Journal of Nanofluids
Vol. 6, pp. 11–17, 2017
(www.aspbs.com/jon)

Direct Synthesis of Nanofluids Containing Novel Hexagonal Disc Shaped Copper Nanoparticles

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Copper nanofluids have been prepared by single step solution phase reduction of copper sulphate by ascorbic acid in the presence of polyvinylpyrrolidone. The synthesized hexagonal disc shaped nanostructures of copper are novel and were characterized by diffraction techniques, microscopic techniques and spectroscopic analysis. Thermal conductivity and rheological measurements were also carried out. Sedimentation measurements showed that the nanofluid was stable up to a period of 3 weeks. The copper nanofluid exhibited Newtonian behavior and enhanced thermal conductivity. The nanofluid showed thermal conductivity of 0.827 $Wm^{-1}K^{-1}$ when the weight fraction of copper nanoparticles was as low as 0.096% owing to higher conductivity of copper, its nano size and uniform distribution of the particles in the fluid. The method is found to be facile, expeditious, economic and reliable technique for synthesis of nanofluids.

KEYWORDS: Nanofluids, Copper, Thermal Conductivity, Viscosity.

1. INTRODUCTION

Nanofluids are considered as advanced heat transfer fluids showing promising role in meeting the ever increasing demand of heat dissipation compared to the conventional heat transfer fluids. It is established that solids like metals, metallic oxides and non metallic oxides have thermal conductivity 1–3 orders higher than the base fluids used for cooling. Nanofluids are nothing but stable suspensions of metal or metal oxide nanoparticles in the conventional base fluids prepared with a goal to enhance the thermal properties of the base fluids.[1] Such nanoparticle suspensions are possible because the interaction of large particle surface is able to overcome the difference in density, which usually result in particles either floating or sinking in the liquid.

Among several nanofluid synthetic techniques single step chemical method is found to be the most advantageous and simplistic in approach.[2–5] It involves simultaneous preparation and dispersion of nanoparticle in the base fluid unlike the two step method in which the nanoparticles are first prepared and then dispersed in the second step.[6–9] In two step methods the nanoparticles are produced initially by methods like chemical vapor deposition, physical vapor deposition, mechanical alloying or other techniques and then dispersed into the base fluids.[1, 10, 11] Two step synthetic methods are not usually very successful in producing nanofluids containing heavier metallic particles.

Single step synthetic techniques could be physical methods like direct evaporation technique, submerged arc nanoparticle synthesis, laser ablation in liquid, dual plasma synthesis, pulsed wire evaporation, solution plasma process etc. or chemical methods like solution phase synthesis or polyol technique.[2, 4, 5, 12–15] The single step chemical method overcomes the drawbacks of other techniques like agglomeration which would result in clogging and poor dispersion leading to low thermal conductivity.[14] But only few single step chemical methods have been reported.[16–19] Keeping the above facts in view an attempt to synthesize copper nanofluids using single step solution phase method has been made. Herein we report the synthesis of copper nanofluids containing unusual hexagonal particles for the very first time showing high thermal conductivity for very low weight fraction and Newtonian behavior with a stability of 3 weeks.

2. MATERIALS AND METHODS

2.1. Synthesis of Nanofluids

Copper nanofluids were prepared by simultaneous *in situ* solution phase synthesis of nanoparticles and their dispersion into base fluid. In a typical experiment, 15 mL aqueous solution of 0.1 M $CuSO_4 \cdot 5H_2O$ was mixed with 5 mL solution of 0.01 M polyvinylpyrrolidone (PVP) in ethylene glycol and 45 mL water and stirred for 15 minutes. Later 30 mL of 0.5 M ascorbic acid solution in ethylene glycol was added. Further the stirring was continued at 75 °C. The color change during the process was from blue to brownish red. After being cooled to room temperature

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Received: 15 September 2016
Accepted: 5 October 2016

naturally, copper nano fluid was obtained. The synthesis was also carried out at varying concentrations of ascorbic acid, PVP and various dilutions. In order to investigate the effect of microwave radiation the same reaction was subjected to microwave irradiation at 50% power for 5 minutes. Experiments were also carried by varying the ratio of the reactants, microwave power and the reaction time.

