Communications in Physics, Vol. 26, No. 4 (2016), pp. 351-360
DOI:10.15625/0868-3166/26/4/8705

THERMAL CONDUCTIVITY OF ETHYLENE GLYCOL BASED COPPER NANOPARTICLE DECORATED GRAPHENE NANOFLUIDS

PHAM VAN TRINH[1,†], NGUYEN NGOC ANH[1], LE DINH QUANG [1], BUI HUNG THANG[1], PHAN NGOC HONG[1,3], NGUYEN TUAN HONG[2], PHAN HONG KHOI[2] AND PHAN NGOC MINH[1,2,3]

[1]*Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Str., Cau Giay Distr., Hanoi, Vietnam*

[2]*Center for High Technology Development, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Str., Cau Giay Distr., Hanoi, Vietnam*

[3]*Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Str., Cau Giay Distr., Hanoi, Vietnam*

[†]*E-mail:* trinhpv@ims.vast.vn

Received 25 July 2016
Accepted for publication 26 December 2016

Abstract. *In this paper, thermal conductivity of ethylene glycol based copper nanoparticle decorated graphene (Cu/Gr) nanofluids are successfully synthesized by a chemical reduction technique using ascorbic acid antioxidant agent. Nano-sized copper nanoparticles are decorated on functionalized graphene, and then dispersed uniformly in ethylene glycol (EG) to make the nanofluids. Morphology, phase composition and thermal conductivity of nanofluids are investigated in detail. Thermal conductivity of the nanofluid containing Cu/Gr with mass ratio of 5:1 shows an enhancement about 10% and 29% at 30°C and 60°C comparing with the EG fluid only. The results show the high potential application of Cu/Gr nanofluids in heat transfer fields.*

Keywords: graphene, copper decorated graphene, nanofluid, thermal conductivity.

Classification numbers: 81.05.ue, 81.70.Pg, 44.90.+c.

I. INTRODUCTION

The modern electronic systems integrated of numerous nano-sized components generate a huge amount of heat once operating, which deteriorates the performance of the devices and decreases their reliability by time. Thus, heat transfer for working electronic devices is one of the most important issues, which had been receiving a great attention of scientists, engineers and manufacturers etc. Among many proposed solutions, the heat transfer fluids are shown great promising due to both cost-effectiveness and great performance [1]. However, conventional fluids such as water, ethylene glycol (EG), oil, etc, have not shown sufficient capability for heat transfer applications due to their poor thermal performance. Several reports are demonstrated that the thermal performance of conventional fluids could be enhanced by adding solid particles [2,3]. Recently, a new class of heat transfer fluids have been investigated and developed by adding intro the fluids nanosize materials such as Ag, Cu, Ni Al_2O_3, Fe_3O_4, CuO, TiO_2 [4,5]. Since the discovery of carbonaceous materials such as carbon nanotube (CNT), graphene, graphene oxide (GO) with very high thermal conductivity [6], several hundred studies concerning to carbonaceous materials based nanofluids (NFs) have been conducted and presented. It demonstrated that a significant thermal conductivity enhancement of nanofluids is obtained both in theoretical and in experimental studies [7–9]. Thang *et al.* proposed a modified model for predicting the thermal conductivity of CNT-nanofluids, which matched correctly the enhancement observed in experimental data [10]. In an experimental study on CNT-nanofluids, Halelfadl and coworkers also showed the enhancement in density, thermal conductivity and viscosity of the water-based nanofluids containing 0.0055% to 0.278 vol.% CNT [11]. Zubir *et al.* reported that the thermal conductivity enhancement of 27% with nanofluid containg 0.05 wt.% [12]. Ghozatloo *et al.* studied on a functionalized graphene-nanofluid with different concentrations from 0.01 to 0.05 wt%, the enhancement of thermal conductivity increases from 3.8 to 17% [13]. Similarly, Ma *et al* also reported that the enhancement is up to 18.9% with silicon based fluid containing 0.007 wt.% functionalized graphene [14]. The enhancement of thermal conductivity of nanofluids containing graphene is higher than the one of the metal-nanofluids due to the high thermal conductivity of graphene as reported by Sen Gupta and coworkers [15]. Recently, several studies are also focused on using the graphene decorated metal or ceramic particles for heat transfer nanofluid. For example, Li *et al.* reported that the enhancement up to 20% could be obtained with SiO_2-decorated graphene based EG nanofluid [16]. Baby and Sundara studied on using silver nanoparticles and copper oxide decorated graphene for EG based nanofluids and showed a thermal conductivity enhancement up to 14% and 23%, respectively [17, 18]. The presence of metallic nanoparticles is able to avoid the stacking of graphene sheets, increases the overall surface area and thus leads to enhance the heat transfer performance of the nanofluids [19].

