JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 24, No. 2, April–June 2010

Technical Note

Microfluidic Method for Synthesizing Cu_2O Nanofluids

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DOI: 10.2514/1.48984

I. Introduction

NANOFLUIDS, fluid suspensions of nanometer-sized particles, have recently been demonstrated to have thermal conductivities far superior to that of the liquid alone [1–4]. This and their other distinctive features offer unprecedented potential for many applications in various fields, including energy, biological, pharmaceutical, chemical, electronic, environmental, material, medical, and thermal engineering industries [1–8]. Yet the functional outcomes of existing nanofluids have not been satisfactory because of the inadequacies of conventional synthesis approaches in engineering microstructures and properties of nanofluids [1–9].

For creating nanofluids by design, we have recently developed a one-step chemical solution method (CSM) that is capable of synthesizing nanofluids of various microstructures [9–11]. The method has been successfully applied to produce the nine kinds of nanofluids [9–11]. The nanofluids synthesized by the CSM have both higher conductivity enhancement and better stability than those produced by other methods. The CSM is also distinguished from the others by its controllability. The nanofluid microstructure can be easily varied and manipulated by adjusting synthesis parameters such as temperature, acidity (pH), ultrasonic and microwave irradiation, types and concentrations of reactants and additives, and the order in which the additives are added to the solution [9–11].

Problems with the CSM come from that reactions take place in macroscale batch reactors such as beakers and flasks. The CSM uses a bottom-up approach to generate nanoparticles through chemical reactions in the liquid phase, and thereby it has the potential to manipulate atoms and molecules for synthesis of tailor-made nanofluids. However, the difficulty of controlling the microscale while operating at the macroscale is insuperable. Mixing in a macroscale batch reactor is usually achieved by stirring. In this case, the fluid entity is broken into fragments by circular motion. The last part of mixing takes place based on molecular diffusion. In the diffusion process, the mixing time t depends on the diffusion path d in the form of $t \propto d^2/D$, where D is the diffusion coefficient. Therefore, if the diffusion path becomes smaller, the mixing time becomes shorter. However, it is very difficult to make small-sized fragments by conventional stirring in solution phase. At the macroscale, therefore, mixing time is usually much larger than reaction time. The reaction rate is normally determined by the mixing time and is usually very low. Moreover, the longer mixing time and lack of effective ways to accurately control mixing also lead to poor product selectivity of competitive parallel reactions and competitive consecutive reactions, thereby yielding poor quality of synthesized nanofluids containing some undesired side products. Because of the work-up demand, a batch-model operation is not commercially economical. The repeatability of nanofluids' structures is also poor with the batch-model operation.

To resolve these critical issues, we propose to replace batch-based macroreactors in the CSM by continuous-flow microfluidic microreactors, allowing a continuous and scalable (simply by numbering-up) synthesis of nanofluids with a more accurate and effective control over particle microstructures such as the size, distribution, and shape. Here, we report such a microfluidic system for synthesizing Cu_2O nanofluids: suspensions of Cu_2O nanoparticles in water.

II. Synthesis

Synthesizing the Cu_2O nanofluids by the CSM is based on following chemical reactions, in order [11]:

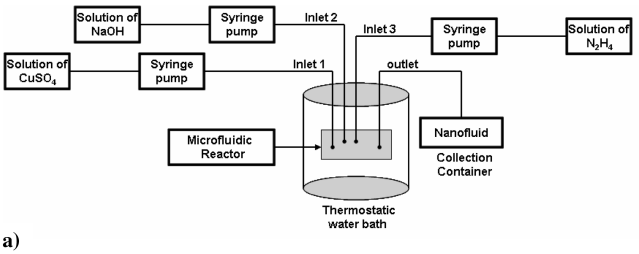
$$Cu\,SO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4 \tag{1}$$

$$Cu\,(OH)_2 \triangleq CuO + H_2O \tag{2}$$

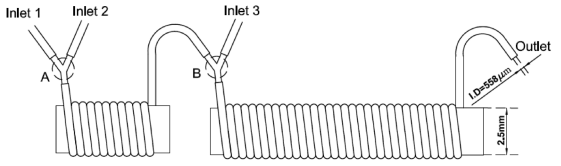
$$4CuO + N_2H_4 = 2Cu_2O + N_2 + 2H_2O \tag{3}$$

The reaction between cupric-sulfate ($CuSO_4$) and sodium-hydrate (NaOH) yields cupric-hydroxide ($Cu(OH)_2$) and sodium sulfate (Na_2SO_4) [Eq. (1)]. The cupric-hydroxide $Cu(OH)_2$ will quickly decomposed into cupric-oxide (CuO) and water (H_2O) under some heating [Eq. (2)]. The cupric-oxide (CuO) is then reduced into cuprous-oxide (Cu_2O) with the hydrazine-hydrate (N_2H_4) as the reducer and nitrogen (N_2) and water (H_2O) as the byproducts [Eq. (3)].

