Preparation and thermophysical properties of graphene oxide–silver hybrid nanofluids

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Abstract. Ethylene glycol (EG)-based hybrid nanofluids containing graphene oxide–silver nanosheets (GO–Ag) were simply prepared without using any surfactant. The graphene oxide–silver composites were characterized using X-ray diffraction analysis, transmission electron microscope, infrared and UV–visible spectroscopy. The stability of GO–Ag nanofluids was estimated by UV–visible spectroscopy. The GO–Ag/EG hybrid nanofluids has good stability without significant sedimentation for 60 days. A few thermophysical properties of GO–Ag/EG nanofluids with 0.1, 0.2 and 0.3 wt% nanosheets were analysed experimentally at different temperatures ranging from 20 to 50°C.

Keywords. Graphene oxide–silver; hybrid nanofluids; thermal conductivity.

1. Introduction

Nanofluid is a multiphase system with stably suspended nanoparticles and a base fluid, which can be used to improve heat transfer. Metal nanoparticles, metal oxide nanoparticles, carbon-based particles are all used as additives of nanofluids [1–3]. Carbon nanotubes (CNTs), graphene nanoplatelets and graphene oxide (GO) nanosheets have excellent thermal conductivity, and make them advantageous candidates for preparing normal and hybrid nanofluids [4–6].

The nanofluids containing graphene exhibit good thermal conductivity and heat transfer coefficient. Graphene is expected to be a good additive of nanofluids. The layered structure of graphene makes it have specific surface area and unique electronic migration performance [7]. It can be used as a good carrier. Metal oxides, metals, conductive polymers or surfactants can be used to modify graphene [8–12]. Graphene or GO hybrid composites are prepared by assembling carrier and metal nanoparticles to exhibit excellent properties. Currently, many researchers have been focused on graphene and metal nanoparticles (Ag, Au and Pt) hybrid materials to prepare nanofluids [8,12–14]. The new hybrid nanofluids with graphene or GO hybrid materials have shown potential applications in the areas of heat transport [9,11,15], catalysis [16] and sensors [17,18]. Aravind and Ramaprabhu [19] studied the stability of nanofluids composed of graphene-coated multi-walled CNTs by UV–visible spectrophotometry. Munkhbayar *et al* [20] evaluated the stability of Ag/CNTs hybrid nanofluids by UV–visible spectrophotometry. Yarmand *et al* [21] determined the stability of functionalized graphene/Pt hybrid

nanofluids with different mass fractions by UV–visible spectrophotometry. Suresh *et al* [22] examined the stability of Al_2O_3/Cu–water hybrid nanofluids by zeta potential measurements. Chang *et al* [23] measured the stability of Ag/Fe nanofluids by zeta potential method. Hossein *et al* [24] used three dispersants containing polyacrylic acid group to stable Fe_2O_3–CNT nanoparticles in the base fluid and measured the zeta potential to evaluate the stability of water-based Fe_2O_3/CNT hybrid nanofluids.

Graphene tends to form agglomerates because of its surface properties in the processing of preparing and has a poor dispersion stability in water, ethylene glycol (EG) or oil. The performance of graphene with high thermal conductivity in nanofluid system was limited. Graphene can be chemically modified with hydroxyl, carboxyl and epoxy groups. And these functional groups attach to the edges of graphene, which formed GOs. GO has high dispersibility in water and EG. Nanofluids formed by GO suspended in the base fluids can improve the thermal conductivity of conventional fluids [25]. GO decorated with metal nanoparticles is used to prepare hybrid nanofluid. Both GO and metal nanoparticles are effective for heat transfer enhancement in the nanofluids. In this study, the Ag nanoparticles modified by oleic acids are highly monodispersed on GO sheets. The EG-based GO–Ag nanofluids were made by dispersing the GO–Ag hybrid nanomaterials in EG. The viscosity and thermal conductivity of GO–Ag/EG hybrid nanofluids were measured. Silver nanoparticles dispersed uniformly on the surface and edge of GO sheets can enhance the thermal conductivity of base fluids. The study of the hybrid

nanofluid is beneficial for the applications in the fields of thermal transfer and management.

