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# Synthesis and thermal conductivity of $Cu_2O$ nanofluids

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ABSTRACT

We apply the chemical solution method to synthesize $Cu_2O$ nanofluids: suspensions of cuprous-oxide ($Cu_2O$) nanoparticles in water, and experimentally study the effect of reactant molar concentration and nanofluid temperature on the thermal conductivity. Substantial conductivity enhancement up to 24% is achievable with the synthesized nanofluids. The nanoparticle shape is variable by adjusting some synthesis parameters. The thermal conductivity shows both sensitivity and nonlinearity to the reactant molar concentration and the nanofluid temperature.



## 1. Introduction

The last decade has witnessed a rapid development of nanofluids, suspensions of nanometer-sized particles in fluids [1]. Thermal conductivity enhancement of nanofluids has been reported by many researchers [1–5]. Such substantial increases in thermal conductivity come from the thermal waves and resonance at the macroscale [6–9] and the nanoparticle Brownian motion, the liquid layering at the liquid–particle interface, the nanoparticle cluster and the nature of heat transport in the nanoparticle from a microscale point of view [1,10–12]. Their high conductivity value and the other distinctive features of nanofluids offer an unprecedented potential for many applications in various fields including energy, bio- and pharmaceutical industry, and chemical, electronic, environmental, material, medical and thermal engineering.

The nanofluids have often been synthesized either by a two-step approach that first generates nanoparticles and subsequently disperses them into base fluids [10–12] or by a single-step *physical* method that simultaneously makes and disperses the nanoparticles into base fluids [4,13–16]. In addition to the challenge of how to effectively prevent nanoparticles from agglomerating or aggregating, the key issue in either of these two approaches is the lack of effective means for synthesizing nanofluids with various microstructures and properties due to either the limitation of available nanoparticle powers in the two-step method or the limitation of the system used in the single-step physical method. In an attempt to synthesize high-quality nanofluids with controllable microstructures, we have recently developed a chemical solution method (CSM) that is a single-step *chemical* method [9,17]. This method enables us to vary and manipulate nanofluid microstructures effectively through adjusting synthesis parameters including the reactant concentration and pH value. Here we apply this method to synthesize two kinds of novel cuprous-oxide ($Cu_2O$) nanofluids: suspensions of spherical $Cu_2O$ nanoparticles in water and suspensions of octahedral $Cu_2O$ nanoparticle in water, and show the variation of their microstructure and conductivity with the reactant concentration. Also reported is the variation of the nanofluid thermal conductivity with the temperature.

## 2. Synthesis

Synthesizing these two types of $Cu_2O$ nanofluids by the CSM is based on following chemical reactions in solution:

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4; \tag{1}$$

$$Cu(OH)_2 \overset{\Delta}{=} CuO + H_2O; \tag{2}$$

$$4CuO + N_2H_4 = 2Cu_2O + N_2 + 2H_2O. \tag{3}$$

The reaction between cupric-sulfate ($CuSO_4$) and sodium-hydrate (NaOH) yields cupric-hydroxide ($Cu(OH)_2$) and sodium-sulfate ($Na_2SO_4$). Under the heating by a constant-temperature (40 °C) water bath with the magnetic stirring (JB-2, Shanghai Leici Equipment Ltd., China), $Cu(OH)_2$ is decomposed into cupric-oxide (CuO) and water ($H_2O$). The hydrazine-hydrate ($N_2H_4$) is then added as a reducer to reduce the cupric-oxide (CuO) into cuprous-oxide ($Cu_2O$). Nitrogen ($N_2$) and water ($H_2O$) are also produced at the same time. To enhance the nanofluid stability and

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**Nomenclature**

| | |
|---|---|
| $a$ | wire radius |
| CV | coefficient of variation |
| $k$ | fluid thermal conductivity |
| $k_r$ | thermal conductivity of residual fluid |
| $m$ | slope |
| $q$ | applied electric power |
| $t$ | time |
| $T$ | temperature |
| $T_{ref}$ | reference temperature |

*Greek symbols*

| | |
|---|---|
| $\alpha$ | thermal diffusivity |
| $\gamma$ | Euler's constant |
| $\sigma_d$ | stand derivation of particle diameter |

*Subscripts*

| | |
|---|---|
| $m$ | mean |
| $r$ | residual |
| $ref$ | reference |

prevent the particle aggregation, some polyvinyl pyrrolidone (PVP; chemical surfactant) is added into $CuSO_4$ solution. In the process, the sodium-hydrate (NaOH) serves not only as a reagent, but also as a mean of adjusting the pH value of mixture for changing particle shape. All the chemicals used in our experiments are with a nominal purity higher than 99% and are purchased from Taikangda Ltd., China. The water was prepared in our laboratory by double distillation.