In this study, we present the results on fabrication of thermal conductivity of ethylene glycol based Cu nanoparticle decorated graphene nanofluids. Copper nanoparticles were decorated on functionalized graphene sheet by chemical reduction technique with different concentration, then dispersed in EG to make nanofluids. The thermal conductivity of these nanofluids has been studied at different temperatures.

II. EXPERIMENTAL

II.1. Materials

Graphite rods with purity of 99.99% purchased from Sigma-Aldrich were used as electrodes to synthesize graphene sheets. Sulphuric acid (H_2SO_4, 98%) and nitric acid (HNO_3, 68%) supplied by Shantou Xilong Chemical Factory, Guangdong, China were used for functionalization process. Copper (II) sulfate pentahydrate salt ($CuSO_4.5H_2O$, 99.5%) purchased from Aladin was used as a precursor for synthesizing copper nanoparticles. Sodium borohydride (NaBH4, 99%) and ascorbic acid (98%) purchased from Shanghai Aladdin Bio-Chem Technology Co.,LTD (China) were used as reducing and antioxidant agent. Sodium hydroxide (NaOH, $>$ 98%, Xilong, China) was also used to control the pH. Aqueous solutions were all made in ethylene glycol. Ethylene glycol (EG, 99%) supplied by the Xilong Chemical Factory was used as base fluid.

II.2. Nanofluid preparation

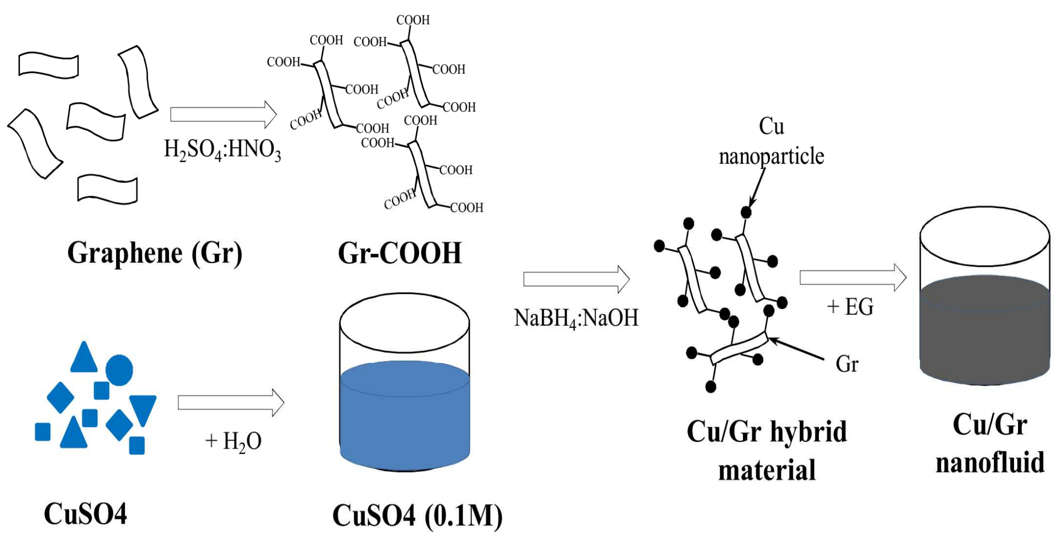

Fig. 1. Schematic synthesis of ethylene glycol based Cu nanoparticle decorated graphene nanofluids.

