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On Synthesis of a Highly Effective and Stable Silver Nanofluid Inspired by Its Multiscale Modeling

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A recently developed multiscale model of heat transfer in nanofluids has shown that significant heat transfer can take place within a few picoseconds during the collision of a nanoparticle with the heat source. Depending on the properties of particles and base fluid, frequent collision of large number of nanoparticles with the heat source followed by dissipation of the heat of nanoparticles to base fluid results in a substantial enhancement in the thermal conductivity. The model then predicts that for a given loading of 4 nm size nanoparticle in water, the thermal conductivity enhancement in case of Ag-nanofluid would be about 6.8 times that of water-based Cu-nanofluid, although the thermal conductivities of the two metals differ only by ∼7%. Inspired by the results of simulation, surface capped Ag nanoparticles produced by a chemical reduction method have been well-dispersed in water to produce the Ag-nanofluids. Thermal conductivity of the Ag-nanofluid, measured by the transient hot-wire method, has shown a sharp linear increase with the volume fraction of nanoparticles (up to 0.09%) in water, as predicted by the model. More than 100% enhancement in thermal conductivity has been achieved for a loading of only 0.09 vol.% Ag nanoparticles. Moreover, the Ag-nanofluid remained highly stable for more than 15 days in stagnant condition at ambient temperature (28 °C).

Keywords: Nanofluid, Thermal Conductivity, Molecular Dynamics.

1. INTRODUCTION

A nanofluid is a colloidal suspension of nanoparticles in a liquid. The most significant property of a nanofluid is its enhanced thermal conductivity compared to that of the base fluid.[1–5] The thermal conductivity of a nanofluid, containing a given volume fraction of nanoparticles is usually much higher than the thermal conductivity of a solid–liquid mixture containing the same volume fraction of millimeter-or-micrometer sized particles. Eastman et al.[3] have experimentally studied the thermal conductivity of ethylene glycol (EG) based nanofluids containing Cu particles of mean diameter < 10 nm and observed 40% enhancement in the thermal conductivity over that of the base fluid for a loading of 0.3 vol.% nanoparticles. Patel et al.[4] have determined the temperature dependence of water based Ag (60–80 nm dia.)-nanofluid and have found 3.2% enhancement in thermal conductivity for a loading of 0.001 vol.% of Ag nanoparticles at a temperature of 30 °C. The extent of enhancement in thermal conductivity of nanofluids is found to depend on the type of nanoparticle and base fluid,[2] volume fraction of nanoparticles,[2] size distribution of the nanoparticles,[4] temperature of the liquid medium,[5] etc.

Though the experiments have usually shown anomalous enhancement in the thermal conductivity of nanofluids, a concrete model to account for this enhancement is yet to emerge. Conventional models, such as Maxwell model,[6] Hamilton and Crosser model,[7] etc., which are based on the effective medium approximation, cannot explain the anomalous enhancement in thermal conductivity of many nanofluids containing well dispersed nanoparticles. Several models have been developed on the basis of the possible physical phenomena operative in nanofluids[8] like the Brownian movement of nanoparticles,[9–11] interfacial nanolayering,[12] particle clustering,[13] etc; but, a generally accepted model, which has the ability to explain observed thermal conductivity of various types of nanofluids, is still lacking.[14]

Recently, Ghosh et al.[15] have developed a multi-scale model of heat transfer in a nanofluid on the basis of coupled molecular dynamics (MD)-stochastic simulation. The model has shown that the pulse-like heat transfer associated with the collision of nanoparticles with the heat source is one of the key phenomena responsible for the enhancement of the thermal conductivity of nanofluids.

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The simulation has shown that repeated occurrence of such rapid heat transfer (within 10–50 ps) during the collision of particles with the heat source followed by dissipation of the heat acquired by the nanoparticles to the base fluid within 2–5 ms during their subsequent Brownian motion causes a significant enhancement in thermal conductivity of the nanofluid. Moreover, the model has shown for the first time that apart from the thermal properties, the elastic and other physical properties of the nanoparticles would have a role in the heat transfer in a nanofluid.