2.2. Characterization

The prepared copper nanofluid was characterized by several techniques. The nanofluid was diluted with absolute ethanol and centrifuged for one hour. The powder sample obtained was given repeated wash with water and ethanol and finally dried at 80 °C.

X-ray diffraction (XRD) studies were carried out using JEOL X-ray Diffractometer (Model DX GE 2P) using Ni filtered Cu K_α radiation ($\lambda = 1.54178$ Å) with an operating voltage of 30 kV. The scan rate was set at 0.06°/s in the 2θ range 25°–85°. The chemical composition and purity of the products were also examined using Energy Dispersive X-ray (EDX) analysis (JEOL JSM 6380LA model Analytical Scanning Electron Microscope).

The spectroscopic analysis of the nanofluid was carried out using Ocean optics, inc SD2000 fibre optic spectrometer and Nicolet Avatar 330 Fourier Transform Infrared (FTIR) spectrometer at room temperature.

The samples for Transmission Electron Microscopy (TEM) were prepared by sonicating the nanofluid and later placing it on carbon coated copper grid for analysis. The TEM images of the nano fluids and Selected Area Electron Diffraction (SAED) pattern were recorded on a Philips CM200 transmission electron microscope operating with an accelerating voltage of 20–200 kV with a resolution of 2.4 Å. The Field Emission Scanning Electron Microscopy (FESEM) images of the copper particles were taken on a Supra 40VP FESEM having a resolution up to 2 nm.

The thermal conductivity of the as such prepared nanofluid as well as at various particle weight fractions were measured with KD2 pro thermal property analyzer using KS-1 sensor. Measurements were recorded at low power mode with read time of 1 min using vertically oriented sensor. Rheological measurements were made using Brookfield LV DV III ultra rheometer.

3. RESULTS AND DISCUSSION

3.1. Results of Diffraction Studies

The examination of phase structure and the purity of the products were done by XRD studies. The powder XRD pattern of the as obtained copper nanoparticles is shown in Figure 1. The diffraction peaks could be indexed to the face centred cubic Cu [JCPDS Card No. 04-0838, $a = 3.6150$ Å, Space group: Fm3m (225)] corresponding to (111), (200) and (220) planes respectively.

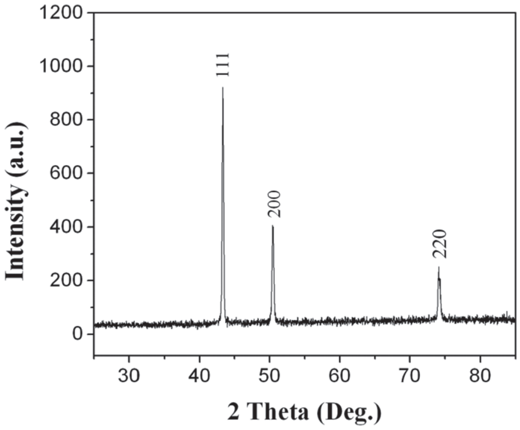

Fig. 1. A typical XRD pattern of the copper nanoparticles.

The average size of the particle is calculated using Scherrer's formula[20] given in Eq. (1).

$$\tau = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where τ is the thickness of the crystal (in Å), K is the shape factor, λ the X-ray wavelength and θ the Bragg angle. The line broadening, B is measured from the extra peak width. No peaks of impurities such as those of cuprous or cupric oxide were detected, suggesting the high purity of the products.

EDX analysis also reveals that there is no contamination and only copper is detected in the EDX spectrum. A typical EDX spectrum of copper nanoparticles is shown in Figure 2(a). This shows that the method is highly efficient in producing copper nanofluid without impurities. The SAED pattern (Fig. 2(b)) of the as-prepared nano fluid shows four fringes, with 2.09 Å, 1.81 Å, 1.28 Å and 1.09 Å as the plane distances, which can be related to (111), (200), (220) and (311) planes of face centered cubic copper.

