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Preparation and thermal conductivity of CuO nanofluid via a wet chemical method

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Abstract

In this article, a wet chemical method was developed to prepare stable CuO nanofluids. The influences of synthesis parameters, such as kinds and amounts of copper salts, reaction time, were studied. The thermal conductivities of CuO nanofluids were also investigated. The results showed that different copper salts resulted in different particle morphology. The concentration of copper acetate and reaction time affected the size and shape of clusters of primary nanoparticles. Nanofluids with different microstructures could be obtained by changing the synthesis parameters. The thermal conductivities of CuO nanofluids increased with the increase of particle loading.

Introduction

Nanofluid is a new class of heat transfer fluids containing nano-sized particles, fibers, or tubes that are stably suspended in a carrier liquid [1-4]. Since the concept of nanofluid was proposed [1], more and more researchers have been committing to it because of the thermal properties and the potential applications associated with heat transfer, mass transfer, wetting, and spreading [1-7].

Preparation of stable nanofluids is the first step and key issue of nanofluid research and applications. At present, some methods, such as dispersion method, direct evaporation condensation method (DECM), submerged-arc nanoparticles synthesis system (SANSS), laser ablation method, and wet chemical method, etc. [2-4,8-12], have been applied to synthesize nanofluids. Dispersion method is a two-step method [13-18], in which commercial nanoparticles are dispersed into base fluid under ultrasonic agitation or mechanical stirring. The advantage of this method is that it could prepare nanofluids in a large scale. However, nanoparticle aggregations are difficult to breakup under ultrasonication or stirring. Thus, stability and thermal conductivity of nanofluids prepared with dispersion method are usually not ideal. DECM, SANSS, and laser ablation method are one-step physical methods [19-22], in which metal materials are vaporized by physical technology and cooled into liquids to obtain nanofluids. These physical methods provide excellent control on the particle size and can produce stable nanofluids. However, it is difficult to synthesize nanofluids in a large scale. Our team has developed a wet chemical method with which several kinds of nanofluids have been produced successfully [23-25]. It has the advantages in terms of controlling the particle size, reducing agglomeration of the nanoparticles, and producing nanofluids in a large scale. This method is a promising technique for commercial synthesis of nanofluids. However, the research about the influences of synthesis parameters on nanofluids microstructure and properties are scarce, though it is very important for industrial synthesis of nanofluids.

In this study, CuO nanofluid was synthesized with a wet chemical method. The influences of synthesis parameters, such as kinds and amounts of copper salts, reaction time, were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), and particle size analyzer. The thermal conductivity of CuO nanofluids was also studied.

Experimental section

All of the reagents used in the experiment were of analytic purity. Figure 1 shows the preparation process. The synthesis process is based on the following chemical reactions in solution:

$$Cu^{2+} + 2NaOH = Cu(OH)_2 + 2Na^+ \quad (1)$$

$$Cu(OH)_2 \triangleq CuO + H_2O \quad (2)$$

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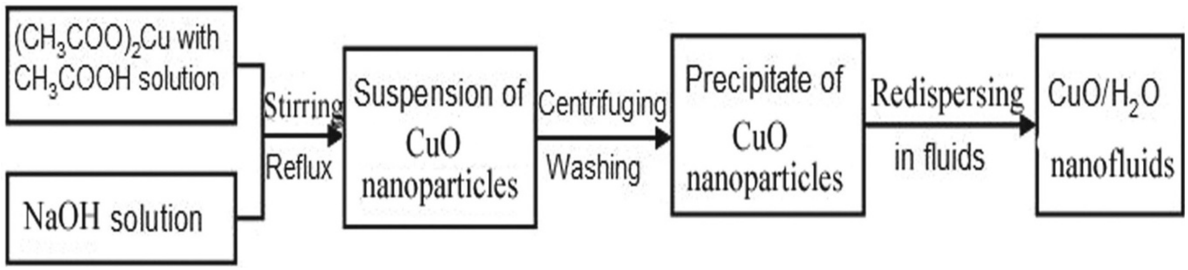

Figure 1 Preparation process of CuO aqueous nanofluids.

