

Study on the Production and Transport Properties of Nanofluids

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THESIS

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NOMENCLATURE

Acronyms and Abbreviations

BM	Brownian Model
CMOS	Complementary metal–oxide–semiconductor
CNT	Carbon Nanotubes
DLS	Dynamic Light Scattering
EMT	Effective Medium Theory
GNPs	Gold Nanoparticles
HPLC	High-Performance Liquid Chromatography
MDS	Molecular Dynamics Simulations
MEMS	Microelectromechanical Systems
NEMS	Nanoelectromechanical Systems
PAO	Poly-alpha-olefin
PZC	Point of Zero Charge
RCF	Relative Centrifugal Force
SANSS	Submerged Arc Nanoparticle Synthesis System
TEM	Transmission Electron Microscope
VEROS	Vacuum Evaporation onto a Running Oil Substrate

Symbols

a	Radius
a_K	Kapitza radius

NOMENCLATURE (continued)

Symbols (continued)

A	Empirical constant
B	Bias error
d	Particle diameter [nm]
k	Thermal conductivity [W/m·K]
K_B	Boltzmann constant [1.3807×10^{-23} J/K]
l	Mean free path
L	Length
m	Empirical constant
n	Sample size
Pr	Prandtl number
q	Input power per unit length [W/m]
r^2	Correlation coefficient
R	Resistance [Ω or $k\Omega$]
R_b	Kapitza resistance (thermal boundary resistance)
Re	Reynolds number
S	Slope between natural logarithmic time ($\ln t$) and variation of temperature (ΔT)
t	Time
$t_{\lambda,95\%}$	Repeated measurement at 95% confidence
T	Temperature [$^{\circ}\text{C}$ or $^{\circ}\text{K}$]
u	Uncertainty

NOMENCLATURE (continued)

Symbols (continued)

V	Voltage [V]
V_0	Input voltage [V]
$\bar{x}$	Sample mean (in t -distribution)

Greek Letters

α	– Chapter II: Temperature coefficient of resistance of platinum wire – Chapter III: $\alpha = a_K / a_p$
β	– Chapter I: $\beta \equiv [k_p - k_{BF}] / [k_p + 2k_{BF}]$ – Chapter II: Temperature coefficient
ϕ	Volume fraction or volume concentration of particles
λ	Degree of freedom (in t -distribution)
μ	– Chapter II: Mean (in t -distribution) – Chapter III: Dynamic viscosity [$\text{N}\cdot\text{s}/\text{m}^2$ or $\text{kg}/\text{s}\cdot\text{m}$]
σ	Standard deviation (in t -distribution)
σ^2	Sample variation (in t -distribution)

Subscripts

0	Initial value or at 0 °C
BF	Base fluid

NOMENCLATURE (continued)

Subscripts (continued)

k	Thermal conductivity
NF	Nanofluid
p	Particle
q	Input power per unit length
R	Resistance
ref	Reference value
w	Wire
ΔT	Temperature variation
V_0	Input voltage

SUMMARY

A new engineering medium, called nanofluid, has attracted wide attention by research targeting cooling processes in engineering applications. Nanofluids have unique thermal transport properties and superior performance that are unavailable in traditional heat transfer fluids or conventional particle fluid suspensions. These novel nanofluids show great promise as next-generation heat transfer fluids for innovative applications related to nuclear power generation, buildings, transportation, aerospace, electronics, tribology, and medicine among others.

A conventional ultrasonic bath was used in this work to examine the feasibility of forming aqueous spherical gold nanoparticles (GNPs) under atmospheric conditions. The effects of ultrasonic energy on the size and morphology of GNPs were investigated. Gold nanofluids with highly monodispersed spherical GNPs were successfully synthesized by sodium citrate reduction in a conventional ultrasonic bath, without additional heating or magnetic stirring, as evidenced by ultraviolet–visible spectra and transmission electron microscopy. Ultrasonic energy was shown to be a key parameter for producing gold nanofluids with spherical GNPs of tunable sizes (20 to 50 nm). A proposed scheme for understanding the role of ultrasonic energy in the formation and growth of GNPs is discussed. The simple single-step method demonstrated in this study offers new opportunities in the production of aqueous suspensions of monodispersed spherical GNPs.