A schematic synthesis of the nanofluid is shown in Fig. 1. Firstly, graphene sheets synthesized by a plasma-assisted electrochemical exfoliation process [20] were functionalized with carboxyl (-COOH) by treatment in the mixture of acids (HNO_3:H_2SO_4, 1:3) at 70˚C in 5 hours under continuous magnetic stirring, then cleaned by distiller water and dispersed in EG to make Gr-EG solution with concentration of 0.3 g/L by ultrasonication in 30 min. To prepare Cu/Gr hybrid material, a desired amount of CuSO4 (0.1M) solution was added into the Gr solution to get different mass ratio to be 7:1, 5:1, 3:1 and 1:1 of Cu decorating on graphene sheets under continuous stirring. After 30 min, a solution of ascorbic acid (0.1M) was added in solution of

Graphene/Cu^{2+} under strong stirring for 30 min. After that, a reducing solution containing a mixture of $NaBH_4$ and NaOH was added to the previous solution. After reducing process completion, the solution was filtered and washed with distiller water. A fixed concentration (0.3 g/L) of Cu/Gr hybrid materials containing different Gr:Cu mass ratios was dispersed in ethylene glycol to make nanofluids by ultrasonication in 45 min under ice water and noted as F1, F2, F3 and F4. The detail concentration and optical image of the nanofluids are presented in Table 1.

Table 1. The desired nanofluids containing different copper/graphene mass ratio.

Sample	Base fluid	Concentration (g/L)	Gr:Cu mass ratio
EG	EG		
Gr	EG	0.3	
F1	EG	0.3	7:1
F2	EG	0.3	5:1
F3	EG	0.3	3:1
F4	EG	0.3	1:1

II.3. Characterization

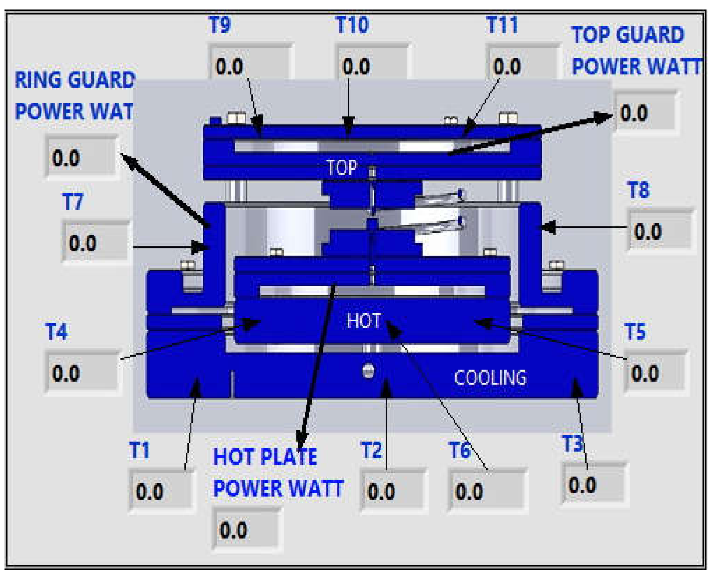

Fig. 2. Experimental procedure for measuring the thermal conductivity of nanofluids.

The morphology of the samples was characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S4800). XRD pattern was recorded by a XRD Bruker D8 Endeavor equipped with CuKα radiation in a 2θ range of 10^o to 90^o with a step size of 0.01. The thermal conductivity (K) of the nanofluids was measured using a HTL-04 thermal conductivity of liquid

(Eee, India) in range from 30^o to 60°C. The apparatus for thermal conductivity of liquid is designed and developed according to the principal of guarded hot plate method as shown in Fig. 2. Thermocouple T1, T2, T3 used for measuring cold plate temperature, T4, T5, T6 used for measuring hot plate temperature and T7, T8, T9, T10, T11 used to adjust the temperature of top guard and ring guard. Temperature of hot plate, ring guard and top guard are controlled by hot plate power (P1), ring guard power (P2) and top guard powder (P3). The K of fluid is calculated by using Eq. (1):

$$K = \frac{P1}{A} \times \frac{S}{Th - Tc} \;\; (W.m^{-1}.K^{-1}) \tag{1}$$

where A is mean area for heat flow, S is thickness of liquid, Th and Tc are average hot plate and cold plate temperature, respectively.