In a typical procedure, 600 ml 0.2 M copper acetate ($Cu(CH_3COO)_2{\cdot}H_2O$) solution and 2 ml glacial acetic acid (CH_3COOH) were added into a round-bottomed flask and heated to boiling under magnetic stirring. Then, 30 ml 8 M sodium hydroxide (NaOH) solution was poured into the flask. The color of the solution turned from blue to black immediately, and a black suspension formed simultaneously. The reaction was carried out under stirring and boiling for 2 h. The mixture was cooled to room temperature and centrifuged. Then, a wet CuO precipitate was obtained. The wet precipitate was washed twice with distilled water to remove the impurity ions. CuO nanofluids of different volume fractions were obtained by re-dispersing the wet precipitate into different amounts of distilled water under ultrasonic vibration (120 W, 40 Hz).

To study the influences of synthesis parameters on the final products, the kinds and amounts of copper salts, reaction time were changed while keeping all other experimental parameters same as in the typical run.

The XRD pattern of the powder (obtained by drying the washed wet precipitate) was recorded on a Rigaku D/Max r-A diffractometer. TEM images were captured on a JEM-2000EX instrument. The nanofluids were diluted with distilled water and dispersed by ultrasonic. Then, one drop was placed on a carbon-coated copper grid and left to dry at room temperature. Particle size distributions of the nanoparticles in nanofluids were measured with a Zetasizer 3000HS (Malvern) particle size analyzer. The samples were also prepared by diluting the nanofluids with distilled water and dispersed by ultrasonic. Thermal conductivity was measured using a KD2 Pro Thermal Property Analyzer (Decagon Inc., Pullman, WA, USA) based on the transient hot wire method. The nanofluids were sonicated for about 30 min before measurements so that the samples would have the same dispersity.

Results and discussion

Characterization of typical sample

Figure 2a is the XRD pattern of the typical sample. All the peaks on the XRD pattern can be indexed to that of monoclinic CuO according to the literature (JCPDS, FileNo 80-1916). The average crystal size is 10.4 nm calculated using Debye-Scherrer formula. Figure 2b shows a TEM image of the typical sample. The size of primary particles is about 10 nm, which is in good agreement with the result of XRD. The primary particles aggregate to chain-like clusters with width of 10 nm and length of 50-150 nm (5-15 primary particles). Figure 2c is the size distribution of the typical sample. The particle size is about 20-80 nm, and the size distribution is narrow. The larger particle size is due to the short clusters shown in the TEM image. Figure 2d is the real photo of the products. The obtained CuO nanofluids could remain stable for 5 months with no visible precipitation at the bottom.

Influences of copper salts

By replacing $Cu(CH_3COO)_2{\cdot}H_2O$ with $CuCl_2{\cdot}2H_2O$ and $Cu(NO_3)_3{\cdot}3H_2O$, respectively, different CuO nanofluids were prepared with all other experimental parameters unchanged. Figure 3 is the TEM images of above two nanofluids. When using $CuCl_2{\cdot}2H_2O$ as copper source (Figure 3a), the obtained particles in nanofluids are flake-like particles with width of 10-80 nm and length of 100-300 nm. When using $Cu(NO_3)_2{\cdot}3H_2O$ (Figure 3b), the particles are aggregations of thin sticks and particles of about 15-50 nm. It has been approved by some researchers that the anions could affect the growth orientation and process of nanoparticles by adsorption or coordination interaction of anions with special crystal face of particles [26]. Therefore, by changing copper source, we could obtain particles with different morphology.

Influences of copper acetate concentration

Figure 4a,b are the TEM images of CuO nanofluids prepared with copper acetate concentration of 0.1 and 0.4 $mol{\cdot}l^{-1}$, respectively. Compared with typical nanofluids (obtained with concentration of 0.2 $mol{\cdot}l^{-1}$), it is clear that the size of primary nanoparticles remain almost the same (about 10 nm), but the morphology and size of nanoparticles cluster change with copper