3.2. Results of Spectroscopic and Microscopic Analysis

Figure 3 shows Ultra Violet-Visible spectrum of copper nanofluid. The absorption peak at 572 nm indicates the peak due to copper nanoparticles.[16, 17, 21]

A mixture of water and ethylene glycol was used as base fluid. To know whether ethylene glycol has any role in reducing copper ions FTIR spectroscopy was used since there were chances of ethylene glycol acting as reducing agent. The FTIR spectra of pure ethylene glycol (a) stacked with copper nanofluid (b) are shown in Figure 4. It is seen that the two spectra resemble indicating that the ethylene glycol is not oxidized. This suggests that ascorbic acid is the one acting as reducing agent and not ethylene glycol. The polyol reduction processes usually requires heating the reaction mixture to a very high temperature.[22] But the currently reported method requires heating only upto 75 °C for the synthesis of copper nanoparticles. Thus

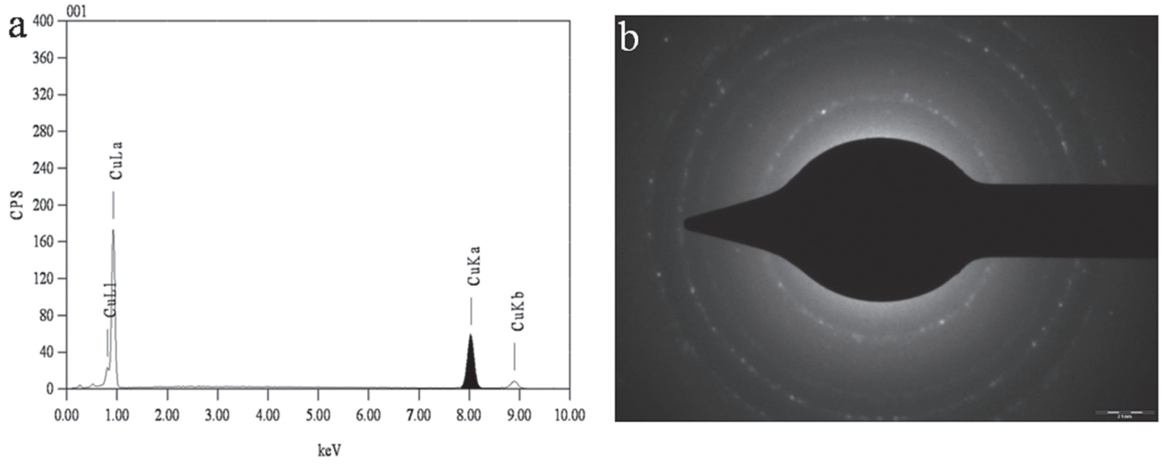

Fig. 2. (a) A typical EDX spectrum of copper nanoparticles; (b) SAED pattern of copper nanofluid.

this method preserves the advantages of the polyol process and aqueous chemical reduction method as well.

The representative FESEM image is shown in Figure 5. The copper nanostructures are somewhat hexagonal disc like in shape. For the first time copper nanoparticles with hexagonal disc shaped structure synthesized through solution phase synthesis has been reported. The surface of the disk shows crystallite flakes which indicate that the second nucleation process had commenced which seized due to lack of copper ions. If the concentration of the copper solution was increased and the reaction was allowed to proceed further these seeds would have further grown into disk shaped particles. It is interesting to note that previously copper nanofluids containing octahedral particles have been reported using copper nitrate as precursor while in the present study hexagonal disks are formed when copper sulphate is used as precursor indicating that the interaction of the precursor with the stabilizing agent plays a crucial role in deciding the morphology of the particle formed.[16] The results of variation in reaction parameter on the size of the particle have been discussed below.

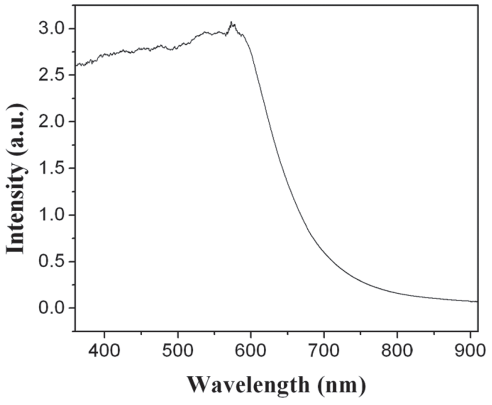

Fig. 3. UV-Visible spectrum of the copper nanofluid.