In our synthesis of nanofluids by the CSM, the used solution amount is 5 ml, 20 ml, 25 ml and 2 ml for $CuSO_4$, PVP, NaOH and $N_2H_4$, respectively. The PVP and NaOH mass fractions in the solution are fixed at 25 g/L and 0.004 g/L, respectively. The pH value of NaOH solution and the molar concentration of $N_2H_4$ solution are 10 and 0.1 mol/L for synthesizing spherical-$Cu_2O$ nanofluids, and 12 and 0.3 mol/L for synthesizing octahedral-$Cu_2O$ nanofluids.

Figs. 1 and 2 show the pictures of the synthesized nanofluids with different values of $CuSO_4$ molar concentration 24 h after its preparation. The fluid is very stable, and no bulk phase separation has been observed. Figs. 3 and 4 typify the SEM images of nanoparticles (Leo 1530FEG, Oxford Instruments, UK), showing that the particles can be changed from a spherical shape to an octahedral one by varying the pH value of NaOH solution and the molar concentration of $N_2H_4$ solution. The average diameter of particles for the case shown in Fig. 3 is 200.5 nm, with a coefficient of variation (CV) of 0.365 (measured by dynamic light scattering system; Delsa Nano C, Beckman Coulter, USA). Here CV is defined by $CV = \sigma_d/d_m$ where $\sigma_d$ is the stand derivation of the diameter and $d_m$ is its mean value. The particles are not so monodispersed mainly because of the difficulty in precisely controlling reactions at microscale while operating at the macroscale (macroreactors). Further studies are required regarding limitations (such as the smallest particle size that could be achieved by the CSM) and improvements of the CSM.

**Fig. 1.** Spherical-$Cu_2O$ nanofluids 24 h after their preparation ($CuSO_4$ molar concentration from 0.01 mol/L to 0.05 mol/L).

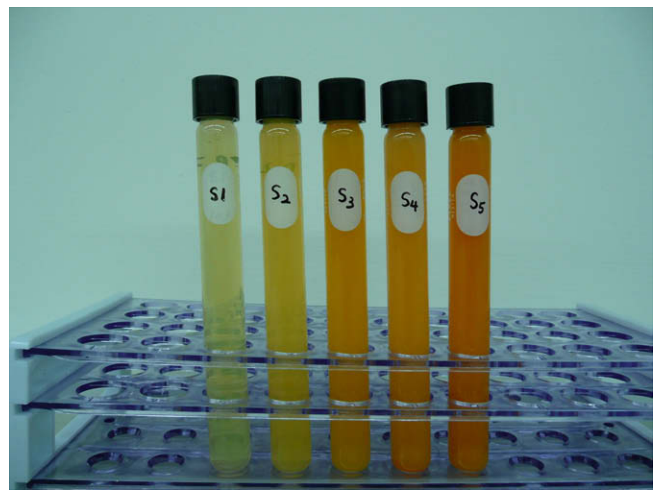

**Fig. 2.** Octahedral-$Cu_2O$ nanofluids 24 h after their preparation ($CuSO_4$ molar concentration from 0.0025 mol/L to 0.002 mol/L).

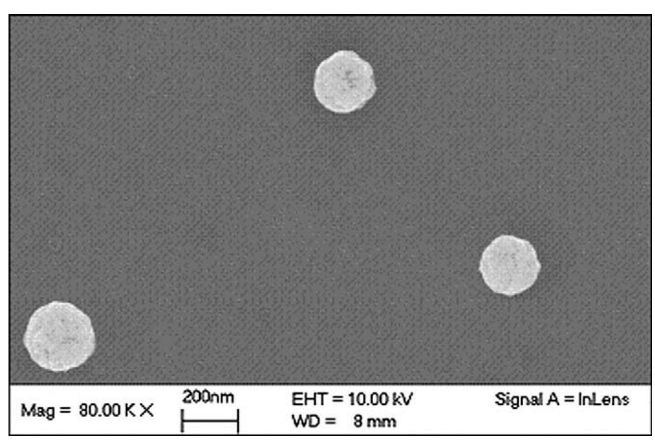


**Fig. 3.** SEM image of some spherical $Cu_2O$ nanoparticles ($CuSO_4$ molar concentration: 0.01 mol/L; at ambient temperature).

