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Enhancement of thermal conductivity of silver nanofluid synthesized by a one-step method with the effect of polyvinylpyrrolidone on thermal behavior

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A one-step chemical method has been developed for the preparation of stable, non-agglomerated silver nanofluids. Silver nanofluid is prepared by using silver nitrate as a source for silver nanoparticles, distilled water as a base fluid, and sodium borohydride and hydrazine as reducing agents by means of conventional heating using polyvinylpyrrolidone (PVP) as surfactant. This is an *in situ*, one-step method that seems to be valuable with high yield of product with less time consumption. The characterization of the nanofluid is done by particle size analyzer, X-ray diffraction topography, UV-visible absorption spectroscopy, and transmission electron microscopy followed by the study of thermal conductivity of nanofluid by the transient hot wire method. The results show that Ag-water nanofluids with low concentration of nanoparticles, i.e., below 1000 ppm, have noticeably higher thermal conductivities than the water base fluid without Ag. Moreover, the amount of PVP in silver nanofluid can have a significant effect on magnitude and behavior of the thermal conductivity enhancement. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4809998]

Nanofluids, a group of fluids contains suspended solid nanoparticles, have created interest in many researchers because of their unique properties such as high thermal conductivity, ^{1,2} superior critical heat flux (CHF), ^{3,4} minimal clogging in flow, ⁵ enhanced mass transport, ⁶ and improved heat transfer coefficient. ⁷ These distinguished features of nanofluids make them potentially useful in a plethora of applications such as in cooling of electronic equipments, vehicle engines, nuclear reactors, biomedical engineering, and energy efficiency enhancement. ^{8,9}

Preparation of nanofluids is the first key step in the use of them. They are not a simple liquid-solid mixture. Stable and durable suspension, negligible nanoparticles agglomeration, and no chemical change are some essential requirements in nanofluid preparation. Two kinds of methods are applied to produce nanofluids, namely, one-step and two-step methods. Each of these methods has some advantages and disadvantages.

In two-step method, dry nanoparticles/nanotubes are first produced by chemical or physical techniques and then they are dispersed in a suitable liquid host with the help of intensive magnetic force agitation, ultrasonication, highshear mixing, homogenizing, and ballmilling. 10 Despite this method is the most economic method to produce nanofluids in industrial production levels, due to the high surface area and surface activity, agglomeration of nanoparticles may take place in the preparation of the nanofluids from nanoparticles on the one hand and in the process of drying, storage, and transportation of nanoparticles on the other hand. The agglomeration will result in the settlement and clogging of microchannels and affect the nanofluid properties. In spite of some techniques such as adding surfactants to the fluids or chemical modification of the nanoparticles surfaces for minimizing the particle aggregation, making a stable and durable dispersion by two-step method remains a challenge.

In one-step method, nanoparticle manufacturing and dispersing the particles in the fluid are done concurrently. Therefore, in this method, the processes of drying, storage, transportation, and dispersion of nanoparticles are avoided, so the agglomeration of nanoparticles is minimized, and the stability of fluids is increased. For producing nanofluids by metal nanoparticles, this method should be applied to prevent oxidation of nanoparticles in contact with surrounding air. ^{10–12}

In the quest to develop nanofluids of superior properties, the synthesis of silver nanofluids has been carried out in the present study. Silver nanoparticles are of great interest because of their high thermal conductivity (429 W/m K at $300\,\mathrm{K})^{13}$ and are therefore expected to have good heat transfer properties ideally suitable for thermal applications. Moreover, Ag is generally regarded as a safe material for human being and animals. 14

An attempt has been made to synthesize silver nanofluid by one-step method using silver nitrate as a source for silver nanoparticles, water as a base fluid, and sodium borohydride and hydrazine as reducing agents by means of conventional heating using polyvinylpyrrolidone (PVP) as surfactant.

