Synthesis and characterization of thermal conductivity of nanofluids based on Ag decorated-CNTs/graphene hybrid materials

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Abstract:

In this work, we present a new nanofluid based on silver nanoparticles decorated on the functionalized carbon nanotubes-graphene sheet (hybrid) materials. Briefly, carbon nanotubes and graphene sheets were first functionalized with a hydroxyl group and carboxyl group respectively. The hybrid material was decorated with silver nanoparticles via chemical reduction method with the assistance of sodium hydroxyl. Finally, the obtained Ag-hybrid material was dispersed in ethylene glycol solution (EG) to form the nanofluid without any surfactant. The thermal conductivity of nanofluid was measured for different weight concentrations at different temperatures. The results showed an increase in thermal conductivity of up to 86% for 0.045% weight concentration at 55°C. This enhancement was due to the high thermal conductivity of graphene, carbon nanotubes (CNTs), and Ag nanoparticles as well as the higher surface area of Ag nanoparticles decorated on graphene and CNTs structures. The results of Transmission Electron Microscope (TEM), X-rays diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) indicated that the silver nanoparticles were formed on the surface of carbon nanotubes and graphene sheets.

Keywords: ***CNTs, graphene, nanofluids, silver nanoparticles, thermal conductivity.***

Classification numbers: ***5.1, 5.5***

Introduction

For a decade, the development of nanotechnology has not only minimized the size but also improved the working speed of electronic devices. A serious problem in electronic devices is heat generation during the process of working at high power, leading to a decrease in their performance and lifetime. In order to solve this problem, there are several methods for heat dissipation, i.e. utilization of fans, thermal grease or fluids. Most of the electronic devices use fluids for heat dissipation such as distilled water or ethylene glycol. However, these basic fluids have poor thermal conductivity, resulting in the lower efficiency of heat transfer. Therefore, it is enormously important to increase the heat transfer capability of fluids. One of the most promising methods is the addition of solid particles with high thermal conductivity which acts as heat carriers for fluids.

In 1873, Maxwell was the first person who proposed the idea of adding solid particles into fluids to enhance their thermal conductivity [1]. Subsequently, researchers dispersed microparticles into fluids to increase the thermal conductivity of the fluids. Nevertheless, the added microparticles would aggregate and settle down [2]. To address this negative aspect, a great deal of research was carried out by dispersing nanoparticles into fluids.

In 1995, the term "nanofluid" was introduced the first time by S. Choi and J.A. Eastman at Argonne National laboratory [3]. Generally, nanofluid is the fluid having stable suspension of nanomaterials such as nanoparticles, nanofibers, nanorods, nanotubes, nanowires, and nanosheets, which are typically less than 100 nm in size. There are two phases in the system, one phase is a liquid phase and the other one is a solid phase. The nanoparticles used in nanofluids are metals, oxides, carbides, and diamond [4-7].