III. RESULTS AND DISCUSSION

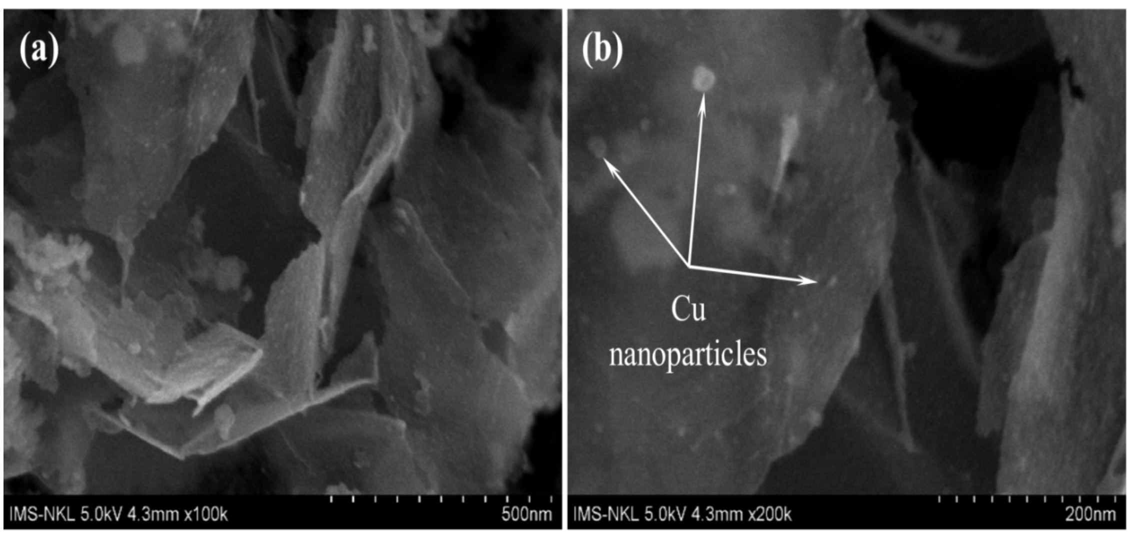

Fig. 3. SEM images of Cu/Gr hybrid material obtained of F2 nanofluid (a) lower magnification and (b) higher magnification.

Figure 3 shows the FE-SEM image of Cu nanoparticle decorated graphene sheets prepared by chemical reduction method. The surface morphology shows a coating of Cu nanoparticles on graphene sheet and the particle size estimated from the SEM image is smaller than 20 nm. The decoration of Cu nanoparticles on graphene sheets is similar to in Gr-CNT hybrid materials which has been developed and reported by our previous study [21]. The bonding between Cu nanoparticles and graphene sheets or CNTs was clarified by HRTEM analysis and FTIR spectra [21]. Both studies confirm that the functional groups (-COOH) attached on surface of graphene sheets not only improved the dispersion and stability of nanofluids but also acted as bridge to connect the Cu nanoparticles [21]. X-ray diffraction (XRD) was performed to study the formation of crystallinity of the samples. Fig. 4 shows the XRD of Cu decorated graphene sample collected from

F2. Some representative peaks of graphite were indicated at $2\theta = 26.3^{\circ}$, 53.3°, and 77.83° corresponding to (002), (004) and (100) planes, respectively. In addition, some peaks corresponding to Cu are also detected, the peak at $\sim 43.192^{\circ}$, 50.300° and 73.888° corresponds to the (111), (200), and (220) planes of Cu nanoparticles, respectively. There are no representative peaks of CuO phases detected; it means that no oxidation phases were formed in sample during chemical reduction process. In other words, using the ascorbic acid solution as reducing and antioxidant agent could restrict the formation of oxidation phases, this also in agreement with other reports in literature [22, 23]. From both morphology and XRD studies, they demonstrate that Cu nanoparticles were successfully synthesized on graphene sheets by the chemical reduction technique.