Figure 1a shows the microfluidic system in which these chemical reactions take place. The $CuSO_4$ and NaOH fluids are pumped by



a)



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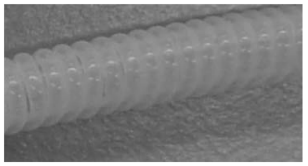

c)

Fig. 1 Microfluidic one-step chemical solution method for Cu_2O nanofluids synthesis: a) test setup, b) microfluidic reactor, and c) PTFE microbore tubing coil.

Received 19 January 2010; revision received 1 February 2010; accepted for publication 2 February 2010.

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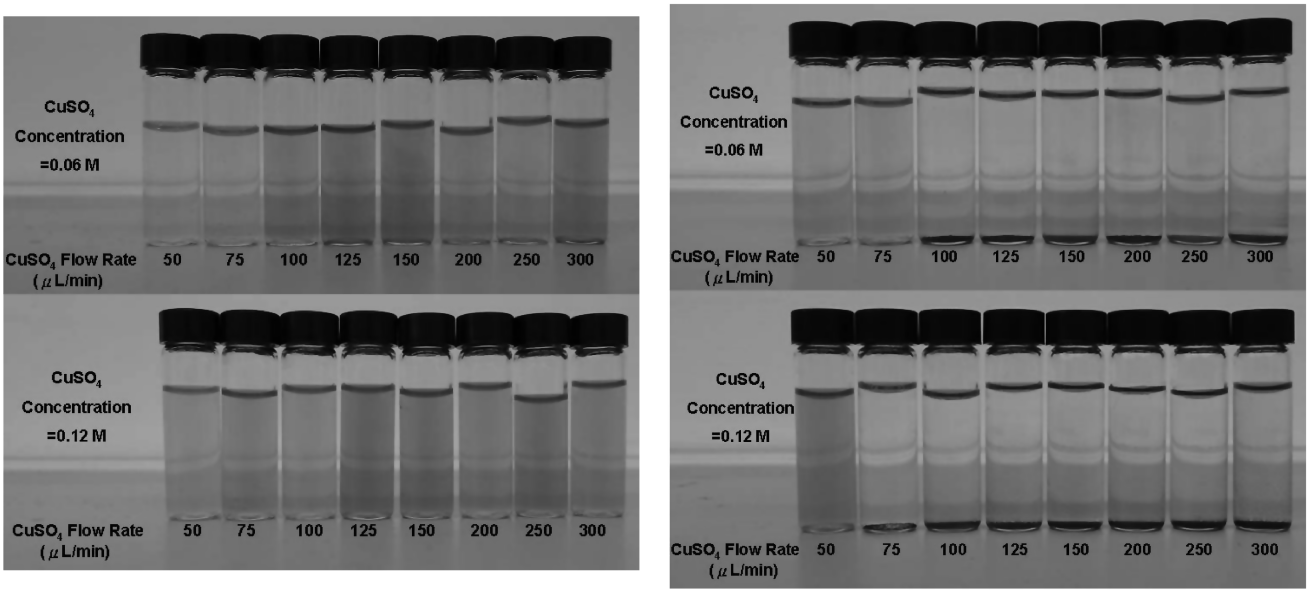
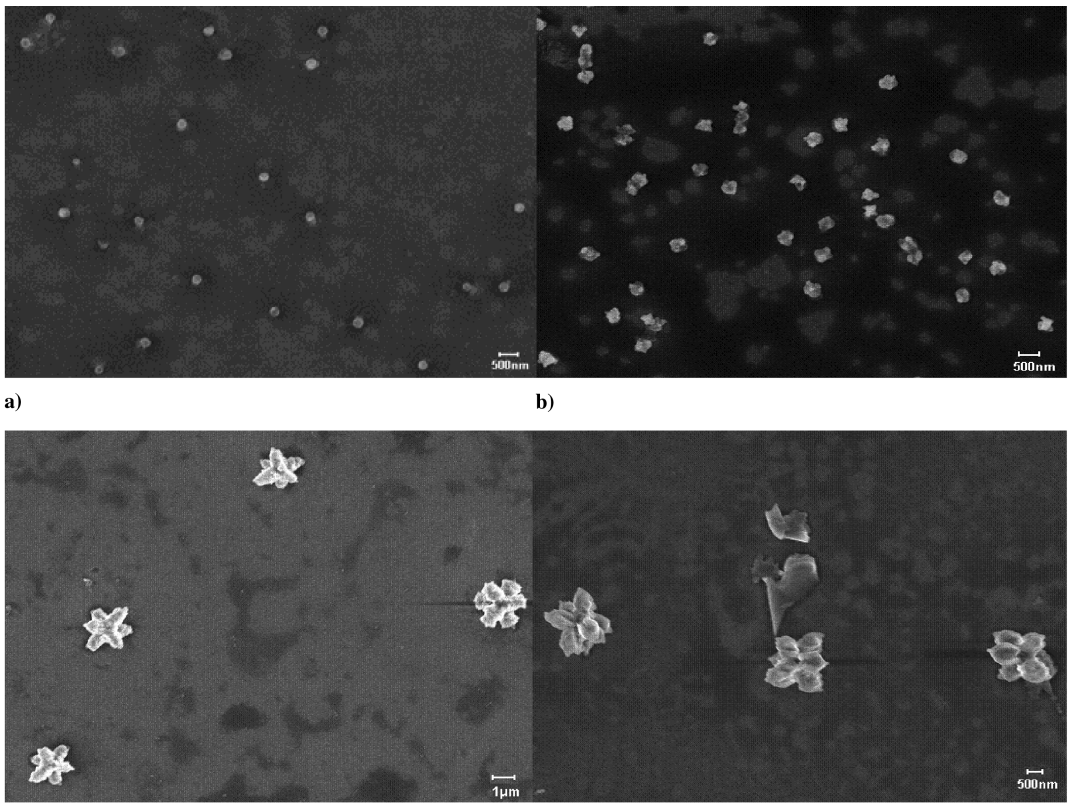