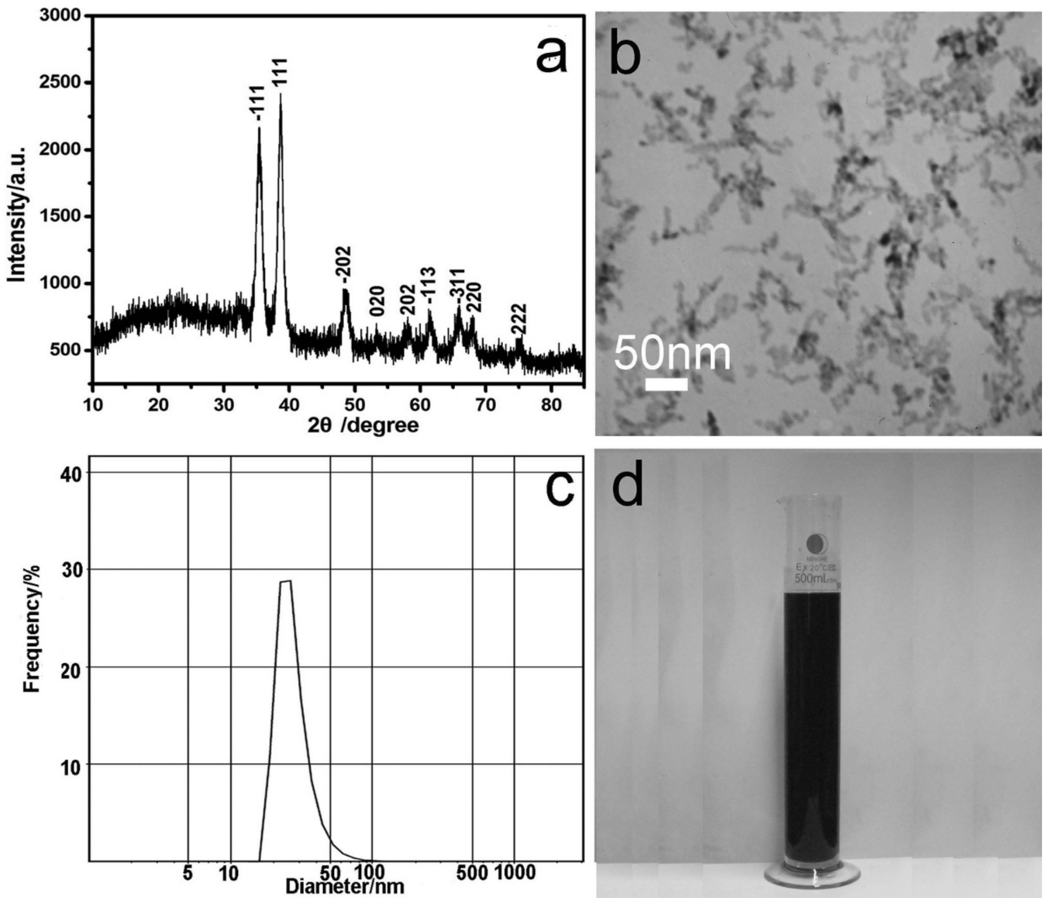

Figure 2 Characterization of the typical sample. **(a)** XRD pattern; **(b)** TEM image; **(c)** size distribution; **(d)** real photo.

acetate concentration. When the concentration is 0.1 mol·l^{-1}, the clusters are also chain-like structures with lengths in the range of 100-200 nm. It is longer than the clusters in typical samples. When the concentration is 0.4 mol·l^{-1}, the primary nanoparticles aggregate and form irregular clusters consisted of 2-30 primary nanoparticles. The formation of chain-like cluster may be due to the orientation adhesion mechanism [27]. When the concentration of copper acetate is low, the collision probability of primary CuO nanoparticles is

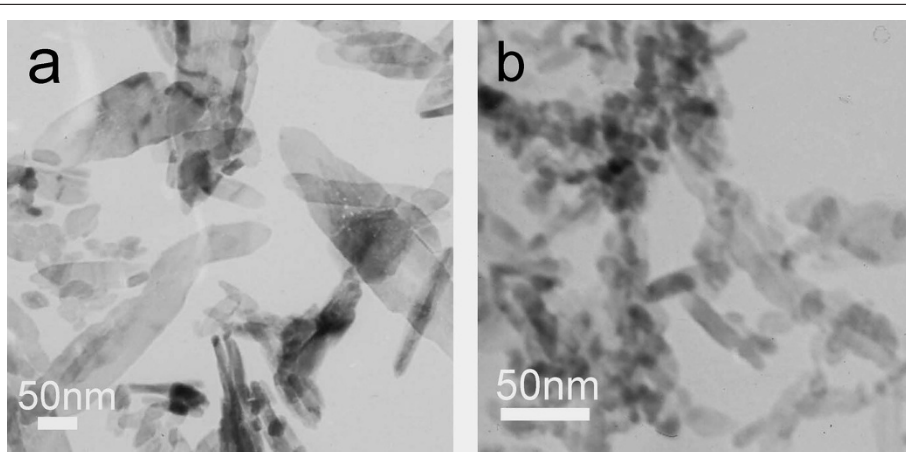

Figure 3 TEM images of CuO nanofluids prepared with different copper salts. **(a)** $CuCl_2·2H_2O$; **(b)** $Cu(NO_3)_2·3H_2O$.