3.3. Effect of Concentration of Reducing Agent

To study the effect of reaction conditions on the size as well as stability of the nanofluid, various reaction parameters were varied. Synthesis was carried out at different concentrations of ascorbic acid to study its effect on size of the copper nanoparticle formed. In thermal conditions the size decreased as follows 70 nm, 62 nm, 57 nm and 48 nm with increase in molar ratio of ascorbic acid to copper sulphate from 10 to 40 with 10 units increase each time and under microwave irradiation it decreased from 64 nm to 59 nm to 46 nm to 39 nm respectively. The reduction of copper ion by ascorbic acid is as shown in Eq. (2).

$$Cu^{2+} + C_6H_8O_6 \rightarrow Cu + C_6H_6O_6 + 2H^+ \tag{2}$$

According to this equation rate and amount of electrons supplied to copper ions is determined by concentration of reducing agent. At lower concentration of ascorbic acid, the copper ions get reduced to copper very slowly and hence only a few nuclei are formed at the nucleation step. Precipitating copper atoms at the later period of reactions are mostly involved in particle growth by collision with already generated nuclei rather than formation of new particles. This leads to the formation of larger sized particles. With increase in concentration of reducing agent, reduction rate is enhanced, leading to the formation of smaller particles. At higher reduction rate the number of precipitating copper clusters increases steeply and hence more number of nuclei is formed during the nucleation period. Eventually the size of the particles decreases because the amount of solute available for particle growth per growing particle decreases with increasing number of nuclei.[17, 23]

3.4. Effect of Dilution

To study the effect of dilution, different amounts of water was added to the reaction mixture. It was seen that dilution of the reaction mixture had a bearing on the reaction rate since it decreased the overall concentration of the solution. It was found that the particle size increased with dilution.

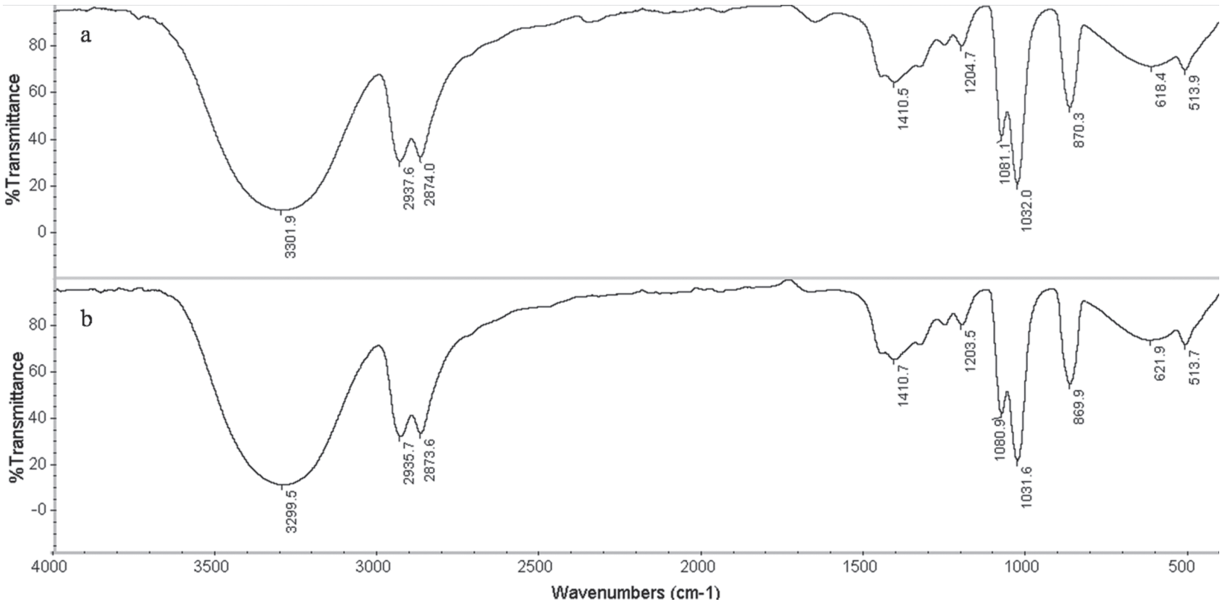

Fig. 4. FTIR spectra of pure ethylene glycol (a) and copper nanofluid (b).

