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Technical Notes

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$CePO_4$ Nanofluids: Synthesis and Thermal Conductivity

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Introduction

NANOFLUIDS, fluid suspensions of nanometer-sized (less than 100 nm) particles, tubes, and fibers, have recently been demonstrated to have thermal conductivities far superior to that of the liquid alone [1]. Such substantial increases in thermal conductivity come from the thermal waves and resonance from a macroscale point of view [2–4] and the nanoparticle Brownian motion, the liquid layering at the liquid–particle interface, the nanoparticle cluster/aggregate effect, and the nature of heat transport in the nanoparticle from a microscale point of view [1,5–7]. This and their other distinctive features offer unprecedented potential for many applications in various fields including energy, biomedical 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 [5–7] or by a single-step *physical* method that simultaneously makes and disperses the nanoparticles into base fluids [8–12]. 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), a single-step *chemical* method [13]. By the CSM, we can easily vary and manipulate nanofluid microstructures through adjusting synthesis parameters including the reactant concentration. Here we report a novel nanofluid synthesized by the CSM, the aqueous suspension of $CePO_4$ nanofibers, and show its microstructure and conductivity variation with the reactant concentration. Also reported is the variation of the nanofluid thermal conductivity with the temperature.

Synthesis and Thermal Conductivity

Synthesizing cerium phosphate ($CePO_4$) nanofluid by the CSM is based on the following chemical reaction in the solution:

$$H_3PO_4 + Ce(NO_3)_3 = CePO_4 + 3HNO_3$$

Therefore, the substance amount of phosphoric acid (H_3PO_4) must be equal to that of cerium nitrate ($Ce(NO_3)_3$) for a theoretically-complete reaction. This requires that CV, where C is the molar concentration and V is the volume of the solution, is the same for the H_3PO_4 solution and the $Ce(NO_3)_3$ solution. In our experiments, we fix V at 15 ml and keep the C value the same for both of the solutions.

By the CSM, we slowly mix the H_3PO_4 solution into the $Ce(NO_3)_3$ solution in a beaker under vigorous ultrasonication (Ultrasonic Cell Processor KS-250C, Haishukesheng Ultrasonic Equipment, Ltd.). The ultrasonication power, frequency, and time are fixed at 250 W, 20 KHz, and 40 min, respectively, for all synthesized samples to isolate the molar concentration effect. To remove the heat from the ultrasonication and reaction, we put the beaker into an ice-water bath.

Figure 1 shows the picture of the synthesized nanofluid with 10 values of molar concentration three months after its preparation. The fluid is very stable, and no bulk phase separation has been observed.

Under the fixed other synthesis parameters, variation of reactant molar concentration changes mixing and reaction process between H_3PO_4 and $Ce(NO_3)_3$ and, thus, the nanofluid microstructure. It also changes the nanofluid acidity mainly by the amount of nitric acid (HNO_3) in the nanofluid. Figure 2 typifies the SEM (scanning electron microscope) images of $CePO_4$ nanofibers from "drying" samples of synthesized nanofluids (Leo 1530FEG, Oxford Instruments, Unuted Kingdom). As the reactant molar concentration increases, the $CePO_4$ nanofibers become thicker, shorter, and straighter. The nanofluid pH values are measured by the acidity meter (PHS-25, Shanghai Precision and Scientific Instrument Company, Ltd.) and listed in Table 1. As the reactant molar concentration increases, the amount of nitric acid (HNO_3) in the nanofluid increases and thus the pH value reduces.

The thermal conductivity of nanofluids can be measured by transient hot-wire (THW), temperature oscillation (TO), and steady-state (SS) methods [1,5–7,14,15]. The first method is well established as the most accurate, reliable and robust measurement technique for the thermal conductivity of nanofluids [1,5–7,14,15]. Therefore, we use a THW system for the thermal conductivity measurement.