Centrifugation is used in the production method of nanofluids with the two-step method in the present study. The study shows that three alumina nanofluids, which have three different

SUMMARY (continued)

sizes of nanoparticles, can be produced from the same original nanoparticle dispersion by means of centrifugation and without involving any dispersants or surfactants. Measurements of thermal conductivity of alumina nanofluids were conducted over a broad range of temperatures from 10 to 80 °C. The experimental results were compared to the effective medium theory (EMT) models and the calculated Brownian velocity. The experimental results clearly show the strong size- and temperature-dependency on the thermal conductivity enhancement. Moreover, it is found that the temperature effect strongly depends on the particle size. In other words, there is a coupling dependency on the size of nanoparticles and temperature in heat conduction enhancement of alumina nanofluids. Finally, it can be concluded that the Brownian velocity is the key factor of the temperature- and size-dependent thermal conductivity of alumina nanofluids.

PREVIOUSLY PUBLISHED MATERIAL

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I. INTRODUCTION

A. **Background**

Cooling technology plays a critical role that controls the performance of industrial, consumer, and medical devices and systems. For example, very high density electronic devices (i.e., those with 8-nm features) are predicted to generate local heat fluxes as high as 10^5 W/cm^2 and heat fluxes at the die level of 10^3 W/cm^2 , 10 times those of present-day CMOS devices (ITRS, 2008). Inefficient dissipation of the immense amount of heat generated in dense electronics and electronic systems would reduce or limit their performance. Therefore, the thermal management of electronics and electronic systems has been the most important contemporary technology driver for thermal scientists and engineers. Similarly, innovations in the thermal management of the power electronics must be achieved for hybrid electric vehicles (FCPEEM, 2006). Besides the need for enhanced cooling performance, the increasing demand for energy-savings and emissions reduction makes energy efficiency a pressing issue in the buildings, transportation, power generation, manufacturing, and many other sectors. However, the inherently poor thermal properties of conventional heat transfer fluids, such as water, oil, and ethylene glycol, are a major barrier to innovations in thermal management and energy efficiency. The development of nanoscale materials provided enormous opportunities across a wide spectrum of critical technologies. In the area of heat transfer fluids, nanoparticles can provide new innovative technologies with potential to tailor the heat transfer fluid's thermal properties through control over particle size, shape, composition, etc. Realizing the unique properties of nanoparticles and their potential to overcome the intrinsic limitation of conventional heat transfer fluids, Choi conceived the concept of nanofluids (Choi, 1995). The term *nanofluids*, coined by

Choi, is defined as a new class of nanotechnology-based heat transfer fluids that are engineered by stably suspending nanosized particles, fibers, sheets, or tubes with average sizes below 100 nm in traditional heat transfer fluids in low volume concentrations (≤ 1 vol.%) (Choi, 2009).

Numerous experimental studies have shown that nanofluids significantly enhance thermal conductivities (Choi *et al.*, 2001; Chopkar *et al.*, 2006; Das *et al.*, 2003c; Eastman *et al.*, 2001; Hong *et al.*, 2006; Jana *et al.*, 2007; Li and Peterson, 2006; Patel *et al.*, 2003), convective heat transfer coefficient (Ding *et al.*, 2006; Hwang *et al.*, 2009; Nguyen *et al.*, 2007; Wen and Ding, 2004b; Xie *et al.*, 2010; Xuan and Li, 2003), and other properties, such as wetting and spreading of nanofluids (Wasan and Nikolov, 2003) and heat absorption rate (Kim *et al.*, 2006). Because of these unique thermal transport properties and superior performance that are unavailable in traditional heat transfer fluids or conventional particle fluid suspensions, nanofluids have been of great scientific interest to researchers worldwide over the past decade (Choi, 2009). These novel nanofluids show great promise as next-generation heat transfer fluids for innovative applications in industries such as nuclear power generation, buildings, transportation, aerospace, electronics, tribology, and medicine among others (Choi, 2009; Wang and Fan, 2010). Besides enhanced thermal properties, nanofluids have other potentially useful properties, such as the formation of nanoporous structures on heated surfaces. Therefore, today's nanofluids technology can be useful to broader applications of nanofluids as nanostructured materials.