a) 24-hour standing **b) 100-hour standing**

Fig. 2 Cu_2O nanofluids synthesized at different $CuSO_4$ molar concentrations and flow rates: a) after 24 h standing; b) after 100 h standing.

high-precision syringe pumps (Cole-Parmer Instrument Company) and forced to flow through the microfluidic reactor (Fig. 1b) that is immersed in a thermostatic water bath with a fixed temperature 40°C (IKA RCT Basic and EDS-D5). As they travel from point A to point B and receive heat from the water bath, the chemical reactions (1) and (2) take place. The N_2H_4 fluid is injected into the microfluidic reactor from inlet 3 (Fig. 1b) also by the high-precision syringe pump (Cole-Parmer Instrument Company); and the chemical reaction (3) takes place as the fluid streams travel further in the microfluidic reactor towards its outlet (Fig. 1b). The output channels of the microfluidic reactor allow the nanofluids to vent to the collecting container at atmosphere pressure.

By this method, we can continuously synthesize Cu_2O nanofluids whose microstructures can be varied by adjusting synthesis parameters such as reactant concentrations, flow rates of reactant fluids and geometry of microfluidic reactor. All the chemicals used in our experiments are with a nominal purity higher than 99% and used as received (Taikangda, Ltd.). The water is prepared in our laboratory by double distillation. NaOH solution is prepared to have a fixed pH value 12. The N_2H_4 concentration is fixed at 0.3 M. To enhance the



a) **b)**

c) **d)**

Fig. 3 SEM images of some Cu_2O particles showing $CuSO_4$ concentrations and $CuSO_4$ flow rates, respectively, of a) 0.12 M and 300 μL/min, b) 0.06 M and 75 μL/min, c) 0.06 M and 100 μL/min, and d) 0.06 M and 250 μL/min.

Table 1 Variations of particle average diameter (nm) with the $CuSO_4$ concentration and flow rate

	$CuSO_4$ flow rate, μL/ min							
$CuSO_4$ concentration	50	75	100	125	150	200	250	300
0.06 M	103.4	81.7	116.0	131.1	84.3	154.3	129.7	199.2
0.12 M	271.6	374.9	194.1	147.9	176.2	211.6	329.8	197.8

nanofluid stability and prevent the particle aggregation, 5 g/L polyvinyl pyrrolidone (PVP, a chemical surfactant) is premixed with $CuSO_4$ solution. We fix the $CuSO_4$ molar concentration at 0.06 and 0.12 M, respectively, to investigate its effect on the nanofluids microstructure and thermal conductivity. For each of two $CuSO_4$ concentration values, we examine the effect of fluid flow rates by setting the $CuSO_4$ flow rate at 50, 75, 100, 125, 150, 200, 250, and 300 μL/ min, respectively, and keeping the flow rate ratio of $CuSO_4$, NaOH, and N_2H_4 fluids as 1:1:2. The flow rates are controlled and measured by the syringe pumps.