All the reagents used in our experiments were of analytical purity and were used without further purification. The beakers used in this procedure were cleaned by an ultrasonic cleaner in an ultrasonic bath (Starsonic 35, 120 W). In this procedure, 485 ml of deionized water (DW) solution was taken in a 500 ml beaker. Then, 0.8 g silver nitrate and 10 g of PVP were added. The reaction mixture was subjected to magnetic stirring for 15 min in a magnetic stirrer/heater with temperature of 70 °C. Then 1 g of sodium borohydride and 3 g of hydrazine were added and the magnetic stirring was

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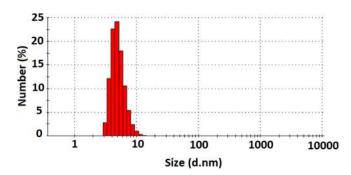


FIG. 1. The particle size distribution of Ag nanoparticles in nanofluid.

continued for another 60 min. The color of the mixture turned from white to dark brown after the reaction. Silver nanofluid was obtained after cooling the reaction mixture to room temperature. Chemical reaction involved is given in the following Scheme

$$N_2H_4 + AgNO_3 + e^- \rightarrow Ag + N_2 + 2H_2 + NO_3^-$$

$$NaBH_4 + AgNO_3 + 4H_2O \rightarrow B(OH)_4 + Ag + NaNO_3 + 4H_2$$

Characterization of the silver nanofluid was done by particle size analyzer, X-ray diffraction topography, UV-vis analysis, and transmission electron microscopy (TEM).

Dynamic light scattering was used for measuring the size of particles. The obtained graph is shown in Fig. 1. The silver nanofluid was separated by a high revolution centrifuge, 6000 rpm, and was then washed with absolute ethanol and acetone. Further, it was vacuum dried at 80 °C for 2 h. X-ray diffraction topography of the obtained powder was performed on a X'Pert MPD model using Cu tube radiation. The X-ray diffraction topography pattern of the sample is shown in Fig. 2.

Silver is an inorganic species, which shows characteristic absorption that can be identified qualitatively by UV-vis spectroscopy. The result of UV-vis analysis is shown in Fig. 3. The peak at about 400 nm in the visible region shows the existence of silver nanoparticles. ¹⁵

TEM image of the Ag nanoparticles suspensions is shown in Fig. 4. The TEM image reveals that the Ag nanoparticles are spherical in shape with sizes around 5 nm which is in agreement with size distribution in Fig. 1. The silver particles are well dispersed in colloidal solution as evidenced by TEM micrographs.

The effective thermal conductivities of nanofluids were typically measured using a transient hot-wire (THW)

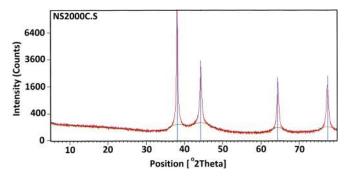


FIG. 2. The XRD patterns of Ag nanoparticles.

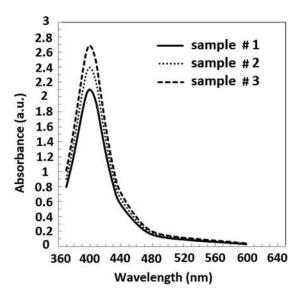


FIG. 3. Analysis pattern of silver nanofluid by UV-vis method for three samples with different amounts of PVP.

technique. 1,16 Measuring the thermal conductivity by this method is accurate and very fast compared with other techniques. In the present study, the thermal conductivity of nanofluids at different concentrations was measured using a KD2 Pro thermal properties analyzer (Decagon devices, Inc., USA), which is based on the transient hot wire method. The KD2 meter is equipped with a probe, 60 mm long and 0.9 mm in diameter, in which a heating element and a thermo-resistor are embedded. The probe is connected to a microprocessor for controlling the heat addition and recording the measurements necessary for the calculation of the thermal conductivity. The accuracy of measurements is ±5%. Before measurements, the KD2 Pro was calibrated using distilled water. The thermal conductivity of distilled water as base fluid was obtained 0.546 W/m K at 20 °C. This value is in good agreement with the reference data¹³ within the accuracy of instrument. Moreover, the accuracy of the temperature measurement is ± 0.1 °C.