B. Literature Review

Published papers which are related to nanofluids are summarized in this section. The objective is to present a review of the open literature describing recent results on the synthesis of

nanofluids, and their general heat transfer characteristics, in particular focusing on thermal conductivity, including both experimental and theoretical investigations.

1. **Synthesis methods of nanofluids**

Synthesis is the first key step and main issue in experimental studies of nanofluids, since the stability and durability of nanofluids can affect their thermal properties. Nanofluids do not simply refer to liquid-solid mixtures. Some requirements are essential for synthesis of nanofluids, such as suspension uniformity, stability and durability, low particle agglomeration, and no chemical change of the suspending fluids (Xuan and Li, 2000). Thus, various synthesis methods have been used for preparation of suspensions, such as changing the pH, using surface activators and/or dispersants, and using ultrasonic vibration. All these fabrication techniques are intended to change the surface properties of suspended particles and to prevent formation of particle clusters in order to obtain stable suspensions. Generally, three different methods, such as the one-step physical method, the one-step chemical method, and the two-step method (or dispersion method), have been used to prepare nanofluids.

a. **One-step physical method**

Physical methods for producing nanoparticles involve condensing nanophase powders from the vapor phase precursor directly into the flowing fluid. The mean size and size distribution of nanoparticle can be controlled by the control of quenching conditions. Akoh *et al.* (1978) developed the single-step direct evaporation method, which is known as the VEROS (Vacuum Evaporation onto a Running Oil Substrate) technique. The original idea of this method was to produce nanoparticles (Kimoto *et al.*, 1963), but it is difficult to subsequently separate the particles from the fluids to produce dry nanoparticles. Wagener *et al.* (1997) proposed a modified direct-condensation method. They used high pressure magnetron sputtering

to produce suspensions containing metallic nanoparticles, such as Ag and Fe. A direct evaporation system was developed by Eastman *et al.* (1997; 2001). The stable Cu/ethylene glycol nanofluids were synthesized by the direct evaporation-condensation process. Lo *et al.* (2005b) employed a vacuum-SANSS (Submerged Arc Nanoparticle Synthesis System) method to synthesize Cu nanofluids with different dielectric liquids. They used de-ionized water, with 30%, 50%, and 70% volume solutions of ethylene glycol and pure ethylene glycol as base fluids. They found that the thermal conductivity of the dielectric liquids is the main factor to influence and determine different morphologies. CuO, Cu₂O, and Cu nanofluids also can be synthesized by this technique. Moreover, Chang *et al.* (2005) developed a combined vacuum arc-submerged nanoparticle synthesis system (ASNSS) for preparing CuO nanofluids and a Ni nano-magnetic fluid was also produced by Lo *et al.* (2005a) using the SANSS method. Laser ablation (Phuoc *et al.*, 2007) was also used to synthesize nanofluids. A target is irradiated by a focused pulsed laser beam to ablate the material which is rapidly quenched during its expansion as a plasma plume in this process (Phuoc *et al.*, 2007).