2.   Experimental

2.1   *Materials*

Natural graphite flake was supplied by Alfa Aesar. $AgNO_3$ (99%), potassium permanganate (99%), concentrated sulphuric acid (36.5%), phosphoric acid ($\geq$85.0%), hydrogen peroxide (30%), absolute ethanol and toluene were all supplied by Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran ($\geq$99.5%), oleic acid ($\geq$99%) and EG ($\geq$99%) were supplied by Aladdin. All reagents were used without further purification.

2.2   *Synthesis of graphene oxide–silver composites*

The GO was prepared through oxidizing natural graphite flake and carried out using simplified Hummers' method [21], Briefly, 1.5 g graphite flakes were mixed with the blends of H_2SO_4 and H_3PO_4 (180 ml:20 ml) using a magnetic stirrer. After adding $KMnO_4$ (9 g), the mixture was left for stirring at 50°C for 6 h. Later, an H_2O_2 solution was added to the mixture, which made the colour of the mixture change to bright yellow. The graphite oxide formed was separated by centrifugation at 10000 rpm and washed with deionized water until a pH of 6–7. The obtained GO was dried in a vacuum oven at 70°C for 24 h. Silver nanoparticles capped with oleic acid were synthesized by reducing $AgNO_3$ with ascorbic acid solution at 100°C [26]. A quantity of 15 mg GO was added into deionized water and sonicated with 400 W powder for 0.5 h. The oleic acid-capped Ag nanoparticles (60 mg) were dispersed in a heptane/dichloromethane mixture (50 ml) and then added into the suspension of GO. The above mixture of nano Ag and the suspension of GO was kept stirring at 25°C for 10 h. The GO–Ag composites were prepared and purified using tetrahydrofuran. Then the GO–Ag composites were centrifuged at 10000 rpm for 10 min and dried.

2.3   *Preparation of nanofluids*

The GO–Ag hybrid nanosheets were weighted accurately and added to 30 g EG as base fluid, to prepare EG-based GO/Ag nanofluid with various mass fractions (0.1, 0.2, 0.3 wt%). The suspensions were sonicated for 20 min.

2.4   *Characterization of nanofluids*

X-ray diffraction patterns (XRD) of GO/Ag were obtained by a D8 Advance powder X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) of GO/Ag was measured by an ESCALAB 250XI multifunctional imaging electron spectrometer. IR spectra were reported with a Nicolet 5700 FT-IR spectrometer. Transmission electron microscope images (TEM) were obtained from a JEM-2100 transmission electron microscopy. The UV–visible absorption spectra of the hybrid nanofluids were determined with a UV-1700 spectrophotometer.

2.5   *Measurement of thermophysical properties*

The viscosities of the nanofluids were determined by a viscometer (DV2T, Brookfield Engineering Labs, USA). A refrigerated bath circulator (Julabo, 200F) was used to keep the samples at the desired temperature during measurements. The thermal conductivity of the nanofluids was determined using a KD2 Pro thermal properties analyzer.

3.   Results and discussion

3.1   *Material characterization*

The oleic acid-capped Ag nanoparticles were hydrophobic and well dispersed in nonpolar organic solvents. The GO sheets act as a good carrier for the Ag nanoparticles. The Ag nanoparticles were dispersed well on the GO sheets [27]. The GO sheets are also a stabilizer, which can avoid Ag nanoparticle aggregation. The TEM pictures of GO sheets, Ag nanoparticles and GO–Ag hybrid nanosheets are shown in figure 1. The TEM image of GO clearly shows that the transparent sheets are flake-like. The oleic acid-capped Ag nanoparticles (4–7 nm) are highly stable and homogeneous dispersions. The Ag nanoparticles have excellent compatibility in non-polar solvents because of the surface capping. GO–Ag hybrid nanosheets were prepared by heptane/dichloromethane and water two-phase method. The mixture reaction lasted 12 h to ensure that the Ag nanoparticles were well assembled on GO sheets on the two-phase interface. It was shown that the Ag nanoparticles bound and monodispersed well on GO nanosheets without aggregation (figure 1c). Silver nanoparticles can bind to GO through electrostatic binding, physical adsorption [13,27]. GO as a good stabilizer and support of Ag nanoparticles can avoid agglomeration of Ag nanoparticles. The GO–Ag hybrid nanosheets are hydrophilic and can well disperse in water or EG because of a large number of carboxyl and hydroxyl groups on the surface of GO sheets.