Three samples of silver nanofluids have been prepared by the above mentioned one-step method. The difference between these samples is the amount of PVP. This amount in samples 1, 2, and 3 is 10 g, 12.5 g and 15 g, respectively. The role of PVP in nanofluid is to protect the agglomeration and

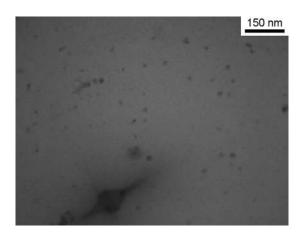


FIG. 4. The TEM image of Ag nanoparticles.

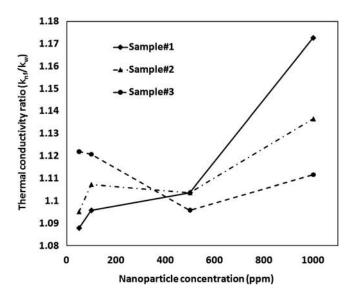


FIG. 5. Thermal conductivity enhancement of Ag nanofluids in different concentrations. Sample #1 contains 10 g PVP, sample #2 contains 12.5 g PVP, and sample #3 contains 15 g PVP.

growth of nanoparticles by steric effects. The amount of PVP in aqueous solutions influences the thermal properties of the solution. The UV-visible absorption spectra of these three samples have been measured and shown in Fig. 3. It is found that the 400 nm luminescence peak positions of the samples remain unchanged, but their peak absorption values increase with increasing PVP magnitude. The peak absorption values are 2.1, 2.4, and 2.7 for sample 1, sample 2, and sample 3, respectively, which shows that the ratio of number of Ag particles to the number of Ag⁺ ions increases with increasing PVP magnitude. Since the amount of silver nitrate is equal in all three samples, the higher peak absorption values mean that the higher amount of silver nanoparticle exists in suspension because of surface plasmon resonance. ^{18,19}

The ratio of the thermal conductivity of nanofluids to that of the distilled water at different nanoparticle concentrations has been shown in Fig. 5. It can be clearly seen that the existence of nanoparticles in the base fluid leads to thermal conductivity enhancement. The enhancement of the thermal conductivity of the nanofluids is approximately between 9% and 18% for sample 1, between 9% and 14% for sample 2, and between 9% and 12% for sample 3. Various mechanisms such as Brownian motion, ²⁰ liquid layering at liquid/particle interface, and nature of heat transport in nanoparticles ²¹ have been proposed for explaining the enhancement of thermal conduction of nanofluids using various assumptions. Recently, it was shown that nanoparticle migration under heating or cooling conditions can lead to a different dynamic thermal conductivity in nanofluids. ²²

The results shown in Fig. 5 can be described in two cases of low and high nanoparticle concentrations. In the low nanoparticle concentrations (i.e., less than 500 ppm), the thermal conductivity enhancement decreases from sample 3 to sample 1. This behavior may be related to the amount of PVP which in sample 3 is higher than other samples. Higher amount of PVP leads to a higher ratio of Ag nanoparticle numbers to the Ag⁺ ion numbers, which was also confirmed

by the UV-visible absorption spectra of three samples in Fig. 3. On the other hand, in high nanoparticle concentrations (i.e., more than 500 ppm) despite of larger Ag nanoparticle numbers, the high concentration of PVP may behave like a thermal resistance layer 17 around the nanoparticles. This can restrict the conductive behavior of Ag nanoparticle and consequently reduce the thermal conductivity enhancement of nanofluid.

In conclusion, a one-step method was developed to synthesize Ag-PVP nanofluids having different concentrations of silver nanoparticles. The non-agglomerated and stably suspended silver nanofluids are obtained in a short time and the UV-visible spectra, XRD, and TEM image confirm the formation of crystalline silver nanoparticles dispersed in PVP. It was showed that synthesized silver nanofluid has superior thermal conductivity. It is also found that the amount of PVP plays an important role in the thermal behavior of prepared nanofluids. Finally, the synthesized silver nanofluid in the present work may be used as an effective coolant in the industry in place of the conventional fluids that are currently in use.

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