Dilution with 100 mL water resulted in increase in size to 76 nm from 70 nm which was obtained at 45 mL dilution. It further increased to 81 nm for 150 mL dilution. For 200 mL dilution the particle size was 83 nm with reaction proceeding very slowly. The observations can be explained by the influence of reaction rate on the nucleation. At a low overall concentration, on dilution of the reaction mixture, the reduction of copper sulphate by ascorbic acid takes place slowly and only a few nuclei of copper are formed in the early period of the reaction. Since the rate of the reaction is slow, the subsequently formed copper atoms get deposited on the already existing nuclei rather than forming new nuclei. As a result of the rate of nucleation being slower than the rate of particle growth, fewer numbers of particles with bigger size are obtained.

3.5. Effect of Addition of Polymer Stabilizer

To prepare stable copper nanofluids 0.01 M PVP was added as a polymer stabilizer. The concentration of PVP was changed to see its effect on the size of particles. The results are given in Table I. Polymer stabilizers were introduced primarily to form a monolayer on the surface of nanoparticles so as to prevent their agglomeration. The surface interaction of a solid particle and polymer stabilizer during the growth process varies significantly depending on various factors like the surface chemistry of the solid, the polymer, solvent used and temperature.

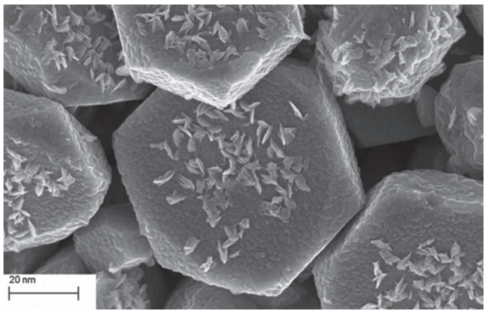

Fig. 5. FESEM image of the copper nanoparticles showing hexagonal discs.

The observed decreasing trend in the size points to PVP acting as a capping agent and effectively restricting the size of the growing particle.[24] The size restriction could be because of two factors: a strong adsorption of polymer stabilizers occupying the growth sites. Secondly, hindering of the diffusion of growth species from solution, to the surface of growing particle due to full coverage of polymer stabilizer and thus reducing the growth rate of nanoparticles. This indicates that it helps in preventing the growth and agglomeration of the particles and in turn achieving required fluid stability by facilitating uniform dispersion and keeping the particles suspended.

The long term stability of nanofluids is a key issue for both scientific and practical application. Sedimentation measurements were used to evaluate the stabilization of nanofluids. In the absence of PVP the solution was not stable. In the presence of PVP nanofluids were found to

Table I. Effect of concentration of PVP on size of copper particles.

Concentration of PVP added (M)	Effective concentration of PVP in the reaction mixture (mM)	Particle size (nm)
0	0	73
0.01	0.53	70
0.05	2.63	58
0.1	5.26	45

be stable up to 3 weeks in stationary state at room temperature. The stability of the as synthesized fluid is better than the one achieved by the two step method where in they could achieve it for one week in case of copper-transformer oil system and 30 h for copper-water system.[25] The higher stability imparted is attributed to the action of PVP which prevents the agglomeration of particles and allows it to remain suspended.

3.6. Effect of Microwave Irradiation Power and Duration

In order to study the effect of power of microwave irradiation on the size of the particles the solution was subjected to varying power for duration of 5 minutes. At 30% the size obtained was 44 nm but the power was not sufficient for the reaction to complete. At 50%, 70% and 90% the average particle size was 64 nm, 58 nm and 52 nm respectively. The microwave radiation causes intense friction and collision of molecules thereby increasing the nucleation rate and reducing the growth of particles.[26, 27]

The effect of reaction time was also studied. Microwave irradiation for a duration of 3 minutes was insufficient for the completion of reaction and yielded particles of size 56 nm. When the reaction time was increased from 5 minutes to 7 minutes to 10 minutes at 50% power the size of the particles increased from 64 nm to 68 nm to 74 nm respectively. The experimental trend can be explained as with increase in the duration of reaction the chances of interaction between the particles increases and hence there is a scope for growth of particles.[28]

