and energy, Guangdong University of Technology, Guangzhou, 510006, China
²GuangDong Provincial Key Laboratory of Functional Soft Condensed Matter, Guangzhou, 510006, China
*E-mail: wuqb@gdut.edu.cn; hyzhang@gdut.edu.cn.

Abstract. Alumina/reduced graphene oxide composite dispersed aqueous nanofluids with various concentrations have been synthesized successfully by a two-step process: synthesis of Al₂O₃/rGO composite via solvothermal reaction method and preparation water-based nanofluids through ultrasonication treatment. The crystal phase structure and morphology of the prepared composite have been characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The suspension stability and thermal conductivity of as prepared Al₂O₃/rGO-water nanofluids with different composite concentration have been studied in detail. The overall value of thermal conductivity increases along with increasing concentration at various temperatures, indicating potential application for heat transfer field.

1. Introduction
Graphene Nanofluid have been studied extensively because of their unique thermal transport characteristics [1,2]. Zhang et al investigated the stability, zeta potential, thermal conductivity, and rheological properties of the reduced graphene oxide-deionized water nanofluids. Significant enhancements in thermal conductivity upon increase of the additive concentration and nanofluids temperature was found with the maximum enhancement of 32.19% at 60°C for a concentration of 1.0 mg/ml [3]. Meanwhile, graphene-based composites attracts more and more attentions for various applications, such as graphene/alumina nanocomposite for monitoring of microbial cell viability [4], 3D flower-like graphene via alumina doping and incorporating Co as oxygen electrode catalyst [5], nitrogen doped graphene anchored cobalt oxides as oxygen reduction and oxygen revolution reaction catalyse [6], Pd/Al₂O₃ hybrid particles decorated graphene sheets for hydrogen storage[7], alumina-coated Fe₃O₄-reduced graphene oxide composite and SiO₂/Al₂O₃/graphene composite as anode materials for lithium ion battery [8, 9]. The hydrothermal or solvothermal process has been used in a wide range for synthesis graphene-based nanocomposites [5, 8, 9, 10]. Currently, a few papers has been reported about the application of graphene-based composites on nanofluids. Wang et al. prepared water-based nanofluids employing TiO₂/reduced graphene oxide composites, which synthesized through the solvothermal reaction method, and found the excellent stability and high thermal conductivity of the nanofluids [10]. Li et al. Reported the enhancement value of thermal conductivities for SiO₂ decorated graphene dispersed nanofluid [11]. Yu et al. found better stability and thermal conductivity for SnO₂/rGO nanocomposite dispersed Nano fluids, compared to rGO water-based nanofluids[12]. Alumina has excellent heat transfer property and has been used as Al₂O₃/water nanofluid widely [13]. Ahammed et al. studied entropy generation analysis of hybrid nanofluid with
adding alumina nanoparticles and graphene nanosheets Entropy generation analysis of graphene-alumina hybrid nanofluid in multiport minichannel heat exchanger [14]. However, to our knowledge, the water-based nanofluids dispersed with alumina/graphene composite have not been reported till now.

In this work, a novel alumina/graphene composite was synthesized by solvothermal process, and the thermal conductivity properties of water-based nanofluids dispersed by the hybrid nanocomposite with various concentrations were investigated in detail.

2. Experimental method
Alumina / reduced graphene oxide composites were synthesized via a kind of solvothermal reaction method. First a small certain amount of aluminium nitrate (Al(NO3)3·9H2O) was dispersed into absolute ethanol under continuous stirring till fully dissolved. Then graphene oxide aqueous solution with density of 2.5 mg/ml was added slowly in the above solution with stirring for 30 minutes for further mixing. The whole mixture suspension was then transferred into an autoclave at 130°C for 6 h to synthesize alumina / reduced graphene oxide composites. The reacting black products were washed with absolute ethanol and deionized water for several times to remove the by-products from the solvothermal reaction completely, and dried at 70°C for 24 h. Finally, the obtained composite powders were dispersed in deionized water by using ultrasonication and without adding surfactants to form nanofluids. The addition amount of the composites was set as 0.02, 0.04, 0.06, 0.08, and 0.1 wt% respectively.

The crystal phase structures and morphologies of the prepared composite powders were identified using X-ray diffraction analysis (XRD, Rigaku, D/MAX-Ultima IV) and transmission electron microscopy (TEM, JEOL, JEM-2100F). The thermal conductivity (k) of the prepared nanofluids at the temperature between room temperature (24°C)-60°C was measured using thermal constants analyser (Hotdisk TPS 500S), based on the transient hot-wire method (THW) technique. In order to ensure the stability of the liquid temperature, the time interval between the two measurements was set as 30 min. The measuring probe was kept flat and completely immersed into the liquid sample during testing.