The one-step physical method combines the synthesis of nanoparticles with the preparation of nanofluids. These one-step physical methods can produce stable nanofluids and the aggregation of nanoparticles in nanofluids can be reduced excessively. However, it is hard to synthesize nanofluids in a large scale due to high production cost and long production time.

b. **One-step chemical method**

The majority of nanoparticles used in nanofluids can be synthesized using a wet chemical method. It is possible to prepare nanofluids using the one-step chemical method that combines the preparation of nanoparticles and nanofluids by modifying the wet chemical method (Wu *et al.*, 2009). Zhu *et al.* (2004) developed a one-step chemical method for

producing Cu/ethylene glycol nanofluids by reducing copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) with sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) in ethylene glycol under microwave irradiation. Experimental results indicated that the addition of sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) and microwave irradiation are two significant factors which affect the reaction rate and the properties of Cu nanofluids. Fe_3O_4 /water (Zhu *et al.*, 2006) and CuO/water (Zhu *et al.*, 2007; 2011) nanofluids were produced by the wet chemical method. The microwave-assisted one-step method has been applied to synthesize stable silver nanofluids in ethanol by reduction of silver nitrate (AgNO_3) (Singh and Raykar, 2008). In their work, polyvinylpyrrolidone (PVP) was used as the stabilizer and reducing agent for silver in solution. Silver nanofluid was also prepared by using silver nitrate (AgNO_3) as a source for silver nanoparticles, distilled water as a base fluid, and sodium borohydride (NaBH_4) and hydrazine (N_2H_4) as reducing agents by means of conventional heating using polyvinylpyrrolidone (PVP) as surfactant (Salehi *et al.*, 2013). The cationic surfactant octadecylamine (ODA) is also an efficient phase-transfer agent to synthesize silver colloids (Kumar *et al.*, 2003). The coupling of the silver nanoparticles with the octadecylamine (ODA) molecules present in organic phase via either coordination bond formation or weak covalent interaction leads to the phase transfer of the silver nanoparticles.

The one-step chemical method also combines the production of nanoparticles with the synthesis of nanofluids. It has several advantages, such as controlling the particle size, yielding the product in less time, and producing metallic nanofluids. However, there are some disadvantages in the one-step chemical method. The presence of residual reactants in the nanofluids due to incomplete reaction or stabilization is one of the most critical issues. It is hard to explain the nanoparticle effect without eliminating this impurity effect. Another disadvantage

is that synthesis of nanofluids with a high volume fraction of particles is hard since agglomeration occurs at high volume concentration of nanoparticles.

c. **Two-step method**

The two-step method is the most widely used method for preparing nanofluids, especially at the early stage of nanofluid investigations. For example, Lee *et al.* (1999) and Wang *et al.* (1999) used this production technique to synthesize Al_2O_3 nanofluids. Murshed *et al.* (2005) also synthesized TiO_2 /water nanofluid using the two-step method. In the two-step method, the first step is the production of dry powders, such as nanoparticles, nanofibers, nanotubes, or other nanomaterials by chemical or physical methods. Then, in the second step, the nano-sized powder is dispersed into the base fluid. Ultrasonic agitation or/and mechanical stirring with the aid of adding dispersants or/and adjusting pH value are the most commonly used techniques to disperse particles in nanofluids. The role of ultrasonication and mechanical stirring is to break down the aggregates of the nanoparticles. Adding dispersants or/and adjusting the pH value was used to prevent and minimize the re-aggregation of nanoparticles. The most common method used to enhance the stability of nanoparticles in fluids is the use of surfactants; nanoparticles have the tendency to aggregate. However, the use of surfactants is compromised in high-temperature applications. The two-step method is the most efficient, economically, for mass production of nanofluids; nanopowder synthesis techniques have been scaled up to industrial production levels by several companies (Kebllinski *et al.*; 2005). This method is useful to prepare nanofluids containing oxides and carbon nano-elements. It has the advantage of producing nanofluids with high particle volume fractions. As mentioned earlier, the two-step method starts with the preparation of the nanoparticles and continues with their dispersion in the base fluids. If agglomerates exist in the dry powders, the stability of nanofluids

is usually not good. Moreover, due to the oxidation or self-ignition of metallic nanoparticles, it is very challenging to synthesize metallic nanofluids by this method.