CNTs and graphene are the materials owning very high thermal conductivity

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(about 3000 W/m.K for CNTs and 5000 W/m.K for graphene) [8-9]. It is reported that by using graphene and CNTs as additives in nanofluids, the thermal conductivity went up significantly. CNTs and graphene are considered as bridges or networks for making heat transfer faster. Rad Sadri, et al. showed that the thermal conductivity rose up to 22.31% for nanofluids containing 0.5wt% of CNTs. This result was obtained after 40 minutes of ultrasonication at 45^{0}C [10]. Zeinab Hajjar, et al. revealed that increasing thermal conductivity depends on the concentration of graphene oxide (GO) dispersing in nanofluids. For example, the thermal conductivity enhancement was 14.75% with 0.05wt % of GO, the thermal conductivity increased by 47.57% with 0.25wt% of GO at 40^{0}C [11]. Mehrauli et al. studied graphene nanofluids with different concentrations of graphene, specifically 0.025, 0.05, 0.075, and 0.1wt%. The result displayed that the maximum thermal conductivity enhanced 27.64% with 0.1wt% of graphene dispersing in nanofluids [12]. Several studies also focused on using metallic or non-metallic nanoparticles decorated on graphene and CNTs to enhance heat transfer capability of nanofluids. For an instant, Baby, et al. studied nanofluids containing copper oxide nanoparticles decorated on graphene. The results depicted that the enhancement in thermal conductivity was approximately 28% with 0.05% volume fraction of CuO-graphene dispersing in DI water-based nanofluids at 25^{0}C and thermal conductivity enhancement was 23% with 0.07% volume fraction in EG-based nanofluids at 50^{0}C [13]. This author group also studied the decoration of silver nanoparticles on graphene and the reported thermal conductivity enhancement was 14% with 0.07% volume fraction of Ag-graphene dispersing in EG-based nanofluids at 70^{0}C [14]. H. Yarmand et al. also showed that the increase in thermal conductivity was 22.22% with 0.1wt% of Ag-graphene at 40^{0}C [15]. Amiri et al. reported an enhancement of thermal conductivity of 25% with 1wt% of Ag-CNTs dispersing in nanofluids. S.S. Aravind, et al. examined nanofluids containing graphene-multiwall carbon nanotubes (graphene-MWCNTs) nanocomposite based on DI water and EG. The results showed that the thermal conductivity enhancement was 10.5% and 87.9% with 0.04% volume fraction of graphene-MWCNTs at 25^{0}C and 50^{0}C in DI water, respectively. Whereas in EG, thermal conductivity enhancement was 13.7% and 24% at 25^{0}C and 50^{0}C, respectively [16]. Recently, T.T. Baby, et al. studied nanofluids containing silver nanoparticles decorated on graphene-MWCNTs based on EG. The results showed that the enhancement of thermal conductivity was 8% and 20% with 0.04% volume fraction of Ag/graphene-MWCNTs at 25^{0}C and 50^{0}C, respectively [17]. The presence of metallic or non-metallic nanoparticles supposed to avoid the stacking of graphene sheets and CNTs [18].

In this study, we present the results of synthesis and thermal conductivity characterization of nanofluids based on EG containing Ag nanoparticles decorated on functional groups of graphene and CNTs by chemical reaction method with different weight concentrations. The Ag-hybrid materials were synthesized by a simple method and performed the enhancement of high thermal conductivity of nanofluids.

Experiment and methods

Materials

CNTs were supported by Laboratory of Carbon Nanomaterials, Institute of Material Science, Vietnam Academy of Science and Technology (VAST). Graphite rod (99.99%) was purchased from Aladdin Bio-Chem Technology Company to be used as an electrode to synthesize graphene sheets. Potassium hydroxide (KOH), ammonia sulfate $(NH_4)_2SO_4$, sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 68%), thionyl chloride ($SOCl_2$), tetrahydrofuran (THF), ethylene glycol (EG), and sodium hydroxide (NaOH) were purchased from Shantou Xilong Chemical Factory Guangdong, China. Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were purchased from Shanghai Aladdin Bio-Chem Technology Co. LTD, China.

Nanofluid preparation

Schematic of the synthesis of Ag nanoparticles decorated on the hybrid material is shown in Fig. 1. Graphene sheets synthesized by a plasma-assisted electrochemical exfoliation process [19] were functionalized with carboxyl (-COOH) group by treatment in the mixture of acid (HNO_3: H_2SO_4, ratio 1:3 respectively) at 70^{0}C for 5 hours under continuous magnetic stirring, then filtered by distilled water and dispersed in EG. CNTs were functionalized with hydroxyl (-OH) group by treatment with $SOCl_2$ at 60^{0}C for 24 hours under continuous magnetic stirring then filtered by distilled water and washed with tetrahydrofuran. After that, they went through a treatment with EG at 120^{o}C for 48 hours under continuous magnetic stirring and dispersed in EG. CNTs-graphene material was dispersed in EG by ultrasonication for 10 minutes. A specific amount of $AgNO_3$ (0.05 M) solution was added to the above solution, under continuous stirring. After 30 minutes, 20 ml of reducing solution (a mixture of $NaBH_4$ and NaOH) was added to the above solution dropwise. The reaction was as follows:

$$AgNO_3 + NaBH_4 \rightarrow Ag + \frac{1}{2}H_2 + \frac{1}{2}B_2H_6 + NaNO_3$$

After the reducing process completes, the solution was filtered and washed with distilled water. A calculated amount of Ag-hybrid material was dispersed in EG to generate nanofluid by ultrasonication.