The model proposed by Ghosh et al.[15] can be potentially utilized to design a wide range of nanofluids by closely tracking the collision behavior of various nanoparticles with the heat source. The elastic modulus of bulk Ag is 36% lower than that of Cu,[16] which is conducive for longer collision period. On the other hand, the thermal conductivity of Ag is about $\sim 7\%$ higher than that of Cu.[16] Hence, the present work has first explored theoretically the effectiveness of nano-sized (4 nm) Ag dispersion in water in comparison to the Cu-nanofluid containing an identical volume percent of Cu nanoparticle (4 nm). The model has predicted that Ag-nanofluid would have remarkably higher thermal conductivity than Cu-nanofluid for identical loading of nanoparticles.

Inspired by this theoretical prediction, water-based nanofluids containing well dispersed Ag nanoparticles have been synthesized by a two-step method. The thermal conductivity of the nanofluids measured by the transient hot-wire method has been compared with that of the theoretical prediction. Moreover, the stability of the nanofluid during prolong storage (up to 400 h) under stagnant condition at ambient temperature (28 °C) has yielded remarkable results, as reported in the "results and discussion" section.

2. MULTISCALE MODELING OF HEAT TRANSFER IN WATER-BASED Ag-NANOFLUID

The model developed by Ghosh et al.[15] earlier aimed at predicting the thermal conductivity of water based Cu-nanofluid, and this has been modified in the present work for the estimation of the thermal conductivity of water based Ag-nanofluid. Imagine, a block of Ag acting as a heat source is in contact with water-based nanofluid containing evenly dispersed 4 nm size Ag particles. The temperature of the heat source is assumed to be 370 K, and that of the fluid is assumed to vary from 370 K adjacent to the heat source to 298 K beyond the thermal boundary layer. Within the thermal boundary layer the temperature of the fluid is assumed to vary linearly. It is natural that the nanoparticles suspended in the nanofluid will undergo Brownian motion in course of which they will repeatedly collide with the heat source with a frequency, which depends on the Brownian motion parameters like temperature and viscosity of the base fluid, size of the nanoparticle, etc. The contact period during each collision is dictated by the impact dynamics.[17] The temperature of the nanoparticle in this period is predicted to increase very fast (within a few ps) due to direct solid–solid contact. Following the approach of Ghosh et al.[15] the heat transfer associated with the collision of Ag-nanoparticles with the heat source has been simulated by the classical MD simulation. The heat transfer due to the collision between the nanoparticles has been ignored in this calculation, because the volume fraction of the nanoparticles in the nanofluids is usually very small (< 0.1 vol.%). Therefore, it would no longer be necessary to track the temperature-modulation of each of the nanoparticles in the fluid to calculate the thermal conductivity of a nanofluid.

After the collision the nanoparticle detaches itself from the heat source, then undergoes Brownian motion through the base fluid (water) and dissipates the excess heat. Stochastic simulation has predicted the phase space of Brownian motion and associated thermal evolution of Ag nanoparticles suspended in water. The initial distance of Ag nanoparticle from the heat source has been varied from 0 to 3.2 mm randomly 3200 times, because preliminary stochastic simulation has revealed that within a time span of 1 s, a 4 nm size Ag particle located at distance more than 3.2 mm from the heat source does not collide with the heat source. MD simulation coupled with the stochastic simulation has estimated the extent of additional heat transfer from the heat source caused by the repeated collision of the nanoparticles with the heat source in 1 s, in order to evaluate the enhancement in thermal conductivity of the nanofluid. It is also found that the extent of this enhancement predicted by the simulation is insensitive to the increase of the above mentioned time span from 1 s to 10 s in the stochastic simulation.