The THW system mainly consists of a thin platinum wire suspended symmetrically in nanofluids in a vertical cylindrical container (Fig. 3). The wire is coated with an electrically insulating and thermally conducting epoxy adhesive and is used as both a heater

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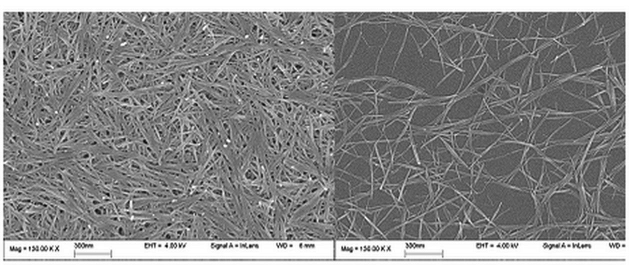
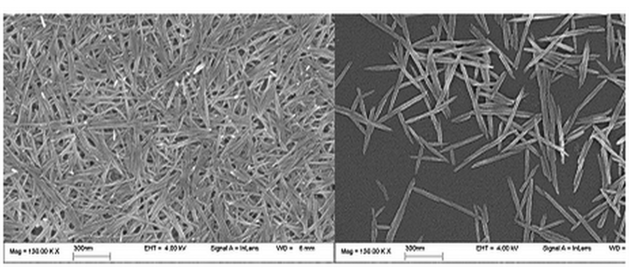
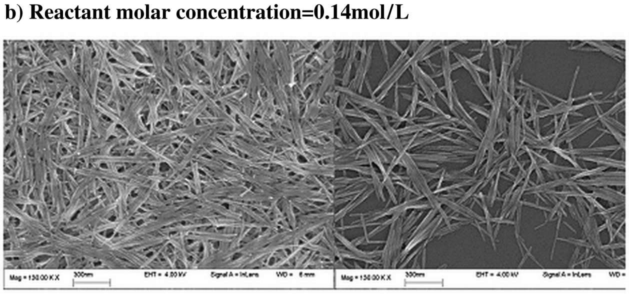
Fig. 1 $CePO_4$ nanofluids three months after their preparation (reactant molar concentration from 0.02 mol/L to 0.2 mol/L).



a) Reactant molar concentration=0.04mol/L



b) Reactant molar concentration=0.14mol/L



c) Reactant molar concentration=0.2mol/L

Fig. 2 SEM images of some $CePO_4$ nanofibers from drying samples of nanofluids.

and thermometer. Platinum is used for the hot wire because its resistance/temperature relationship is well known over a wide temperature range. The temperature of the wire is obtained by measuring its electrical resistance R_w, the latter being measured by a Wheatstone bridge (Fig. 3). The electrical resistance of the

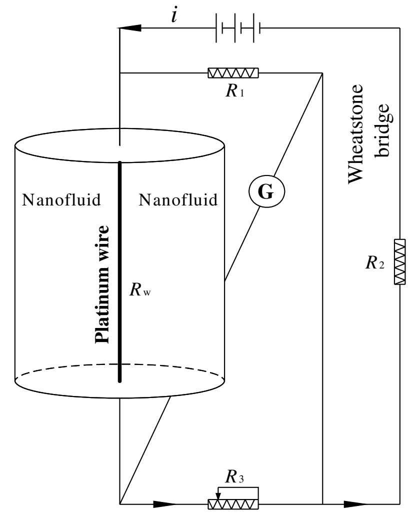


Fig. 3 An embedded platinum hot wire within a nanofluid in a cylindrical container and a Wheatstone bridge for measuring electrical resistance of the wire.

potentiometer R_3 is adjusted until the reading of the galvanometer G shows zero current. When the bridge is balanced at a zero current reading on the galvanometer G, the R_w can be obtained from the known electrical resistances R_1, R_2, and R_3 by using the balanced Wheatstone bridge relationship $R_w = R_1 R_3 / R_2$.

The relationship between the wire temperature change and the thermal conductivity is [1,5–7,14,15]

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

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

$$k = \frac{q}{4\pi m}$$

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 of the platinum wire rises with time after a step change in voltage has been applied to it.