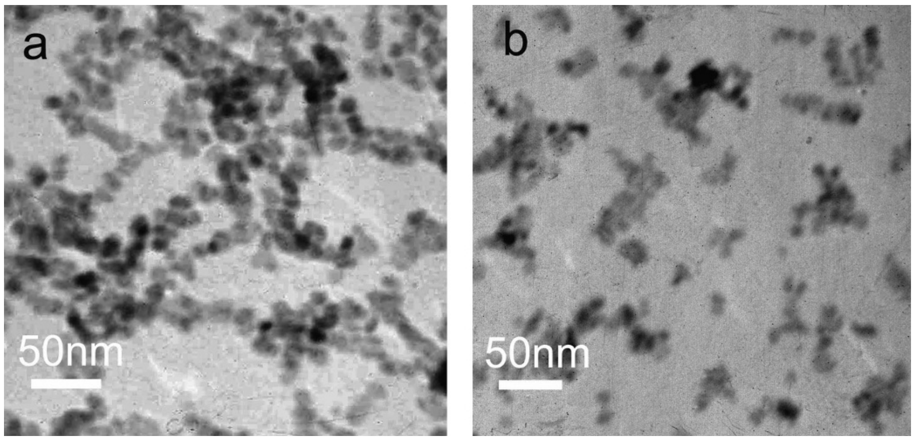

Figure 4 TEM images of CuO nanofluids prepared with different concentrations of $(CH_3COO)_2Cu{\cdot}H_2O$ solution. **(a)** 0.1 mol·l^{-1}; **(b)** 0.4 mol·l^{-1}.

low; thus, the orientation adhesion is preponderant in the reaction process. Therefore, by changing the concentration of copper acetate, the size and structure of cluster could be adjusted.

Influence of reaction time

Figure 5 is the TEM images of CuO nanofluids obtained with different reaction times. When the reaction time is 12 h (Figure 5a), average size of CuO primary nanoparticles is about 10 nm. CuO nanoparticles form flexural chains consisting of 30-50 primary particles. It is longer than the chain in typical sample (Figure 2b). When the reaction time was increased to 25 h (Figure 5b), the size of the primary particles is also about 10 nm, but the chain-like clusters do not exist any more. Instead, there are small aggregates composed of several primary particles. As mentioned above, the formation mechanism of chain-like cluster is orientation adhesion. With the increase of reaction time, the orientation adhesion degree increases; and thus, the length of the cluster increases. Why do the chain-like clusters destroy when the reaction time is 25 h? It needs more detailed research in future studies. The above results show that different microstructures could be obtained through changing the reaction time.

Thermal conductivity of CuO nanofluids

Figure 6 shows the thermal conductivity ratio of the typical sample, defined as k/k_0, where k and k_0 are the thermal conductivities of the nanofluids and the base media (H_2O) respectively, as a function of the particle volume fraction at 25°C. The thermal conductivity of the base fluid (H_2O) was measured, and it had an average value of 0.580 $W{\cdot}m^{-1}{\cdot}K^{-1}$. It can be seen that the thermal conductivity ratio increases as the particle volume fraction increases. This is in good agreement with some research, in which the thermal conductivity of nanofluids also increase linearly with the particle loading [28,29]. On comparing with some reported experimental results of CuO nanofluids, the current

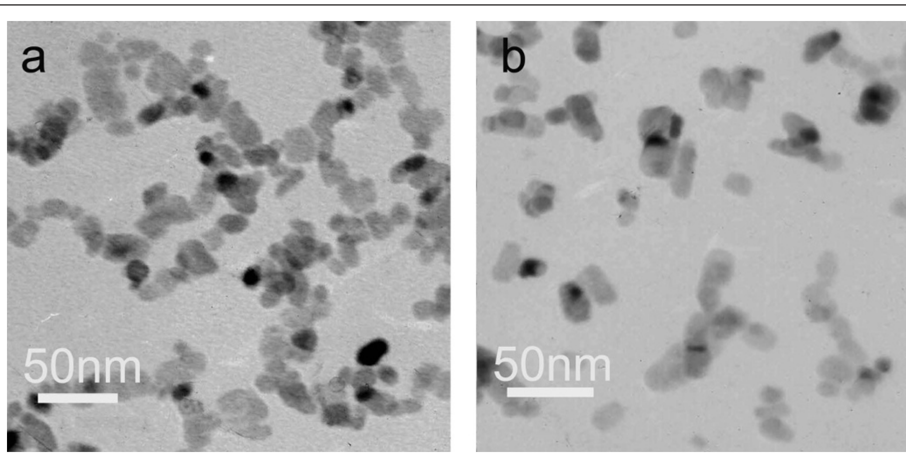

Figure 5 TEM images of CuO nanofluids synthesized under different reaction times. **(a)** 12 h; **(b)** 25 h.