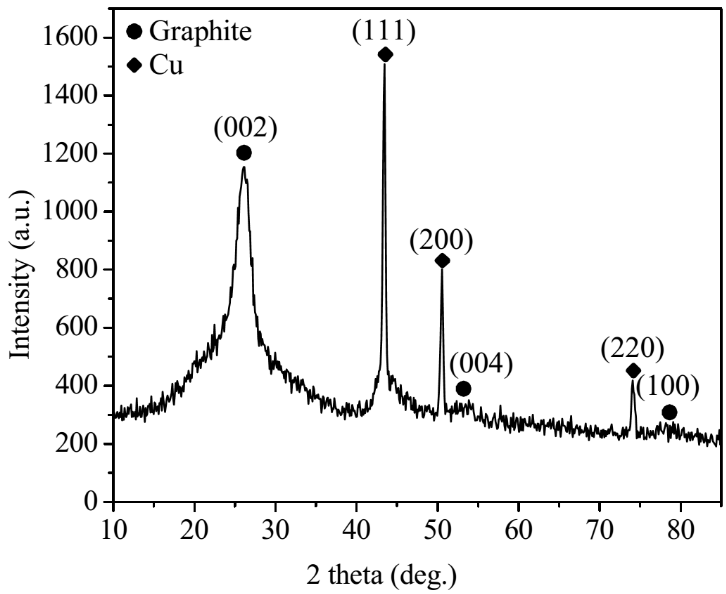

Fig. 4. XRD pattern of Cu/Gr hybrid material.

The thermal conductivity of nanofluids is measured for different Cu:Gr mass ratio at different temperatures. Fig. 5 and Fig. 6 show the experimental results and the comparison of thermal conductivity of nanofluids at different temperatures. It can be observed clearly from graphs that the thermal conductivity of the nanofluid increase as increasing temperature with EG base, Gr+EG, F1 and F2 nanofluid. However, as for F3 and F4 nanofluids, thermal conductivity increases together with temperature below 40°C and decreases with higher temperature. We propose an explanation as follow: for a nanofluid with higher Cu concentration, not only the density of nanofluid increases but also the existence of carboxyl functional groups attached on surface of graphene sheet reduces. Besides, at higher temperature ($> 40^{\circ}$C) the hydrogen bonding between functional group and EG becomes weaker [24]. Therefore, Cu/Gr hybrid material in solution tends to aggregate together to form the larger clusters. These clusters could be a reason led to reduce of thermal conductivity of nanofluids.