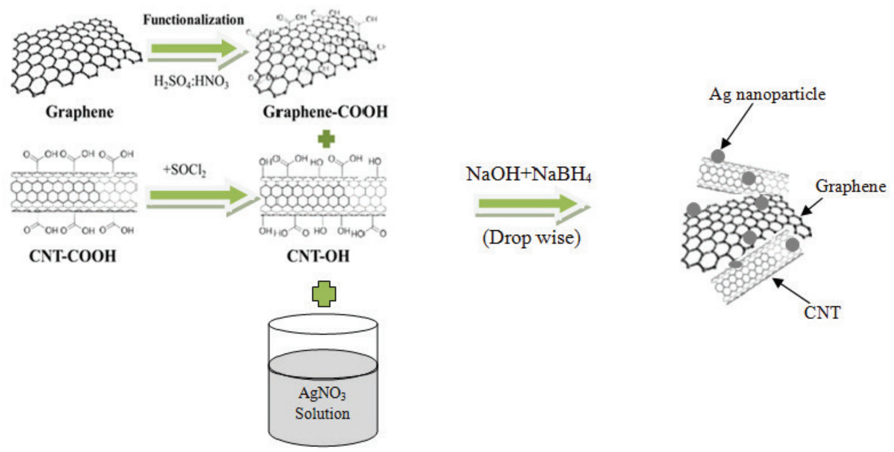

Fig. 1. Schematic of the synthesis of Ag nanoparticles decorated on the hybrid material.

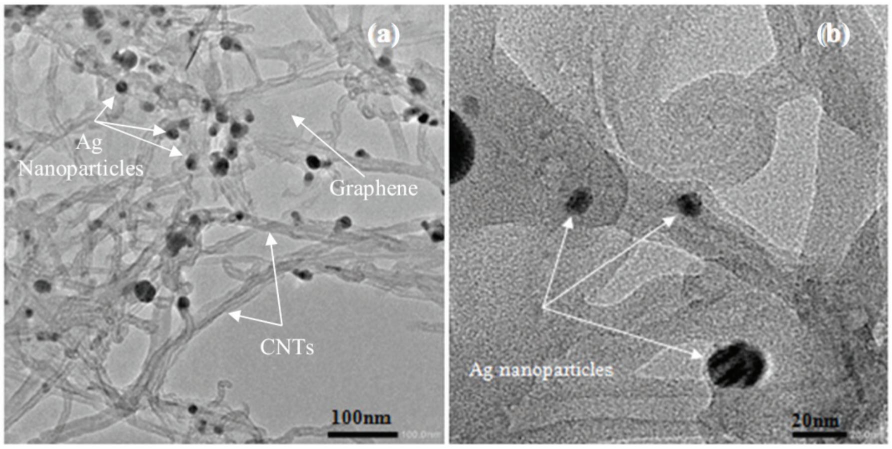

Fig. 2. Transmission electron microscopy (TEM) images of Ag-hybrid materials.

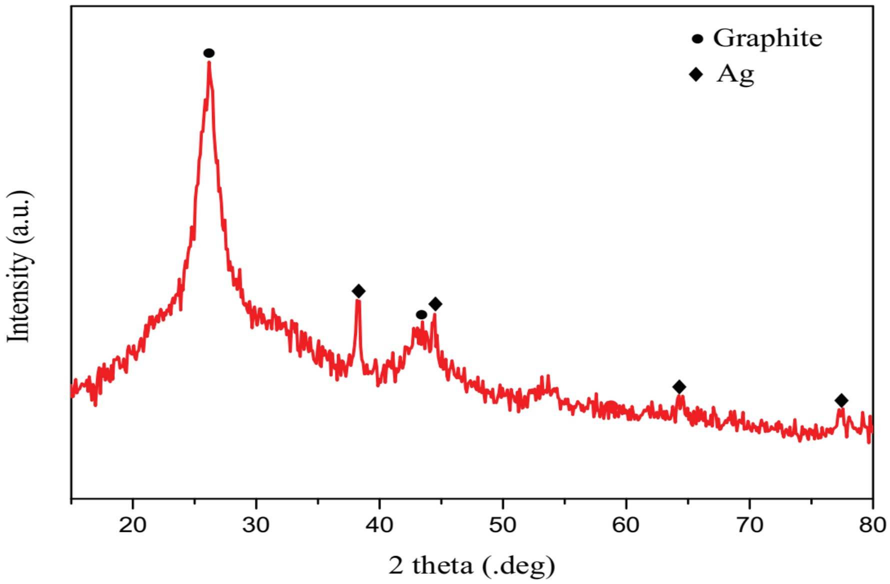

Fig. 3. X-ray diffraction pattern of Ag- hybrid material.