The microfluidic reactor consists of 4-m-long polytetrafluoroethylene (PTFE) microbore tubing coil with an inner diameter of 558 μm (Cole-Parmer Instrument Company), which winds tightly on a cylinder of 2.5 mm in diameter (Figs. 1b and 1c). The two parts of the coil are connected by a Y-type connector (Cole-Parmer Instrument Company); and their lengths are 1 and 3 m, respectively. Both are long enough to ensure the completion of reactions (1) and (2) in the first part and reaction (3) in the second part, respectively. This microfluidic reactor can have a very rapid mixing between reactant fluids due to both the short diffusion length and the centrifugal-force-driven transverse secondary flow in curved channels [12–15].

III. Results and Discussion

Figure 2 shows the synthesized nanofluids with different values of $CuSO_4$ molar concentration and eight sets of fluid flow rates after 24 and 100 h standing, respectively. The fluid is very stable, and no bulk phase separation has been observed for all samples 24 h after its preparation (Fig. 2a). The nanofluids synthesized at the $CuSO_4$ flow rate of 50 and 75 μL/ min are still stable even after 100 h standing (Fig. 2b). This is especially important considering that the PVP concentration used is only one-third of that in [11] and it is typically rare to maintain nanofluids synthesized by conventional approaches in a homogeneous stable state for more than 24 h [2].

Figure 3 typifies the SEM (scanning electron microscope) images of nanoparticles (Hitachi S-4800 FEG SEM, Japan), showing that the particles can be changed from a spherical shape to a polyhedral, starfishlike, and even flowerlike one by varying the $CuSO_4$ concentration and/or fluid flow rates. Variations of particle average diameter with the $CuSO_4$ concentration and flow rate are measured by dynamic light-scattering system (Delsa Nano C, Beckman Coulter) and are shown in Table 1.

Figure 4 shows the variation of conductivity ratio k/k_w with the $CuSO_4$ concentration and flow rate at the room temperature. Here, k and k_w are the thermal conductivity of the nanofluid and the water, respectively, measured by the standard transient line heat source method (KD2 Pro; Decagon Devices, Inc.) [16]. For each data point in Fig. 4, an average value over three readings is used. The error bar indicates the standard deviation calculated based on the procedure described in [17]. A variation of k/k_w from 0.94 to 1.04 is observed. Therefore, the presence of nanoparticles can either enhance or weaken fluid heat conduction, a phenomenon predicted by the thermal-wave theory [9,18,19]. Although the $CuSO_4$ concentration and flow rate can change the shape of nanoparticles significantly (Fig. 3), they vary the conductivity ratio k/k_w only moderately (Fig. 4). Therefore, the conductivity enhancement is insensitive to the particle shape for this type of nanofluids.

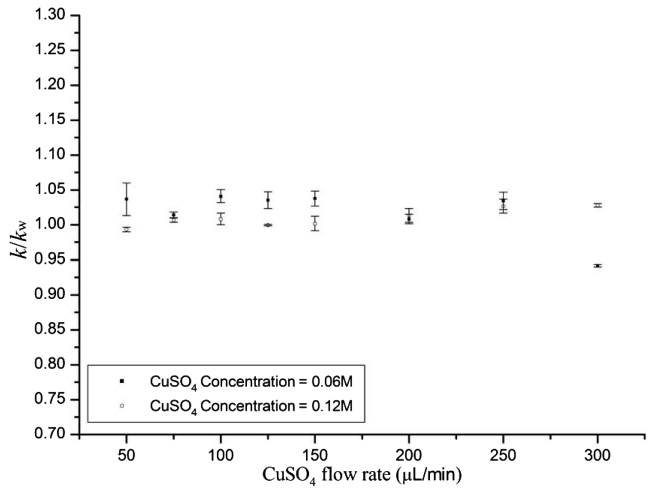


Fig. 4 Variation of k/k_w with $CuSO_4$ molar concentration and flow rate (k is nanofluid thermal conductivity, and k_w is water thermal conductivity).

IV. Conclusions

Conventional nanofluid synthesis approaches have not been satisfactory because of their inadequacies in engineering microstructures of nanofluids. The recently developed one-step chemical solution method (CSM) takes advantage of the ability of manipulating atoms and molecules through chemical reactions in the liquid phase. However, the difficulty of controlling the microscale while operating at the macroscale is insuperable. By replacing batch-based macroreactors in the CSM by continuous-flow microfluidic microreactors, a novel microfluidic one-step CSM is developed for effective synthesis of nanofluids with controllable microstructures. The technique has been successfully applied to synthesize Cu_2O nanofluids with spherical, polyhedral, starfishlike, and flowerlike nanoparticles. The Cu_2O nanofluids synthesized by this method have better stability than those produced by other methods and are with a conductivity enhancement insensitive to the particle shape.

Acknowledgment

The financial support from the Research Grants Council of Hong Kong (GRF718009) is gratefully acknowledged.

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