The multiscale model developed by Ghosh et al.[15] suggests that the collision induced heat transfer depends on the thermal conductivity of the colliding particle as well as the period of collision of the nanoparticle with the heat source. The collision period (Δt_c) is given as:[17]

$$\Delta t_c = \frac{2.94}{V_{\text{coll}}} \zeta r_{\text{np}} \tag{1}$$

where

$$\zeta = \left[\frac{5}{2} \pi^2 \rho V_{\text{coll}}^2 \omega \right]^{2/5} \tag{2}$$

Here V_{coll} is the collision velocity, r_{np} is the radius of the nanoparticle, ρ is the density of the nanoparticle, ω is the elasticity parameter for the particle or heat source material. The elasticity parameter ω is defined by:[17]

$$\omega = \frac{1 - \mu^2}{\pi E} \tag{3}$$

where, μ is the Poisson's ratio and E is the Young's modulus. Therefore, apart from size and collision velocity the elastic properties as well as the density of the nanoparticle

influence the collision period. It is obvious that period of collision of nanoparticle with the heat source, which depends on the elastic modulus along with other parameters of the nanoparticle, significantly influence the phonon transfer during the collision. The lower is the value of elastic modulus, the longer will be the duration of collision, and the consequent time available for phonon transfer from the heat source to the nanoparticle. The thermal conductivity of Ag (425 W m^{-1} K^{-1}) is almost 7% higher than that of Cu (397 W m^{-1} K^{-1}),[16] but the elastic modulus of Ag (83 GPa) is 36% lower than that of Cu.[16] As a result the collision period of a 4 nm Ag particle with an Ag heat source is 1.3 times higher than that of a 4 nm Cu particle colliding with a Cu heat source. The higher collision period is conducive for more phonon transfer and results in higher enhancement in thermal conductivity of Ag-nanofluid compared to Cu-nanofluid. The thermal conductivity estimated on the basis of the present multiscale model has predicted that water based Ag-nanofluid would show an enhancement in thermal conductivity 6.8 times that of water based Cu-nanofluid for the same volume fraction of nanoparticle (4 nm) loading. This prediction has provoked the present attempt to synthesize the water-based Ag-nanofluids for heat transfer applications.

3. EXPERIMENTAL DETAILS

Water based Ag-nanofluid has been produced by a novel two-step method.[18] First, the Ag nanoparticles with organic surfactant capping have been produced by the chemical reduction of silver nitrate.[19] In the present experiment, tri-sodium citrate and sodium formaldehyde sulphoxylate (SFS) were used as reagents for the capping. The process consists of dropwise addition of aqueous solution of trisodium citrate to an aqueous solution of silver nitrate under stirred condition. This is followed by dropwise addition of required amount of sodium formaldehyde sulphoxylate to the reaction product under the same stirred condition. The resultant dark gray precipitate has been filtered off, washed with methanol and then dried to obtain surface capped Ag nanopowder. The as-prepared Ag nanopowder has been characterized by Philips X'pert Pro high resolution X-ray diffractometer. The average crystallite size of the nanoparticles has been estimated from the X-ray diffraction (XRD) peak broadening by Williamson-Hall method,[20] which permits elimination of the contributions of instrumental broadening and microstrain. The particle sizes of the Ag-nanoparticles have been verified from the bright field image observed by a JEOL JEM 2100 transmission electron microscope (TEM).

In the second step, the as-prepared Ag-nanoparticles are dispersed in distilled water by programmed ultrasonic vibration to produce nanofluids with different volume fraction of nanoparticles (< 0.1 vol.%). The particle size distribution in the nanofluid has been determined by the dynamic light scattering (DLS) technique using a Brookhaven 90 Plus instrument. The thermal conductivities of the nanofluids have been measured by the transient hot-wire method[2] under stagnant condition.