3.7. Results of Thermal Conductivity Measurements

The thermal conductivity of the copper nanofluid synthesized was found to be 0.827 $\mathrm{Wm^{-1}K^{-1}}$ when the weight fraction of copper nanoparticles was 0.096%, significantly higher than the reported value of 0.6 $\mathrm{Wm^{-1}K^{-1}}$ and 0.279 $\mathrm{Wm^{-1}K^{-1}}$ for copper nanofluid (0.1%) prepared using sodium hypophosphite, were single step chemical reduction and microwave method was followed, respectively; and 0.259 $\mathrm{Wm^{-1}K^{-1}}$ for copper nanofluid (0.5%) prepared by single step physical method of direct evaporation technique.[2, 14, 29] The thermal conductivity value reported is also significantly higher than the one obtained by micro electrical discharge machining process where PVA and PEG where used as stabilizers and a thermal conductivity of 0.606 $\mathrm{Wm^{-1}K^{-1}}$ in DI water, 0.649 $\mathrm{Wm^{-1}K^{-1}}$ in PVA sample 0.656 $\mathrm{Wm^{-1}K^{-1}}$ in PEG sample was obtained.[30] The variation of thermal conductivity ratio with copper nanoparticle weight fraction of the above synthesized fluid is as shown in Figure 6. The ratio of water and ethylene glycol was maintained 1:1 during the measurements. Similar trend was observed for different ratios of the base fluids. The thermal conductivity also depended on the nature of base fluids. It was observed that for a particular ratio of base fluids, with the increase in the particle concentration the thermal conductivity and in turn the thermal conductivity ratio of the nanofluid increased. This shows that at very low concentrations the thermal conductivity depends on the volume fraction of the nanoparticles.[31] At higher concentrations, the increase in thermal conductivity could be attributed to the higher conductivity of copper, its nano size and uniform distribution of the particles in the fluid.[10, 32, 33] The enhanced thermal conduction in the nanofluids is believed to be due to two mains factors: Brownian motion induced convection and effective conduction through percolating nanoparticle paths. However the latter is considered as the main factor in the enhancement of thermal conductivity according to some reports.[34, 35]

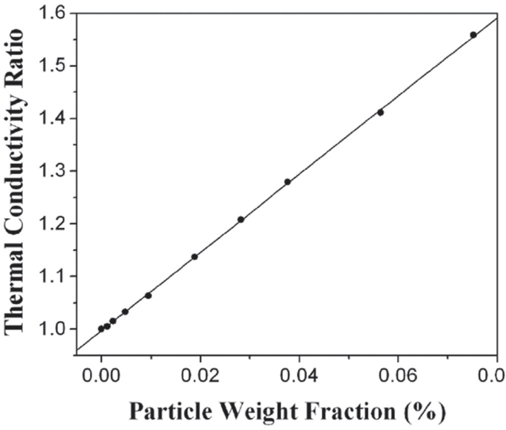

Fig. 6. Variation of thermal conductivity ratio with copper nanoparticle weight fraction.

3.8. Results of Rheological Measurements

Measurements were done to verify whether nanofluid behaves like a Newtonian fluid or non-Newtonian fluid, in order to investigate the rheological behavior, since it is an important attribute in its application. Even though a nanofluid may exhibit higher thermal conductivity, if the viscosity of the fluid is higher then the pumping of fluid through the heat exchanger will require higher power thereby reducing the benefit of the increased conductivity of the fluid.[36] The variation of shear stress with shear rate of copper nanofluid at 30 °C for a particle loading of 0.096% is as shown in Figure 7(a).

The equation governing Newtonian behavior of a fluid is given by (3).

$$\tau = \mu\gamma \tag{3}$$

Where τ is shear stress, μ is the coefficient of viscosity and γ is the shear strain. The linear relation between the shear stress and shear rate demonstrates the Newtonian behavior of the nanofluid.[18, 24] Viscosity as a function of shear rate for 0.096% particle loading at different temperatures, shown in Figure 7(b) demonstrates that viscosity is independent of shear rate.[37, 38] The results for other particle concentrations are similar.