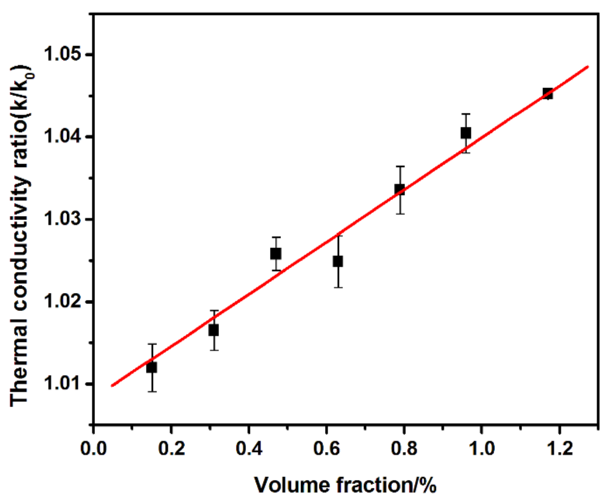

Figure 6 Thermal conductivity ratio as a function of CuO volume fraction at 25°C.

data are found to be close to Lee et al.'s data, Das et al.'s data, and Liu et al.'s data [30-32], suggesting the potential application as heat transfer fluids.

Conclusion

A wet chemical method to synthesize stable CuO nanofluids in a large-scale was developed successfully. The influences of synthesis parameters on nanofluids microstructures were investigated. Different copper salts resulted in different particle morphologies. The concentration of copper acetate and reaction time affected the size and shape of clusters of primary nanoparticles. Nanofluids with different microstructures could be obtained through changing the synthesis parameters. The thermal conductivity of CuO nanofluids increased with the increase of particle loading. It is expected that this method can be extended to synthesize other nanofluids.

Abbreviations

DECM: direct evaporation condensation method; SANSS: submerged arc nanoparticles synthesis system; TEM: transmission electron microscopy; XRD: X-ray diffraction.

Authors' contributions

HZ designed and guided all aspects of the work. DH carried out the experiments and drafted the manuscript. ZM, DW and CZ participated in the design of the study and revised the manuscript.

Competing interests

The authors declare that they have no competing interests.