The XRD patterns of GO and GO–Ag hybrid nanosheets and the XPS spectrum of GO–Ag are shown in figure 2. As shown in figure 2A, the diffraction peak of GO appears around 10°. Comparison with the peaks of GO, the peaks of GO–Ag hybrid nanocomposites have both the
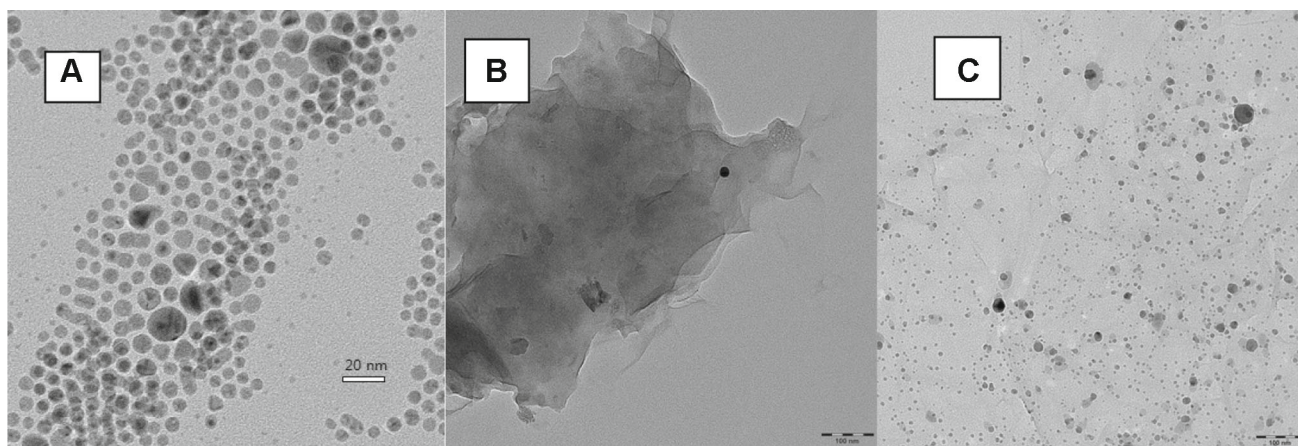
Figure 1. TEM images: (**A**) oleic acid-capped Ag nanoparticles; (**B**) GO and (**C**) GO–Ag hybrid nanosheets.
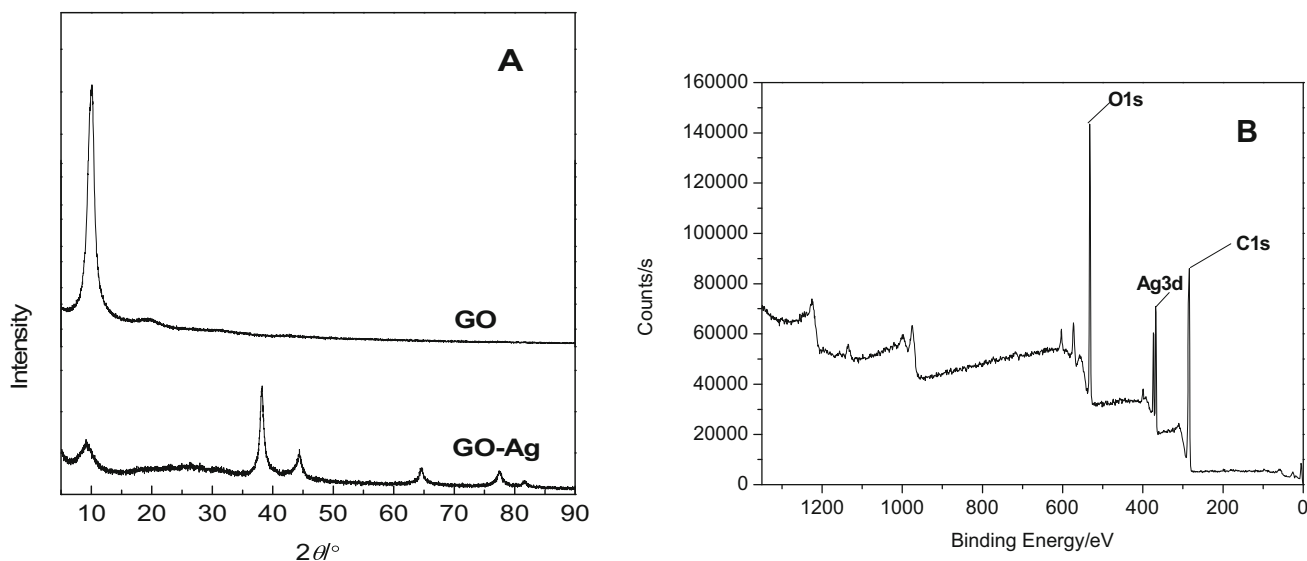