## 3. Thermal conductivity

The thermal conductivity of nanofluids can be measured by transient hot-wire (THW, also called transient line heat source method), temperature oscillation (TO) and steady-state (SS) methods [1,10–12,18–20]. The first method is well established as the

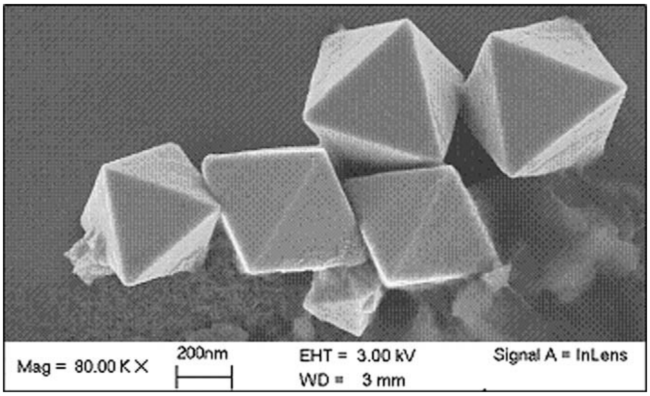


**Fig. 4.** SEM image of octahedral $Cu_2O$ nanoparticles ($CuSO_4$ molar concentration: 0.005 mol/L; at ambient temperature).

most accurate, reliable and robust measurement technique for the thermal conductivity of nanofluids [1,10–12,18,19]. Therefore, we follow [2] in using a THW system for the thermal conductivity measurement.

The THW system used in KD2 system (Decagon Devices, USA) infers thermal conductivity from the temperature response of a thermocouple a short distance away from an electrically heated wire. The relationship between the temperature change and the thermal conductivity is [1,10–12,18–20]:

$$T(t) - T_{ref} = \frac{q}{4\pi k}\left[\ln(t) - \gamma - \ln\left(\frac{a^2}{4\alpha}\right)\right], \tag{4}$$

where $T(t)$ is the temperature at time $t$, $T_{ref}$ a reference temperature, $q$ the electric power applied to the hot-wire, $k$ the thermal conductivity, $\gamma$ the Euler's constant, $a$ the wire radius, and $\alpha$ is the thermal diffusivity of the test fluid. This shows that $\Delta T = T - T_{ref}$ and $\ln(t)$ are linearly related with a slope $m = q/4\pi k$. Linearly regressing $\Delta T$ on $\ln(t)$ yields a slope that, after rearranging, gives the thermal conductivity as

$$k = \frac{q}{4\pi m}, \tag{5}$$

where $q$ is known from the supplied power. Therefore, the thermal conductivity of nanofluids can be determined by measuring the rate at which the temperature rises with time.

The variation of conductivity ratio $k/k_r$ with the $CuSO_4$ molar concentration and nanofluid temperature is shown in Figs. 5 and 6 for the two types of nanofluids, respectively. Here $k$ and $k_r$ are the thermal conductivity of the nanofluid and the residual fluid (the left fluid after removing the nanoparticles by strongly centrifuging the nanofluid sample for 40 min), respectively, measured by the standard KD2 system (Decagon Devices, USA). The probe radius and length in the KD2 system are 0.64 mm and 60 mm, respectively. Its controller waits for 30 s to ensure temperature stability, and then heats the probe for 30 s. It then monitors the cooling rate for 30 s. The accuracy of the KD2 system (5% for thermal conductivity) has been verified by a careful calibration before experiments through measuring thermal conductivities of water and various oils and comparing with those well-documented in the literature [2]. For every sample and temperature, we repeat our measurement three times with a time gap of 5 min in between and an average values over the three readings are used in Figs. 5 and 6.

For both types of nanofluids, the measured conductivity shows a high nonlinearity to both the $CuSO_4$ molar concentration and the temperature, which is consistent with the theory of thermal waves and resonance [6,8,21]. Variation in the $CuSO_4$ molar concentration leads to a change in nanofluid thermal conductivity through changing the nanofluid microstructure. The nanofluid thermal conductivity also shows a strong sensitivity to the temperature. While the fluid conductivity could be reduced by adding the nanoparticles in some cases, an extraordinary conductivity enhancement—up to a 24% enhancement [at the $CuSO_4$ molar concentration of 0.05 mol/L (0.02 mol/L) and the fluid temperature of 30 °C (40 °C) for spherical (octahedral) $Cu_2O$ nanofluids]—is achievable for both types of nanofluids. The measured $k/k_r$ data also show that the conductivity enhancement with spherical $Cu_2O$ nanoparticles is higher than that with octahedral $Cu_2O$ nanoparticles. The fact that $k/k_r$ varies from 0.83 to 1.24 (Figs. 5 and 6) agrees with the finding in