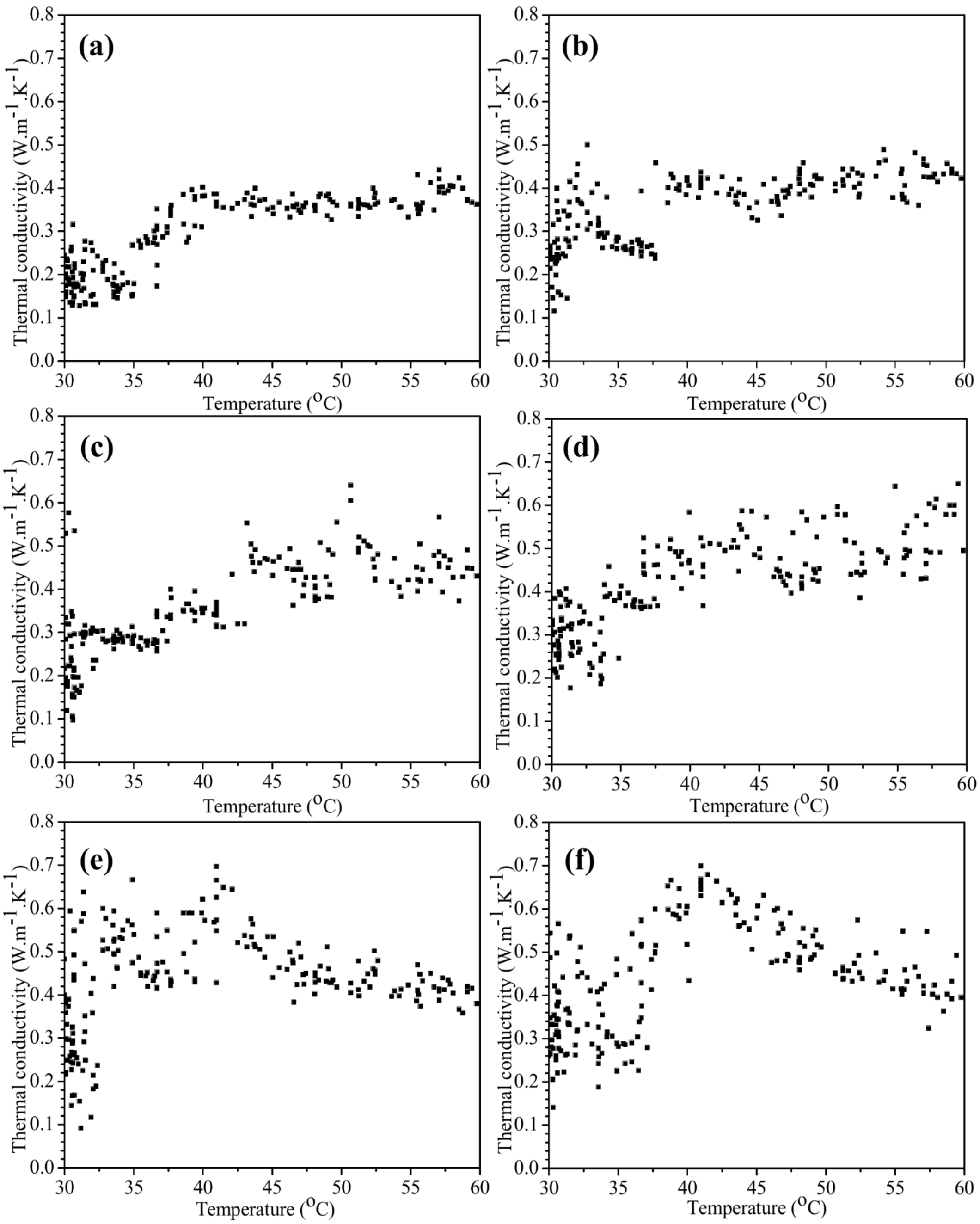

Fig. 5. Experimental thermal conductivity of (a) EG (b) Gr+EG (c) F1 (d) F2 (e) F3 and (f) F4 nanofluids with different temperatures.

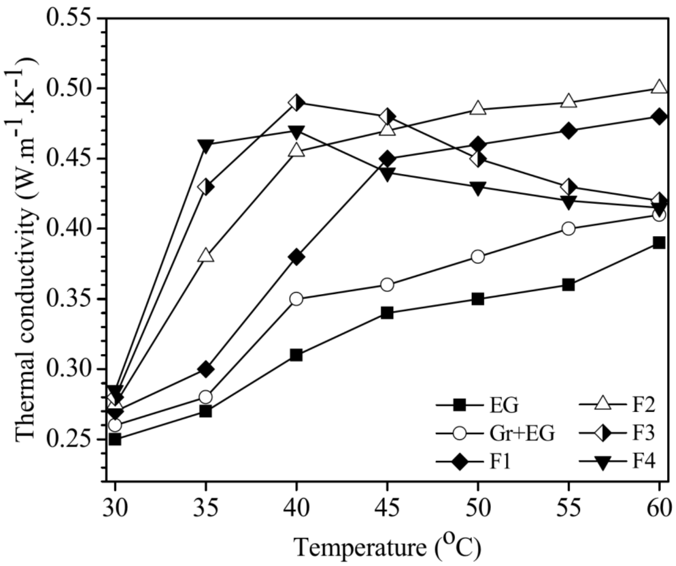

Fig. 6. Comparison of thermal conductivity of nanofluids in the selected temperatures.

The enhancement percentage in thermal conductivity is calculated using Eq. (2):