Figure 2. (**A**) XRD patterns and (**B**) XPS spectra of GO–Ag hybrid nanosheets.

peaks of graphite oxide and the face-centred cubic silver crystals (38.1°, 44. 1°, 64.4° and 77.3°). It shows the major element peaks of Ag 3d, C 1s and O 1s in figure 2B. According to the analysed results of XPS, the mass fraction of Ag nanoparticles in GO–Ag composites is 14.66%. The XRD and XPS results show that the Ag nanoparticles have deposited on the surfaces of GO nanosheets successfully.

The infrared spectra of GO sheets, oleic acid-capped Ag nanoparticles and GO–Ag hybrid nanosheets are shown in figure 3. The absorption peaks at 2918 and 2850 cm^{-1} and the absorption band at 1470 cm^{-1} are corresponded to the stretching vibrations and deformation vibration of CH$_2$ groups, respectively. The absorption at 1710 cm^{-1}

corresponds to the characteristic band of C=O. The absorption at 3000–3700 cm^{-1} represents the characteristic band of O–H. The absorption peaks at 1401 and 1148 cm^{-1} are the deformation vibration of O–H and the expansion vibration of C–OH. The peak at 1003 cm^{-1} characterized the expansion vibration of C–O. It shows that the surfaces of GO and GO–Ag composites contain a large number of oxygen-containing functional groups and the Ag nanoparticles have deposited on the surfaces of GO nanosheets.

The UV–visible absorption spectra of GO nanofluid, Ag nanoparticles colloid and GO–Ag nanofluid are shown in figure 4. The UV–visible absorption of Ag nanoparticles colloid gave characteristic absorptions with the maximum at 418 nm. The spectrum of GO suspension exhibits a
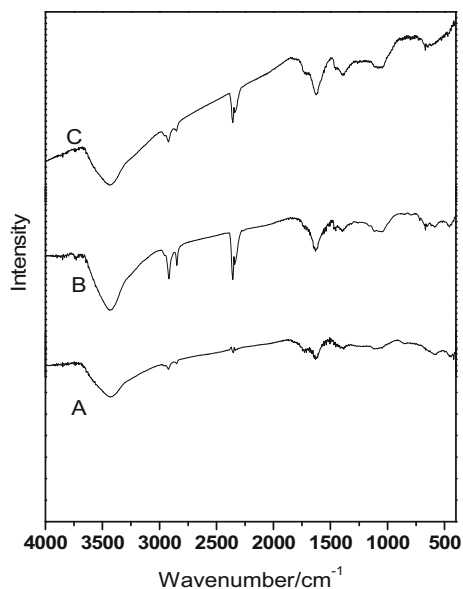
Figure 3. Infrared spectra: (**A**) GO; (**B**) oleic acid-capped Ag nanoparticles and (**C**) GO–Ag hybrid nanosheets.
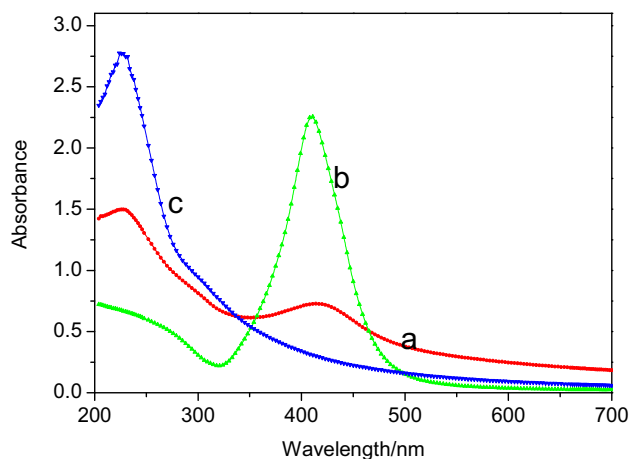

Figure 4. UV–visible absorption spectra of (**a**) GO–Ag, (**b**) oleic acid-capped Ag nanoparticles and (**c**) GO.

maximum at 226 nm. The spectrum of GO–Ag nanofluid exhibits two absorption peaks at 226 and 419 nm (line (a) in figure 4).