4. RESULTS AND DISCUSSION

The XRD pattern of as-prepared Ag-nanopowder obtained using Co target has evidenced the characteristic peaks of fcc Ag. Analysis of the XRD spectrum has yielded the average crystallite size of the Ag-nanopowder as 32 nm. The bright field TEM image in Figure 1 evidences that the particles have faceted structure and plate like geometry. The particle size is in the range of 20–90 nm, and the mean nanoparticle diameter has been estimated as 45 nm. Since, the average crystallite size calculated from the XRD pattern is 32 nm, and the particle size obtained from the TEM images ranges from 20 to 90 nm, most of the as-prepared Ag nanoparticles seem to be polycrystalline.

Figure 2 shows the particle size distribution of the suspended Ag nanoparticles as obtained by DLS measurements. It has been observed that the mean hydrodynamic diameter of the surface capped Ag nanoparticles suspended in water is 58.2 nm. These DLS measurements, therefore, do not provide any evidence of dendritic or fractal agglomeration involving many nanoparticles in the present nanofluid.

The enhancement in thermal conductivity predicted on the basis of the present model as a function of volume fraction of nanoparticles ($< 0.1\%$) for water based Ag-nanofluid as well as water based Cu-nanofluid[15] have been displayed in Figure 3. It shows that the enhancement in predicted thermal conductivity would increase linearly with the volume fraction of nanoparticles ($< 0.1\%$) in both the nanofluids. This type of linear variation was observed experimentally in the case of water based Cu-nanofluid[15]

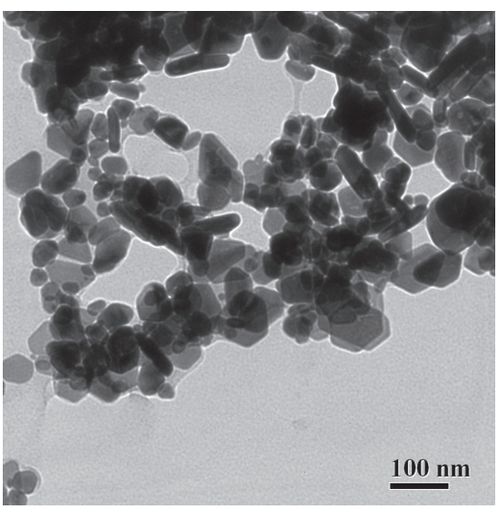

Fig. 1. Bright field TEM image of the synthesized Ag nanoparticles.

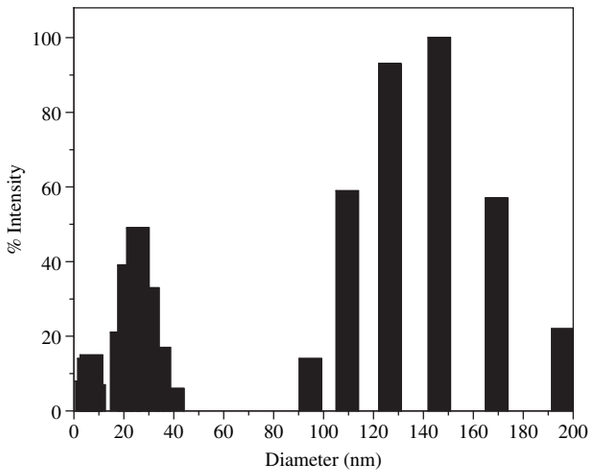

Fig. 2. Particle size distribution of Ag nanoparticles dispersed in water measured by DLS technique.

or water based Cu_9Al_4-nanofluid,[21] for low volume fraction loading. It is interesting to note that enhancement in thermal conductivity predicted by the present model for water based Ag-nanofluid is 6.8 times that of water based Cu-nanofluid for the same volume fraction loading, although Ag has only $\sim 7\%$ higher thermal conductivity than Cu.[16] This is apparently due to different collision period[17] of Ag nanoparticles (16.97 ps) as compared to the Cu nanoparticles (13.59 ps) of same size (4 nm). This potentially makes Ag-nanofluid much more attractive than Cu-nanofluid in heavy heat-flux applications. In Figure 3, the present experimental data of thermal conductivity enhancement measured under stagnant condition for water based Ag-nanofluids have also been superimposed. It is found that for a given volume percent