$$\% = [(k - k_o) \times 100\%]/k_o \tag{2}$$

where k_o is the thermal conductivity of the base fluid and k is that of the nanofluid. The thermal conductivity enhancement of nanofluids at 30˚C and 60˚C is shown in Fig. 7. As seen in Fig. 7 at 30˚C, the enhancement is obtained in all nanofluids and followed the rule of the higher Cu concentration the higher thermal conductivity enhancement. For example, the enhancement is about 8% for Gr+EG nanofluid, 10% for F2 and 14% for F4. However, the enhancement of F4 (6%) and F3 (8%) nanofluid at 60˚C is lower than that of F2 (29%) nanofluid due to formation of clusters as mentioned in above section. The thermal conductivity enhancement of 29% is quite high compared to nanofluids containing either graphene or Cu nanoparticle. For graphene based EG nanofluid, Baby *et al.* [25] and Selvam *et al.* [26] reported enhancements of 7% and 21% at volume fraction of 0.05 and 0.5 Gr loading, respectively. The highest enhancement of 86% reported by Yu *et al.* for nanofluid with very high Graphene oxide concentration of 5 wt.% was added [27]. Using hybrid nanomaterial of Graphene and metal or metal oxide nanoparticles for nanofluids have been also developed and reported [17, 18]. Baby and Sundara developed Ag decorated graphene-based nanofluids and reported an enhancement of up to 14% at a very low concentration [17]. Using CuO decorated graphene for nanofluids also repoted by the same group with an enhancement of up to 23% [18]. Several reports on using Cu nanoparticles for nanofluid have been developed and reported [4, 28, 29]. Garg et al. reported an enhancement up to 12% for nanofluid containing 2 vol.% prepared by using a chemical reduction [28]. Nikkam *et al.* reported the thermal conductivity evaluation of nanofluids consisting of copper nanoparticles in diethylene glycol base liquid with an enhancement of up to 7.2% with 1.6 wt. % Cu nanoparticle concentration [29]. The significantly thermal conductivity enhancement up to 36% has been reported by

Patel et al with nanofluid containing very high Cu nanoparticle concentration of 3 vol.% [4]. The enhancement in thermal conductivity is attributed to the high thermal conductivity of graphene and Cu nanoparticles. When Cu concentration increases, the distance or the mean free path of nanoparticles decreases due to the percolation effect and thus increases the frequency of lattice vibration [17]. In addition, the presence of Cu nanoparticles prevents the stacking of graphene sheets, increases the overall surface area and thus leads to enhance the heat transfer performance of the nanofluids [19].

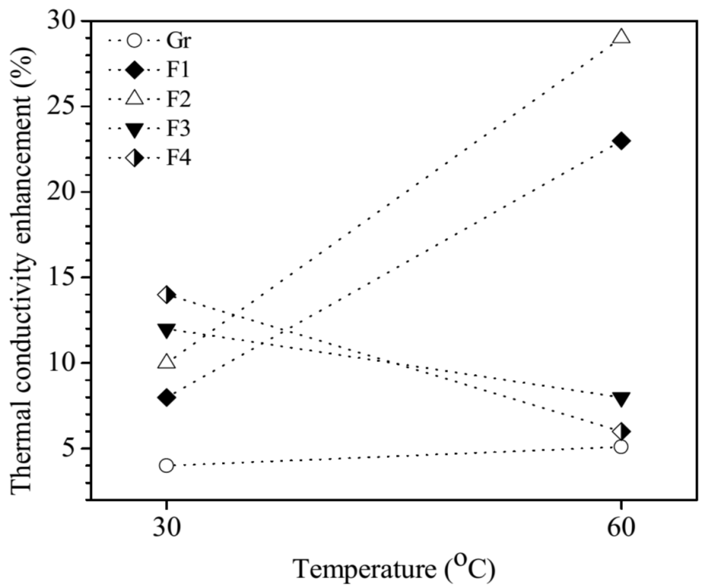

Fig. 7. Thermal conductivity enhancement of nanofluids at 30°C and 60°C.

IV. CONCLUSIONS

Ethylene glycol based Cu nanoparticle decorated graphene nanofluid is synthesized successfully by chemical reduction method. Size of Cu particles is determined smaller 20 nm and no oxidation phase formation is recorded during reduction process. The enhancement is obtained in all nanofluids. The best nanofluid is determined with nanofluid containing Cu/Gr with mass ratio of 5:1 at which the thermal conductivity enhancement is about 10% at 30°C and 29% at 60°C. The enhancement is due to the high thermal conductivity of graphene and Cu nanoparticles as well as higher surface area of Cu decorated graphene structure. Experimental results on the thermal conductivity strongly confirm that EG containing Cu/Gr nanofluids can be used for heat transfer applications.