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References

1. Choi SUS: **Enhancing thermal conductivity of fluids with nanoparticles.** In *Developments and Applications of Non-Newtonian Flows.* Edited by: Singer DA, Wang HP. New York: American Society of Mechanical Engineers; 1995:99-105.
2. Das SK, Choi SUS, Yu W, Pradeep T: *Nanofluids: Science and Technology* New Jersey: John Wiley & Sons, Inc; 2007.
3. Zhu HT, Liu SQ, Xu L, Zhang CY: **Preparation, characterization and thermal properties of nanofluids.** In *Leading Edge Nanotechnology Research Developments.* Edited by: Sabatini DM. New York: NOVA Science Publisher; 2008:5-38.
4. Wu DX, Zhu HT, Wang LQ, Liu LM: **Critical issues in nanofluids preparation, characterization and thermal conductivity.** *Curr Nanosci* 2009, **5**:103-112.
5. Krishnamurthy S, Lhattacharya P, Phelan PE, Prasher RS: **Enhanced mass transport in nanofluids.** *Nano Lett* 2006, **6**:419-423.
6. Coursey JS, Kim J: **Nanofluid boiling: The effect of surface wettability.** *Int J Heat Fluid Fl* 2008, **29**:1577-1585.
7. Wasan DT, Nikolov AD: **Spreading of nanofluids on solids.** *Nature* 2003, **423**:156-159.
8. Choi SUS: **Nanofluids: From vision to reality through research.** *J Heat Transfer* 2009, **131**:0331061-0331069.
9. Li YJ, Zhou JE, Tung S, Schneider E, Xi SQ: **A review on development of nanofluid preparation and characterization.** *Powder Technol* 2009, **196**:89-101.
10. Zhang YX, Jiang W, Wang LQ: **Microfluidic synthesis of copper nanofluids.** *Microfluid Nanofluid* 2010, **9**:727-735.
11. Wei XH, Wang LQ: **Microfluidic method for synthesizing Cu_2O nanofluids.** *J Thermophys Heat Transfer* 2010, **24**:445-448.
12. Karthikeyan NR, Philip J, Raj B: **Effect of clustering on the thermal conductivity of nanofluids.** *Mater Chem Phys* 2008, **109**:50-55.
13. Xuan YM, Li Q: **Heat transfer enhancement of nanofluids.** *Int J Heat Fluid Fl* 2000, **21**:58-64.
14. Choi SUS, Zhang ZG, Yu W, Lockwood FE, Grulke EA: **Anomalous thermal conductivity enhancement in nanotube suspensions.** *Appl Phys Lett* 2001, **79**:2252-2254.
15. Xie HQ, Lee H, Youn W, Choi M: **Nanofluids containing multiwalled carbon nanotubes and their enhanced thermal conductivities.** *J Appl Phys* 2003, **94**:4967-4971.
16. Hong TK, Yang HS, Choi CJ: **Study of the enhanced thermal conductivity of Fe nanofluids.** *J Appl Phys* 2005, **97**:064311-0643114.
17. Ko GH, Heo K, Lee K, Kim DS, Kim C, Sohn Y, Choi M: **An experimental study on the pressure drop of nanofluids containing carbon nanotubes in a horizontal tube.** *Int J Heat Mass Transfer* 2007, **50**:4749-4753.
18. Wu SY, Zhu SY, Zhang XR, Huang J: **Preparation and melting/freezing characteristics of Cu/Paraffin nanofluid as phase-change material (PCM).** *Energy Fuels* 2010, **24**:1894-1898.
19. Eastman JA, Choi SUS, Li S, Yu W, Thompson LJ: **Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles.** *Appl Phys Lett* 2001, **78**:718-720.
20. Lo CH, Tsung TT, Chen LC: **Shape-controlled synthesis of Cu-based nanofluid using submerged arc nanoparticle synthesis system (SANSS).** *J Cryst Growth* 2005, **277**:636-642.
21. Chang H, Chen H, Jwo CS, Chen SL: **Electrostatic and sterical stabilization of CuO nanofluid prepared by vacuum arc spray nanofluid synthesis system (ASNSS).** *Mater Trans* 2009, **50**:2098-2103.
22. Phuoc TX, Soong Y, Chyu MK: **Synthesis of Ag-deionized water nanofluids using multi-beam laser ablation in liquids.** *Opt Lasers Eng* 2007, **45**:1099-1106.
23. Zhu HT, Lin YS, Yin YS: **A novel one-step chemical method for preparation of copper nanofluids.** *J Colloid Interface Sci* 2004, **277**:100-103.
24. Zhu YS, Zhang CY, Liu SQ, Tang YM, Yin YS: **Effects of nanoparticle clustering and alignment on thermal conductivities of Fe_3O_4 aqueous nanofluids.** *Appl Phys Lett* 2006, **89**:0231231-0231233.
25. Zhu HT, Zhang CY, Tang YM, Wang JX: **Novel synthesis and thermal conductivity of CuO nanofluid.** *J Phys Chem C* 2007, **111**:1646-1650.
26. Zhong WZ, Hua SK: **Anion coordination polyhedra and crystal morphology.** *Morphology of Crystal Growth* Beijing: Science Publisher; 1999, 114-126.
27. Teo JJ, Chang Y, Zeng HC: **Fabrications of hollow nanocubes of Cu_2O and Cu via reductive self-assembly of CuO nanocrystals.** *Langmuir* 2006, **22**:7369-7377.

28. Shima PD, Philip J, Raj B: Influence of aggregation on thermal conductivity in stable and unstable nanofluids. *Appl Phys Lett* 2010, **97**:1531131-1531133.
29. Philip J, Shima PD, Raj B: Evidence for enhanced thermal conduction through percolating structures in nanofluids. *Nanotechnology* 2008, **19**:3057061-3057067.
30. Lee S, Choi SUS, Li S, Eastman JA: Measuring thermal conductivity of fluids containing oxide nanoparticles. *J Heat Transfer* 1999, **121**:280-289.
31. Das SK, Putra N, Thiesen P, Roetzel W: Temperature dependence of thermal conductivity enhancement for nanofluids. *J Heat Transfer* 2003, **125**:567-574.
32. Liu MS, Lin MCC, Huang IT, Wang CC: Enhancement of thermal conductivity with CuO for nanofluids. *Chem Eng Technol* 2006, **29**:72-77.

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