Characterization

The morphology of the samples was characterized by field emission scanning electron microscopy (FESEM, Hitachi S4800) and transmission electron microscopy (TEM, JOEL JEM 2100 microscope). XRD pattern was recorded by an XRD Bruker D8 Endeavor equipped with Cu (Kα) radiation in a 2θ range of 10° to 90° with a step size of 0.01. The thermal conductivity (K) of the nanofluids was measured by using an HTL-04 thermal conductivity of liquid (Eee, India) in the range from 30° to 60°C. The apparatus for measuring the thermal conductivity of the liquid is designed and developed according to the principle of guarded hot plate method. Detail of measurement method was presented in our previous studies [20, 21].

Results and discussions

The surface morphology of the samples was characterized by TEM images at low and high magnifications as shown in Fig. 2. The distribution of Ag nanoparticles on CNTs and graphene sheets is visible in TEM images. The surface morphology shows that silver nanoparticles were decorated properly on functional groups of graphene sheets and CNTs. The size of silver nanoparticles was estimated from the TEM images and it was smaller than 20 nm.

Figure 3 illustrates the X-ray diffraction (XRD) pattern of Ag-hybrid materials. XRD pattern was recorded by an XRD Bruker D8 Endeavor equipped with Cu (Kα) radiation in a 2θ range of 10° to 90° with a step size of 0.01. XRD was performed to study the formation of crystallinity and investigate phase compositions of the samples. The result shows some representative peaks of graphite at 2θ = 26.2°, 42°, and 53.6° corresponding to (002), (101), and (004) planes of graphite, respectively. Peaks around 38.2°, 44.3°, 64.2°, and 77.5° are responsible for (111), (200), (220), and (311) planes structure of

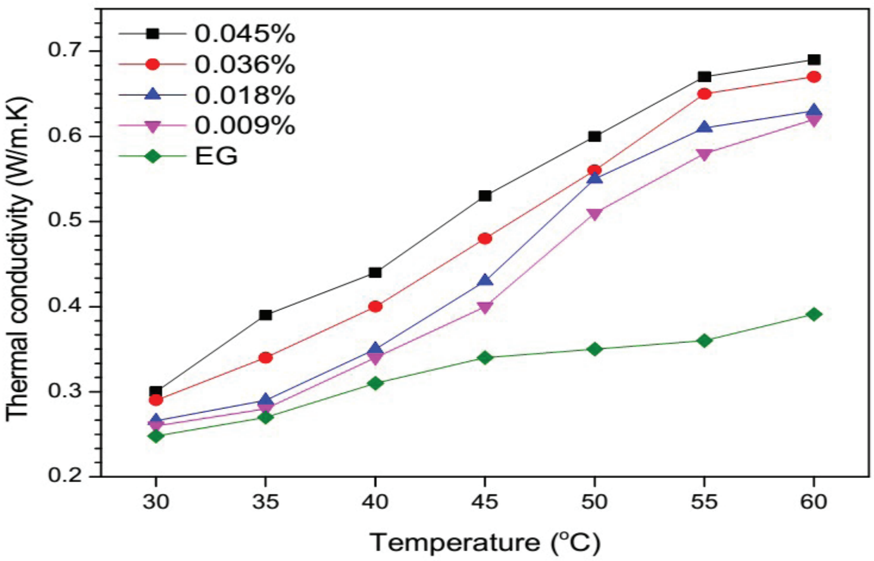

Fig. 4. Thermal conductivity of nanofluids containing EG and Ag-hybrid material at different temperature for different weight concentrations.