ACKNOWLEDGEMENT

The research was financially supported by The National Foundation for Science and Technology Development (NAFOSTED) under a project 103.99.2014.71

REFERENCES

[1] Y. Xuan and Q. Li, *Int. J. Heat Fluid Flow* **21** (2000) 58.
[2] E. V. Timofeeva, W. Yu, D. M. France, D. Singh and J. L. Routbort, *Nanoscale Res. Lett.* **6** (2011) 182.
[3] J. Philip and P. Shima, *Adv. Colloid Interface Sci.* **183** (2012) 30.
[4] H. E. Patel, T. Sundararajan and S. K. Das, *J. Nanopart. Res.* **12** (2010) 1015.
[5] V. Sridhara and L. N. Satapathy, *Nanoscale Res. Lett.* **6** (2011) 456.
[6] A. A. Balandin, *Nat. Mater.* **10** (2011) 569.
[7] H. Xie and L. Chen, *J. Chem. Eng. Data* **56** (2011) 1030.
[8] E. Sadeghinezhad, M. Mehrali, R. Saidur, M. Mehrali, S. T. Latibari, A. R. Akhiani and H. S. C. Metselaar, *Energy Convers. Manage* **111** (2016) 466.
[9] A. Rasheed, M. Khalid, W. Rashmi, T. Gupta and A. Chan, *Renew. Sustainable Energy Rev.* **63** (2016) 346.
[10] B. H. Thang, P. H. Khoi and P. N. Minh, *Physics of Fluids* **27** (2015) 032002.
[11] S. Halelfadl, T. Maré and P. Estellé, *Exp. Therm Fluid Sci.* **53** (2014) 104.
[12] M. N. M. Zubir, A. Badarudin, S. Kazi, N. M. Huang, M. Misran, E. Sadeghinezhad, M. Mehrali, N. Syuhada and S. Gharehkhani, *Exp. Therm Fluid Sci.* **66** (2015) 290.
[13] A. Ghozatloo, M. Shariaty-Niasar and A. M. Rashidi, *International Communications in Heat and Mass Transfer* **42** (2013) 89.
[14] W. Ma, F. Yang, J. Shi, F. Wang, Z. Zhang and S. Wang, *Colloids Surf., A* **431** (2013) 120.
[15] S. Sen Gupta, V. Manoj Siva, S. Krishnan, T. Sreeprasad, P. K. Singh, T. Pradeep and S. K. Das, *J. Appl. Phys.* **110** (2011) 084302.
[16] X. Li, Y. Chen, S. Mo, L. Jia and X. Shao, *Thermochim Acta* **595** (2014) 6.
[17] T. T. Baby and R. Sundara, *J. Phys. Chem. C* **115** (2011) 8527.
[18] T. T. Baby and S. Ramaprabhu, *J. Mater. Chem.* **21** (2011) 9702.
[19] T. Theres Baby and R. Sundara, *AIP Advances* **3** (2013) 012111.
[20] D. Van Thanh, L.-J. Li, C.-W. Chu, P.-J. Yen and K.-H. Wei, *RSC Advances* **4** (2014) 6946.
[21] P. Van Trinh, N. N. Anh, B. H. Thang, N. T. Hong, N. M. Hong, P. H. Khoi, P. N. Minh, P. N. Hong et al., *RSC Advances* **7** (2017) 318.
[22] T. M. D. Dang, T. T. T. Le, E. Fribourg-Blanc and M. C. Dang, *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2** (2011) 025004.
[23] J. Xiong, Y. Wang, Q. Xue and X. Wu, *Green Chem.* **13** (2011) 900.
[24] X. C. Tang, M. J. Pikal and L. S. Taylor, *Pharmaceutical research* **19** (2002) 484.
[25] T. T. Baby and S. Ramaprabhu, *J. Appl. Phys.* **108** (2010) 124308.
[26] C. Selvam, D. M. Lal and S. Harish, *Thermochim Acta* **642** (2016) 32.
[27] W. Yu, H. Xie, X. Wang and X. Wang, *Physics Letters A* **375** (2011) 1323.
[28] J. Garg, B. Poudel, M. Chiesa, J. Gordon, J. Ma, J. Wang, Z. Ren, Y. Kang, H. Ohtani, J. Nanda et al., *J. Appl. Phys.* **103** (2008) 074301.
[29] N. Nikkam, M. Ghanbarpour, M. Saleemi, E. B. Haghighi, R. Khodabandeh, M. Muhammed, B. Palm and M. S. Toprak, *Appl. Therm. Eng.* **65** (2014) 158.