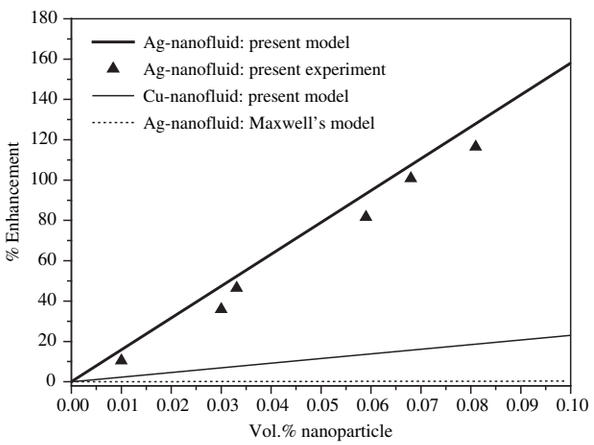

Fig. 3. The enhancement in thermal conductivity of water based Ag-nanofluid (thick line) and Cu-nanofluid (thin line) predicted by the present model as a function of the volume of nanoparticle loading along with the present experimental data for water based Ag-nanofluid (solid triangle). The prediction of Maxwell's model has been depicted by dotted line.

of loading ($< 0.1\%$), the theoretically estimated enhancement in thermal conductivity is somewhat higher than the corresponding experimental values for the water based Ag-nanofluid. This deviation arises due to the fact that the size of nanoparticles considered in the present model (4 nm) is much smaller than the experimentally prevailing size of Ag nanoparticles (20–90 nm). For any given volume fraction of well-dispersed nanoparticles in a fluid, as the average size of particles decreases, their number and surface area to volume ratio increases. Further, the frequency of collision of smaller sized particles is higher, resulting in better enhancement of thermal conductivity. In consequence, for a given fraction of evenly dispersed nanoparticle, the thermal conductivity of nanofluid should decrease with the increase in particle size. In the present study, simulation has been carried out for 4 nm size Ag-nanoparticles to keep MD simulation time within manageable limit. However, the particle size prevailed in the present experimentally produced nanofluid is in the range of 20–90 nm, as revealed by the TEM image. MD simulation for such a large particle size is a formidable task because of the excessive computation time requirement. Hence, the present experimental data for 20–90 nm size Ag-nanoparticles have been compared with the prediction of the present model for 4 nm size Ag-nanoparticles. The results have shown that for a given volume fraction loading of Ag-nanoparticles in water the experimentally produced nanofluid exhibits lower enhancement in thermal conductivity compared to the theoretical predictions. This is expected and can be qualitatively explained in terms of the particle size. Nevertheless, the prediction of present model seems to be in reasonable agreement with the present experimental data. It is noteworthy that more than 100% enhancement in thermal conductivity has been achieved by the addition of only 0.09 vol.% Ag nanoparticles in water.

It is to be noted here that the Ag-nanoparticles synthesized in the present experiment were provided surface capping of organic material in order to increase the stability of the nanofluid. Since the organic capping formed by adding tri-sodium citrate and sodium formaldehyde sulphoxylate (SFS) during synthesis of the nanoparticles normally has low thermal conductivity compared to the metallic nanoparticles, the presence of such capping material on the nanoparticles is expected to lower the extent of heat transfer to some extent during the collision of the Ag-nanoparticles with the heat source. This would result in some reduction in the effectiveness of the nanoparticles in enhancing the thermal conductivity of the nanofluid. This can partly account for the lower enhancement in thermal conductivity of experimentally produced water based Ag-nanofluid compared to the theoretical predictions based on the Ag-nanoparticles free from surface capping. However, in the present simulation the presence of the organic capping material has been ignored during the collision because of the non-availability of interatomic

potentials of Ag with the organic capping material. However, considering the fact that the organic layer enveloping the Ag-nanoparticles is 1–2 molecular layers thick, the reduction in the enhancement in thermal conductivity caused by the capping material is assumed to be negligible.