3. Results and discussion
XRD patterns of GO and Al2O3/rGO composite samples are shown in Figure 1.

![Figure 1. XRD patterns of GO and Al2O3/rGO composite samples](image)

In the GO XRD pattern, a strong diffraction peak of (001) plane at 9.86° was tested clearly, corresponding to the interplanar spacing of 0.896 nm, and indicating a larger spacing than graphite (0.335 nm). A broad diffraction peak at 25.1° is appeared after solvothermal treatment, which should be contributed to the (002) plane of rGO sheets. It means the successful reduction of GO to rGO. Several small peaks could be indexed to orthorhombic phase of Al2O3 (PDF card no. 88-0107) as well, which
revealing the synthesis of alumina crystal during the solvothermal process. The XRD results show that the obtained products are mixtures of alumina and graphitic carbon.

Figure 2 shows the morphology and crystal structure of Al₂O₃/rGO composite samples. TEM and STEM image exhibit clearly that large amount of particles, ranging from 3 to 8 nm in size, are distributed uniformly on the rGO sheets, as shown in Figure. 2 (a) and 2 (b). High-resolution TEM image of Figure 2 (c) reveals that the nanoparticles is crystalline, having a calculated lattice spacing of 0.206 nm, which is consistent with the (212) plane of orthorhombic alumina. The interlayer spacing of 0.370 nm can be identified to the d-spacing of the (002) basal planes in graphite, demonstrating that the Al₂O₃ nanoparticles are successfully synthesized and decorated on the surface of graphene sheets via the solvothermal process. The high crystallinity of alumina, and is in accordance with XRD results as well. TEM observations reveal that the Al₂O₃ nanoparticles are anchored firmly on the rGO surface at high packing density even after a sonication treatment during preparation of TEM samples. The ultrasmall-sized Al₂O₃ nanoparticles should be advantageous to the heat transfer between nanoparticles and G sheets [14].

The sedimentation photographs of as prepared nanofluids with the Al₂O₃/rGO composite loading of 0.02, 0.04, 0.06, 0.08 and 0.1 wt% before and after quiescence for 25 days are exhibited in Figure 3.

No obvious sedimentation is observed for all nanofluids samples, whereas little agglomeration and sedimentation are found in the samples with higher concentration, especially 0.08 and 0.1 wt%. It indicates that the prepared Al₂O₃/rGO-water nanofluids has relatively good dispersion stability at
lower composite concentration. As from TEM observation, intensive Al₂O₃ nanoparticles are distributed on the rGO surface; it is considered that lower density of the nanoparticles should be beneficial to increase suspension stability.

![Figure 4.](image1.png)

Figure 4. Thermal conductivity properties of the water-based nanofluids vs the prepared composite weight fraction concentrations. (a) Thermal conductivity; (b) Thermal conductivity enhancement

Thermal conductivity measurement results at various temperature show clearly that adding the prepared Al₂O₃/rGO composites in water could improve its heat transfer performance to a certain extent, as shown in Figure 4(a) and 4(b). The thermal conductivity at 50°C is 0.67 W/(mK) for 0.02wt%, and it reaches 0.74 W/(mK) for the sample of 0.08wt% while the water sample without adding graphene composites is 0.64 W/(mK). Measurement results of the nanofluids at 60°C is in the similar way. The thermal conductivity enhancement is about 5% when Al₂O₃/rGO composite concentration is 0.02 wt% and it rise to slightly more than 10% when Al₂O₃/rGO composite concentration reaches to 0.08 wt%. The thermal conductivity of the nanofluids at lower temperatures exhibits a slight improvement. The average value of thermal conductivity enhancement is about 5% and display unregularly changing, though the overall value of thermal conductivity increases along with increasing concentration, as shown in Figure 4(b). It can be seen obviously that the thermal conductivity decrease sharply when the concentration reaches to 0.1 wt% at higher temperature. It is supposed that poorer suspension stability of the nanofluids has a major impact on the decline of their thermal conductivities.

4. Conclusions
In summary, a kind of nanocomposite based on reduced graphene oxide (rGO) nanosheets with alumina (Al₂O₃) nanocrystals depositing on their surface has been synthesized by the solvothermal reaction method. Water-based nanofluids with various nanocomposite concentration have been prepared afterwards. Their thermal conductivity measurement results show clearly that adding the prepared Al₂O₃/rGO composites in water could improve its heat transfer performance to a certain extent at different temperature. The maximum value of thermal conductivity enhancement can reach 15% with Al₂O₃/rGO composite concentration of 0.08 wt% at 50°C. Further studies on improving suspension stability and thermal conductivity of the nanofluids can be explored and developed for its thermal transfer application.

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