Figure 4 shows the variation of conductivity ratio k/k_w with the reactant molar concentration and nanofluid temperature for the $CePO_4$-nanofibers/water/HNO_3 nanofluids in Fig. 1. Here k and k_w are the thermal conductivity of the nanofluid and the water, respectively, measured by the standard THW method (KD2, Therm Test, Inc., Canada). In the KD2 system, the wire radius and length 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. The THW system accuracy depends on the ratio of wire diameter over that of the liquid container. We have carefully checked the variation of measured thermal conductivity with the container diameter (11 mm, 20 mm, 40 mm,

Table 1 Variation of nanofluid pH value with the reactant molar concentration at room temperature

Molar concentration, mol/L	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20
pH value	1.45	1.07	0.93	0.91	0.79	0.73	0.51	0.40	0.38	0.26

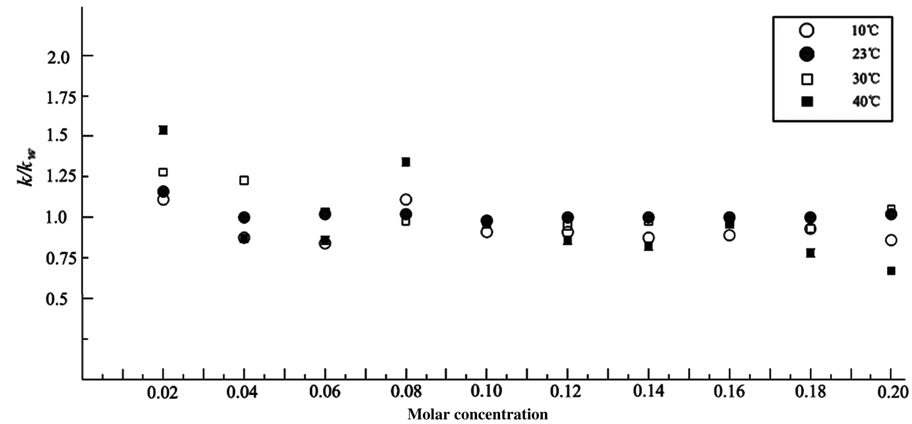


Fig. 4 Variation of k/k_w with the reactant molar concentration and temperature for $CePO_4$-nanofibers/water/HNO_3 nanofluids (k indicates nanofluid thermal conductivity and k_w indicates water thermal conductivity).

and 75 mm). The maximum variation is 1.7%. We have also carefully checked the variation of measured thermal conductivity with the liquid depth (115 mm, 175 mm, 235 mm, and 325 mm; all with the whole wire immersed in liquids). The maximum variation is 1.3%. For every sample and temperature, we measure thermal conductivity three times with a time gap of 5 min. The data shown in Fig. 4 are the average values over the three readings.

Remarkably, an extraordinary conductivity enhancement (up to a 53% enhancement at the reactant molar concentration of 0.02 mol/L and the fluid temperature of 40°C) is obtained. Although a significant increase in thermal conductivity is achieved for some cases, the fluid conductivity could also be reduced by adding the nanofibers for the other cases. The measured conductivity shows a high nonlinearity to both the reactant molar concentration and the temperature, and is consistent with the theory of thermal waves and resonance [2,16]. Variation in the reactant molar concentration leads to a change in nanofluid thermal conductivity through changing the nanofluid microstructure and pH value. The nanofluid thermal conductivity also shows a strong sensitivity to the temperature.

Conclusions

$CePO_4$ nanofluid can be synthesized by using the chemical solution method. Its microstructure and acidity can be varied by changing the reactant molar concentration. Its thermal conductivity can also be controlled by the reactant molar concentration and temperature. Although the fluid conductivity is reduced in some cases, an extraordinary conductivity enhancement up to 53% is achievable with this type of nanofluids.

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References

[1] Das, S. K., Choi, S. U. S., Yu, W. H., and Pradeep, T., *Nanofluids: Science and Technology*, Wiley, New York, 2008.

[2] Wang, L. Q., Zhou, X. S., and Wei, X. H., *Heat Conduction: Mathematical Models and Analytical Solutions*, Springer–Verlag, Berlin, 2008.