In summary, many synthesis techniques have been developed, however, some of the main issues have yet to be resolved: production cost, production time, large-scale production, chemical residue, and agglomeration, to name a few. Thus, the need exists to develop more simple, staple, and eco-friendly nanofluid synthesis approaches in the future. A summary of the merits and demerits of synthesis methods that have been used to date is shown in Table I.

2. **Experimental features of the thermal conductivity of nanofluids**

Several pioneering experiments with nanofluids showed that nanofluids have unprecedented thermal transport phenomena that show remarkable enhancement in thermal properties compared with the base fluid. These phenomena surpass the fundamental limits of macroscopic theories of suspensions and provide avenues to exciting new coolants for a variety of applications. The enhanced transport properties and heat transfer have been studied with varying degrees of thoroughness. Thermal conductivity is a significant parameter in enhancing the heat transfer performance of a heat transfer fluid. It is expected that the suspended particles can enhance the thermal conductivity and heat transfer performance of the combined medium, since the thermal conductivity of solid particles exceeds that of the base fluids. On this aspect, thermal conductivity is the most studied property of nanofluids because it is of great theoretical and practical interest to scientists and engineers. Many researchers have discovered that the heat conduction behavior of nanofluids has novel features that are completely lacking in conventional suspensions of micro- or millimeter-sized solid particles. Moreover, the unprecedented thermal transport phenomena in nanofluids surpass the fundamental limits predicted by effective medium theory (EMT), in which thermal diffusion is the only heat conduction mechanism. In contrast to

these pioneering discoveries, these unexpected heat conduction behaviors are not observed in some experimental studies. In this section, representative experimental studies from both sides are presented.

a. **High thermal conductivity at low concentrations**

Lee *et al.* (1999) and Wang *et al.* (1999) produced oxide nanofluids using a two-step method and showed that the k of oxide nanofluids is slightly greater than that of base fluids or the one predicted by EMT. Therefore, this study did not generate significant interest in oxide nanofluids. Although Eastman *et al.* (1997) and Xuan and Li (2000) were the first investigators to make metallic nanofluids containing Cu nanoparticles using a two-step method, the k of their nanofluids was not superior to that of oxide nanofluids. However, researchers took notice when Eastman *et al.* (2001) demonstrated for the first time that copper nanofluids produced by a single-step method show a dramatic enhancement in thermal conductivity (up to a 40% at a particle concentration of 0.3 vol.%) compared to oxide nanofluids produced by a the two-step method. Conventional particle-liquid suspensions require high concentrations (>10 vol.%) of particles to achieve such dramatic enhancement. Furthermore, they showed that Cu nanofluids have an anomalous enhancement in thermal conductivity far beyond the predictions of conventional effective medium theory even at very low volume concentrations (<1 vol.%). Patel *et al.* (2003) produced gold nanofluids using single-step chemical methods and observed anomalous enhancements in thermal conductivity at vanishing concentrations. Liu *et al.* (2006) synthesized Cu nanofluids using a chemical reduction method with no surfactants and observed that the thermal conductivity was enhanced by up to 23.8% at 0.1 vol.%. Jana *et al.* (2007) observed that Cu-water nanofluids show a 74% increase in conductivity at 0.3 vol.%, far exceeding the previous record of 40% (Eastman *et al.*, 2001).

More recently, Garg *et al.* (2008) measured the thermal conductivity of Cu nanoparticles in ethylene glycol and also found an anomalous increase, i.e., the measured increase in conductivity was twice the predicted value of the Maxwell model (Maxwell, 1873). These studies show that metallic nanofluids truly stand out as high quality nanofluids. Schmidt *et al.* (2008) also reported that the thermal conductivity of Al_2O_3 /decane nanofluids have an anomalous enhancement in thermal conductivity (11% at 1 vol.%) and Philip *et al.* (2008b) reported very exciting results that the thermal conductivity enhancement of Fe_3O_4 nanofluids under a magnetic field can reach up to 216% at 4.5 vol.%.