3.2 *Stability of hybrid nanofluids*

The stability of EG-based GO–Ag nanofluids was investigated with ultraviolet–visible spectra analysis. The EG-based GO–Ag nanofluids with different mass fraction were diluted with EG at a ratio of 1:4 and determined by UV–visible spectrophotometer. The UV–visible spectra of the EG-based GO–Ag nanofluids for different weight concentrations are presented in figure 5. It shows that the peak
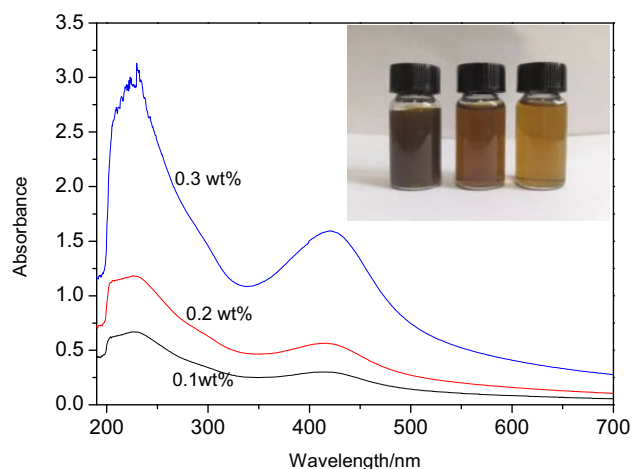

Figure 5. UV–visible absorbance spectrum for diluted EG-based GO–Ag nanofluids with different mass fraction at a ratio of 1:4.

value of absorbance for all samples lies in the range of wavelengths of 220–230 nm and 410–420 nm due to the presence of GO–Ag nanocomposites. The absorbance of the nanofluid with 0.1 wt% GO–Ag was measured at different time intervals for more than 60 days, as shown in figure 6. The stability of EG-based GO–Ag nanofluids is good.

3.3 *Thermophysical properties of EG-based GO–Ag nanofluid*

The viscosity and thermal conductivity of the EG-based GO–Ag nanofluid were determined for different mass fractions at temperatures from 20 to 50°C, respectively. Figure 7 shows viscosity of GO–Ag hybrid nanofluids with EG as base solution at temperatures from 20 to 50°C. The data show that the viscosity decreases with the increase in temperature, which is due to the decrease in the adhesion force between molecules and particles, resulting in the decrease of the viscosity with the increase in temperature. The viscosity of GO–Ag composite nanofluids does not increase significantly compared with that of EG. With the increase of temperature, the difference between the viscosity of GO–Ag nanofluids and that of liquid EG becomes less.