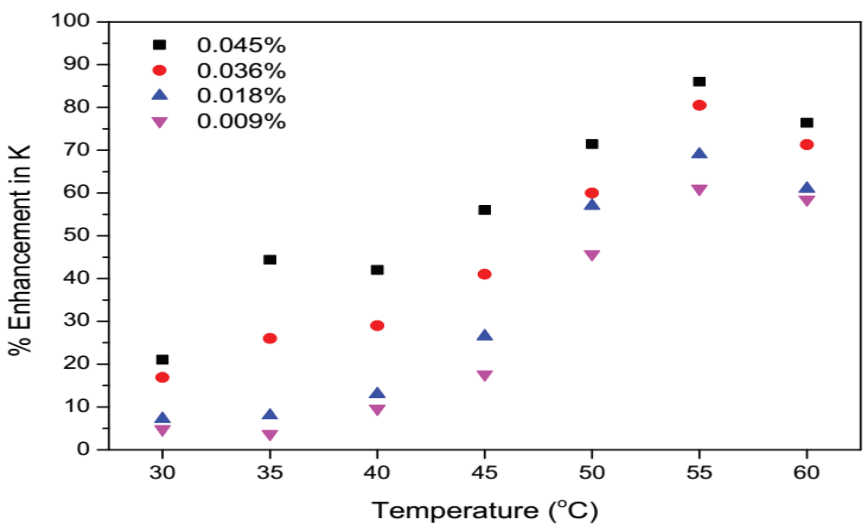

Fig. 5. Thermal conductivity enhancements of nanofluids with different weight concentrations at different temperatures.

Table 1. Summary of experimental results on thermal conductivity of EG based nanofluids.

Ref.	Material type	Material concentration	Temperature	Enhancement
This work	Ag-CNTs/graphene hybrid material	0.009-0.045wt%	30 – 60°C	21-86%
[14]	Ag decorated graphene	0.005-0.07wt%	25-70°C	6-14%
[16]	CNTs-graphene	0.04vol%	25-50°C	13.7-24%
[17]	Ag decorated MWNT-HEG hybrid	0.005-0.04vol%	25-50°C	8-20%
[25]	Graphene oxide nanofluids	2-5wt%	10-60°C	Up to 86%

Ag nanoparticles, respectively. The average size of Ag nanoparticles is approximately 7 nm, which has been calculated with Scherer's formula corresponding to the representative peak of Ag at 38.2°. From both morphology and XRD studies, it is proven that Ag nanoparticles were grown successfully on CNTs and graphene hybrid materials by the chemical reduction method.

The thermal conductivity of the nanofluids was measured for different weight concentrations at different temperatures as showed in Fig. 4. In general, the thermal conductivity of the nanofluids increased together with an increase in the weight concentration or temperature. The enhancement in thermal conductivity is quantified by the following formula:

$$\%K = [(K-K_o) \times 100] / K_o$$

where: K_o is the thermal conductivity of the base fluid and K is that of the nanofluids.

Figure 5 shows the percentage of thermal conductivity enhancement of nanofluids containing different weight concentrations of Ag-hybrid material at different temperatures. The result shows that the enhancement percentage in thermal conductivity of 0.009wt% Ag-hybrid material at 30°C is ~5% and around 58.5% at 60°C. Whereas, the nanofluids containing 0.045wt% show an enhancement of 21% at 30°C and around 76.4% at 60°C. Especially, the percentage enhancement in thermal conductivity experiences a high rate of 86% at 55°C before decreasing. This could be due to the formation of clusters at high temperatures. The thermal conductivity enhancement is mainly due to the Brownian motion of nanoparticles. According to the theory of Brownian motion, the smaller size of nanoparticles, the faster Brownian motion and the higher temperature, the faster Brownian motion, consequently, heat transfer inside nanofluids is faster [22-24]. However, the formation of clusters at high temperatures prevents the Brownian motion, causing a decrease in the enhancement percentage of thermal conductivity at high temperatures (Table 1).

The enhancement is due to the high thermal conductivity of graphene, CNTs, and Ag nanoparticles as well as the higher surface area of Ag nanoparticles decorated on graphene and CNTs structures.

Conclusions

The nanofluid containing Ag nanoparticles decorated on CNTs-graphene is synthesized successfully by chemical reduction method. The average size of Ag nanoparticles is smaller than 20 nm. The nanofluid containing 0.045wt% of Ag-hybrid material shows the best performance with the thermal conductivity increase of 21% at 30^{o}C and 86% at 55^{o}C. Experimental results of the thermal conductivity strongly confirm that EG containing Ag-hybrid can be used for heat transfer applications.

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