[3] Wang, L. Q., and Wei, X. H., "Equivalence Between Dual-Phase-Lagging and Two-Phase-System Heat Conduction Processes," *International Journal of Heat and Mass Transfer*, Vol. 51, Nos. 7–8, 2008, pp. 1751–1756. doi:10.1016/j.ijheatmasstransfer.2007.07.013

[4] Xu, M. T., and Wang, L. Q., "Thermal Oscillation and Resonance in Dual-Phase-Lagging Heat Conduction," *International Journal of Heat and Mass Transfer*, Vol. 45, No. 5, 2002, pp. 1055–1061. doi:10.1016/S0017-9310(01)00199-5

[5] Choi, S. U. S., Zhang, Z. G., and Keblinski, P., "Nanofluids," *Encyclopedia of Nanoscience and Nanotechnology*, Vol. 6, edited by H. S. Nalwa, American Scientific Publishers, Valencia, CA, 2004, pp. 757–773.

[6] Eastman, J. A., Phillpot, S. R., Choi, S. U. S., and Keblinski, P., "Thermal Transport in Nanofluids," *Annual Review of Materials Research*, Vol. 34, 2004, pp. 219–246. doi:10.1146/annurev.matsci.34.052803.090621

[7] Peterson, G. P., and Li, C. H., "Heat and Mass Transfer in Fluids with Nanoparticle Suspensions," *Advances in Heat Transfer*, Vol. 39, 2006, pp. 257–376.doi:10.1016/S0065-2717(06)39003-X

[8] Choi, S. U. S., and Eastman, J. A., "Enhanced Heat Transfer Using Nanofluids," U.S. Patent, US 6,221,275 B1, 2001.

[9] Eastman, J. A., Choi, S. U. S., Li, S., Yu, W., and Thompson, L. J., "Anomalously Increased Effective Thermal Conductivities of Ethylene Glycol-Based Nanofluids Containing Copper Nanoparticles," *Applied Physics Letters*, Vol. 78, No. 6, 2001, pp. 718–720. doi:10.1063/1.1341218

[10] Chang, H., Tsung, T. T., Chen, L. C., Yang, Y. C., Lin, H. M., Lin, C. K., and Jwo, C. S., "Nanoparticle Suspension Preparation Using the Arc Spray Nanoparticle Synthesis System Combined with Ultrasonic Vibration and Rotating Electrode," *The International Journal of Advanced Manufacturing Technology*, Vol. 26, Nos. 5–6, 2005, pp. 552–558. doi:10.1007/s00170-003-2029-8

[11] Lo, C. H., Tsung, T. T., Chen, L. C., Su, C. H., and Lin, H. M., "Fabrication of Copper Oxide Nanofluid Using Submerged Arc Nanoparticle Synthesis System (SANSS)," *Journal of Nanoparticle Research*, Vol. 7, Nos. 2–3, 2005, pp. 313–320. doi:10.1007/s11051-004-7770-x

[12] Lo, C. H., Tsung, T. T., and Chen, L. C., "Shaped-Controlled Synthesis of Cu-Based Nanofluid Using Submerged Arc Nanoparticle Synthesis System (SANSS)," *Journal of Crystal Growth*, Vol. 277, Nos. 1–4, 2005, pp. 636–642. doi:10.1016/j.jcrysgro.2005.01.067

[13] Zhu, H. T., Lin, Y. S., and Yin, Y. S., "A Novel One-Step Chemical Method for Preparation of Copper Nanofluids," *Journal of Colloid and Interface Science*, Vol. 277, No. 1, 2004, pp. 100–103. doi:10.1016/j.jcis.2004.04.026

[14] Vadasz, P., "Nanofluid Suspensions and Bi-Composite Media as Derivatives of Interface Heat Transfer Modeling in Porous Media," *Emerging Topics in Heat and Mass Transfer in Porous Media*, edited by P. Vadasz, Springer–Verlag, Berlin, 2008, pp. 283–326.

[15] Vadasz, P., "Heat Conduction in Nanofluid Suspensions," *Journal of Heat Transfer*, Vol. 128, No. 5, 2006, pp. 465–477. doi:10.1115/1.2175149

[16] Tzou, D. Y., *Macro-to Microscale Heat Transfer: The Lagging Behavior*, Taylor and Francis, Washington, D.C., 1997.