It may be pointed out that Patel et al.[4] have experimentally determined the temperature dependence of water based Ag (60–80 nm dia.) nanofluid and have found 3.2% enhancement in thermal conductivity for a loading of 0.001 vol.% at temperature of 30 °C. Although the present experiment has not determined the thermal conductivity enhancement for such a low volume fraction loading, present MD-stochastic model for 4 nm size Ag particle predicts 1.6% enhancement in thermal conductivity for 0.001 vol.% loading, which is in reasonable agreement with the experimental results of Patel et al.[4]

The variation of thermal conductivity enhancement with the volume fraction of evenly dispersed Ag nanoparticles in water medium, predicted by the classical Maxwell's model[6] has also been shown in Figure 3. It is evident that under the given condition the Maxwell's predictions lie far below the experimental data and hence, the Maxwell's continuum model is unable to account for the present experimental data on thermal conductivity of water based Ag-nanofluid.

In order to assess the stability of the present water based Ag-nanofluid, the variations in enhancement of thermal conductivity of the nanofluid containing 0.086 vol.% and 0.032 vol.% Ag nanoparticle have been tracked under stagnant condition at ambient temperature (28 °C) from the time of their synthesis up to 400 h and 193 h, respectively (Fig. 4). It shows nearly 15% decrease in the enhancement within the first 20 h of holding, beyond which no significant change in the thermal conductivity occurred during prolong holding up to 400 h. The initial decrease in thermal conductivity may be attributed to the settling of the relatively bigger sized Ag particles within first 20 h of nanofluid synthesis. The results in Figure 4, therefore, evidences the excellent stability of the present Ag-nanofluid and more than 100% enhancement in thermal conductivity compared to water has been achieved by addition of only 0.086 vol.% Ag nanoparticles. This potentially makes Ag nanoparticle an attractive dispersoid for the synthesis of water based nanofluids.

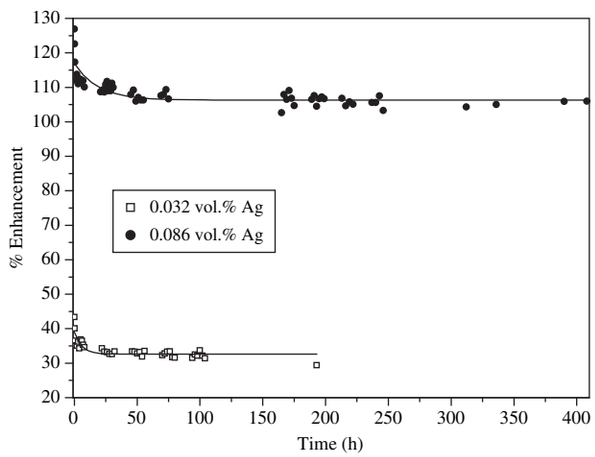

Fig. 4. Variation in enhanced thermal conductivity of water based Ag-nanofluids with time at room temperature under stagnant condition.

5. CONCLUSION

Application of a multiscale heat transfer model for nanofluids proposed earlier[15] has predicted that water based Ag-nanofluid would be far more conductive than the water based Cu-nanofluid for the same extent of loading (< 0.1 vol.%) of nanoparticles. This prediction inspired the development of a novel and simple method for synthesizing water based Ag-nanofluid, as reported here. The theoretical predictions of the thermal conductivity enhancement of this nanofluid show reasonable agreement with the present experimental data, as well as, that in the literature. A linear enhancement of thermal conductivity with the volume fraction of Ag particle loading (< 0.1 vol.%) has been predicted by the present model and manifested by the present experimental data. Moreover, the present Ag-nanofluid remained remarkably stable at ambient temperature (28 °C) for more than 15 days during storage under stagnant condition.

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