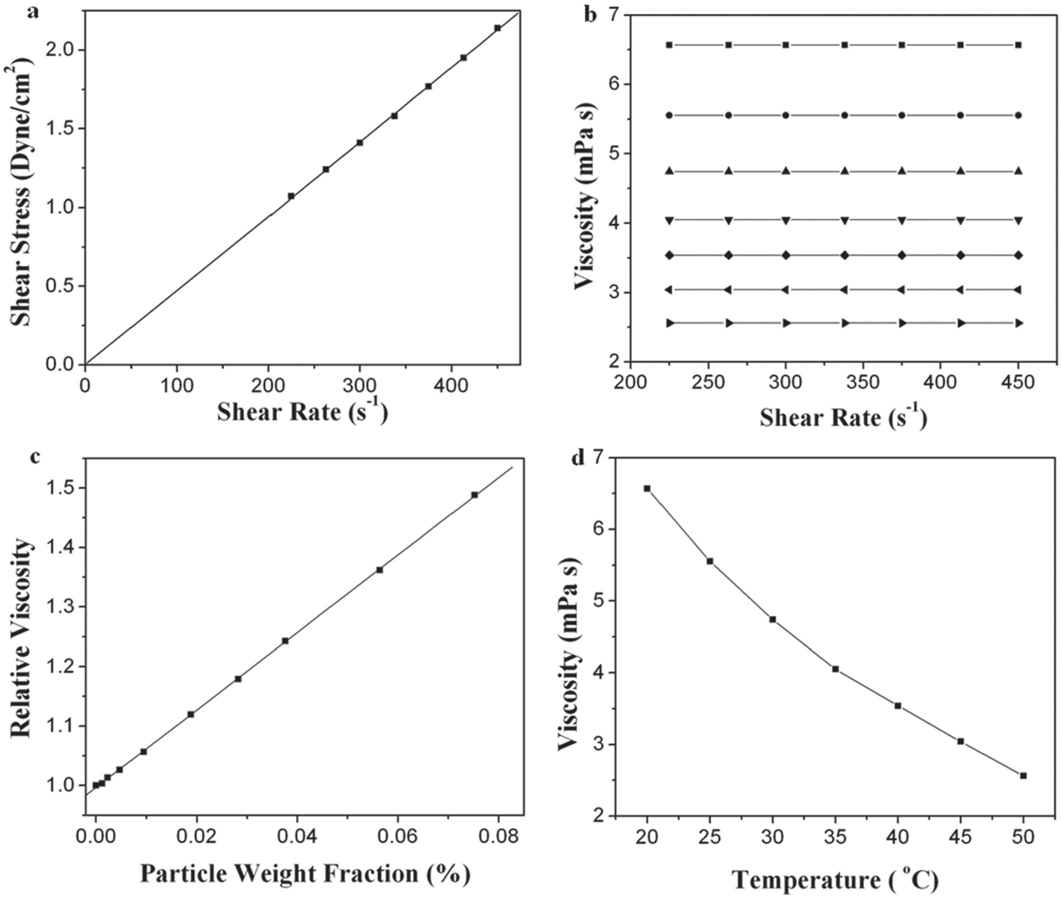

Fig. 7. Rheological measurements. (a) Shear stress versus shear rate at 30 °C for particle loading of 0.096%. (b) Viscosity as a function of shear rate for particle loading of 0.096%. (c) Variation of relative viscosity of the nanofluid with particle weight fraction. (d) Viscosity as a function of temperature for particle loading of 0.096% ► 50 °C, ◄ 45 °C, ♦ 40 °C, ▼ 35 °C, ▲ 30 °C, ● 25 °C, ■ 20 °C.

The viscosity of the above nanofluid was measured at different particle weight fractions at 30 °C and the changes in relative viscosity of the nanofluid with particle weight fraction are shown in Figure 7(c). It is seen from the figure that the viscosity increases with the increase in particle concentration. The effect of temperature on the viscosity of the nanofluid was studied within a range of 20 °C–50 °C and is shown in Figure 7(d). It was seen that the viscosity decreases with the increase in temperature of the fluid. The trend is similar to the one reported earlier.[39, 40]

4. CONCLUSIONS

A method to synthesize copper nanofluid stabilized by PVP has been reported. The method utilizes single step reduction of copper sulphate by ascorbic acid in a mixture of water and ethylene glycol, serving as base fluids. An unprecedented synthesis of hexagonal disc shaped structures of copper nanoparticles by a simple solution phase method has been developed. The variation of synthetic conditions led to the establishment of meticulous control over the particle size. The synthesized fluids were characterized by various techniques and the results were in agreement with each other. The fluid showed Newtonian behavior and stayed stable up to a duration of 3 weeks. An appreciably high thermal conductivity for low particle weight fraction of copper nanoparticles dispersed stably was observed in comparison to that of the thermal conductivity of the base fluid alone.

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