The thermal conductivity of EG-based nanofluids containing 0.1, 0.2 and 0.3 wt% mass fraction GO–Ag composites were measured at temperatures from 20 to 50°C. Figure 8 shows the thermal conductivity ratio (k_{nf}/k_{bf}) of EG-based GO–Ag nanofluids. There was no significant change for the thermal conductivity of the nanofluids compared with the thermal conductivity of the base fluid (EG) at relatively low temperatures of nanofluids (20 and 25°C). The thermal conductivity ratio of GO–Ag nanofluids obviously increases with the increase in temperature, which is due to Brownian motion of the suspended GO–Ag. The maximum enhancement of thermal conductivity is approximately 22% for the EG-based GO–Ag nanofluid with mass fraction of 0.3 wt% at 45°C.
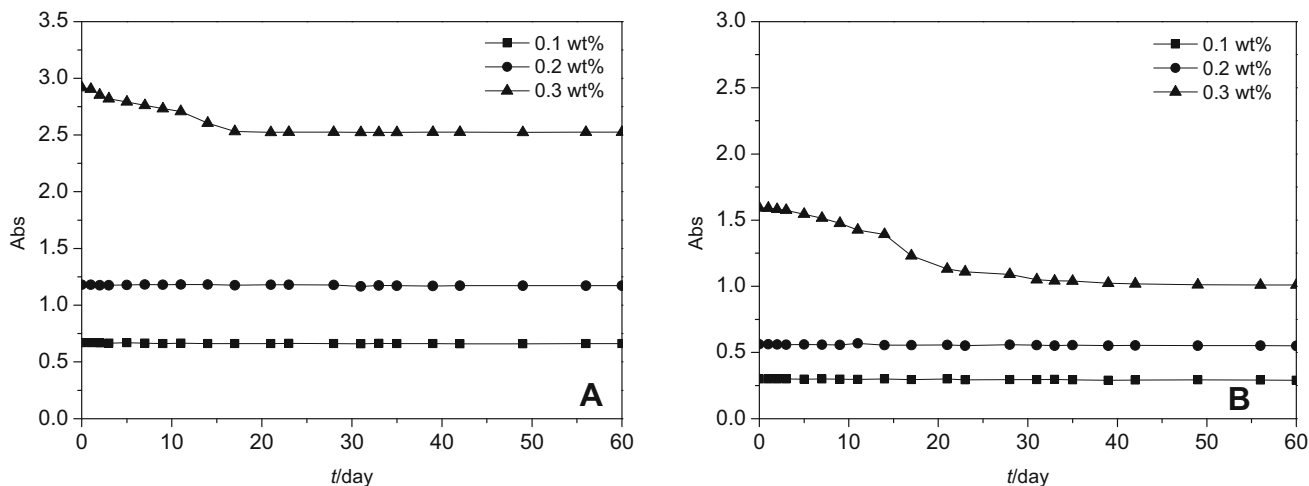
Figure 6. Absorbance of GO/Ag–EG nanofluids for 60 days: (**A**) λ = 226 and (**B**) λ = 419 nm
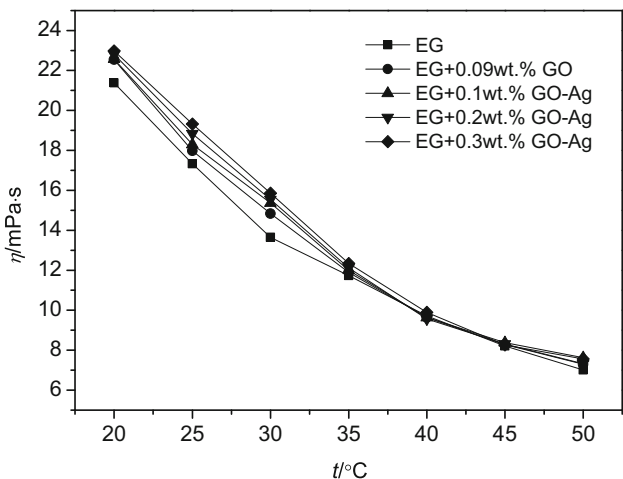

Figure 7. Viscosity of EG-based nanofluids with different mass fraction.
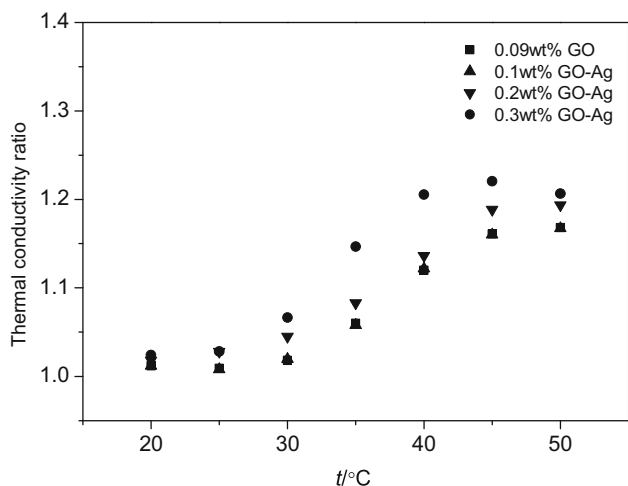

Figure 8. Thermal conductivity ratio of EG-based nanofluids with different mass fraction.

4. Conclusions

EG-based hybrid nanofluids containing graphene oxide–silver nanosheets were prepared without using any surfactant. The EG-based GO–Ag hybrid nanofluids can keep stable and no sedimentation for 60 days. Viscosity properties and thermal conductivity of the GO–Ag nanofluids were measured for different mass fraction. The viscosity of GO–Ag nanofluids increases with increase in mass fraction of GO–Ag and decreases with increase in temperature. The thermal conductivity of GO–Ag nanofluids increases obviously, especially when the temperature exceed 30°C. The maximum enhancement of the thermal conductivity of the nanofluid with mass fraction of 0.3 wt% is approximately 22% at 45°C.

Acknowledgement

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