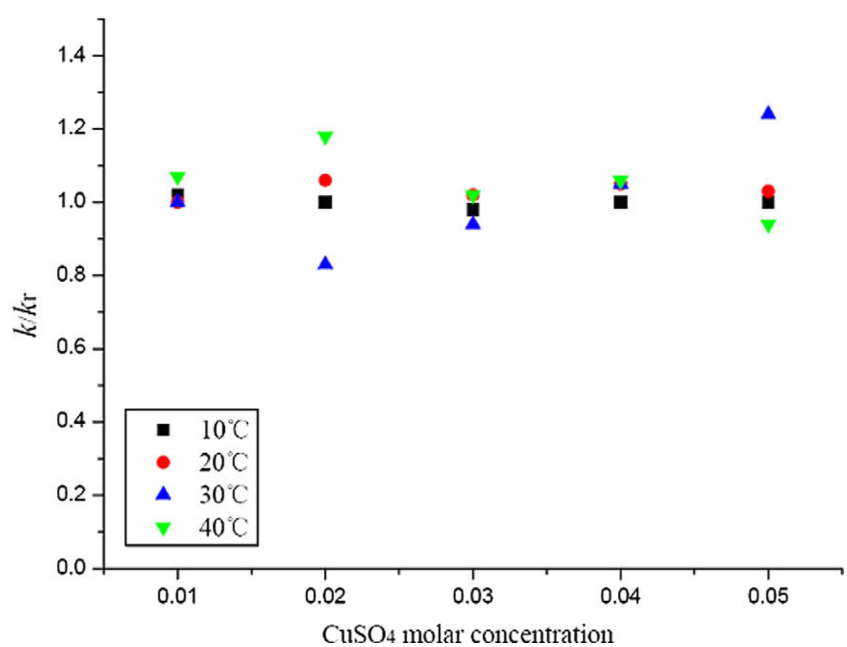


**Fig. 5.** Variation of $k/k_r$ with the $CuSO_4$ molar concentration and the nanofluid temperature for spherical $Cu_2O$ nanofluids ($k$: nanofluid thermal conductivity; $k_r$: residual fluid conductivity).

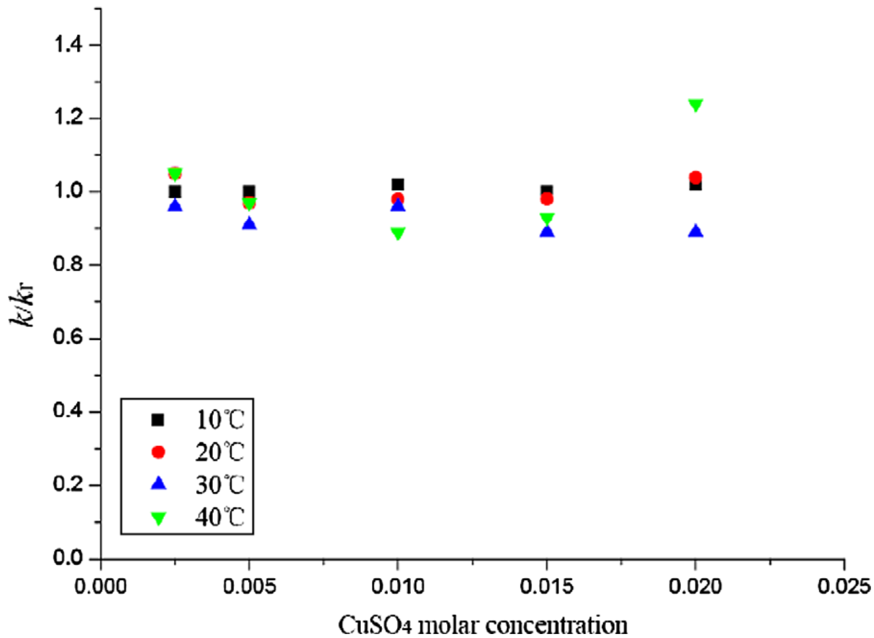


**Fig. 6.** Variation of $k/k_r$ with the $CuSO_4$ molar concentration and the nanofluid temperature for octahedral $Cu_2O$ nanofluids ($k$: nanofluid thermal conductivity; $k_r$: residual fluid conductivity).

[22,23] that high-conductivity nanoparticles not always enhance fluid thermal conductivity.

## 4. Concluding remarks

$Cu_2O$ nanofluids can be synthesized by using the chemical solution method. The nanoparticle can be varied from a spherical shape to an octahedral one by adjusting some synthesis parameters. The nanofluid thermal conductivity can also be controlled by either the synthesis parameters or its temperature. A conductivity enhancement up to 24% is achievable with both types of the $Cu_2O$ nanofluids.

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