In contrast, no anomalous enhancement in thermal conductivity was observed with nanofluids produced by other groups (Buongiorno *et al.*, 2009a; Eapen *et al.*, 2007; Putnam *et al.*, 2006; Timofeeva *et al.*, 2007; Zhang *et al.*, 2006a; 2006b). These contradictory k data highlight the need for more controlled syntheses, accurate characterization and thermal conductivity measurements of nanofluids.

In Figure 1, the thermal conductivity ratio $k_{\text{NF}}/k_{\text{BF}}$ (k of nanofluid to that of base fluid) is plotted for several kinds of nanofluids from different sources as a function of $\beta\phi$, where $\beta \equiv [k_p - k_{\text{BF}}]/[k_p + 2k_{\text{BF}}]$ (Jeffrey, 1973) and ϕ is the volume fraction of nanoparticles, and compared with the prediction from the Maxwell model (Maxwell, 1873) for dilute nanofluids of spherical nanoparticles. The very fact that there are huge differences in k as shown in Figure 1 infers that there are large differences in the quality of nanofluids. Although a number of data seem predictable, some other experimental results (Eastman *et al.*, 2001; Li and Peterson, 2006; Murshed *et al.*, 2006; Patel *et al.*, 2010; Wang *et al.*, 1999; Xie *et al.*, 2002a) show anomalously high thermal conductivity compared with the predictions of the classical EMT-based model. In general, nanofluids produced by one-step methods have well dispersed and stably suspended

nanoparticles and higher thermal conductivities compared to those produced by two-step methods, as shown in Figure 2. Therefore, good dispersion and stable suspension of nanoparticles in the host liquids are prerequisites for the study of nanofluids properties as well as for their applications. This requirement can be achieved using various dispersion and stabilization methods. However, it is important to keep in mind that some nanofluids containing uniformly dispersed and stably suspended nanoparticles do not have any conductivity enhancement for presently unknown reasons.

b. **Nonlinear relationship between conductivity and concentration**

Choi *et al.* (2001) made the first carbon nanotubes (CNTs)-based nanocomposite material with the highest thermal conductivity enhancement ever achieved by dispersing CNTs in a liquid matrix of poly- α -olefin oil (PAO) and discovered that the measured thermal conductivity of the CNT nanofluids is nonlinear with nanoparticle volume fraction at low volume fractions of CNTs. This is another anomalous feature of the k of nanofluids, since predictions by classical EMT show a linear relationship. In an attempt to confirm these results, Xie *et al.* (2003) and Wen and Ding (2004a) made CNT nanofluids and measured the thermal conductivity of their CNT nanofluids, but found smaller enhancements compared to the data by Choi *et al.* (2001). Finally, Shaikh *et al.* (2007) independently confirmed the previous results on both the large magnitude of enhancements and the nonlinear trend in the thermal conductivity of the CNT/PAO oil nanofluids Choi *et al.* (2001) reported six years ago, as shown in Figure 3. This shows that it is neither straightforward nor speedy to reproduce high-quality nanofluids and their anomalous thermal properties. Interestingly, Murshed *et al.* (2005), Hong *et al.* (2005) and Chopkar *et al.* (2006) showed that nanofluids containing spherical nanoparticles also have strong

nonlinear behavior, thereby demonstrating that nonlinear relationship is not limited to particles (CNTs) with a high aspect ratio.

c. **Temperature-dependent thermal conductivity**

Das *et al.* (2003c) were the first to show that nanofluids containing spherical nanoparticles have strongly temperature-dependent thermal conductivity. They found that the conductivity enhancement of Al_2O_3 or CuO nanofluids is two to four times that of the base fluid over a temperature range between 20 °C and 50 °C. Li and Peterson (2006) found that the temperature effect is stronger compared to the data of Das *et al.* (2003c). This new discovery was confirmed by other research groups (Chon *et al.*, 2005; Jha and Ramaprabhu, 2008; Li and Peterson, 2007b; Mintsu *et al.*, 2009; Murshed *et al.*, 2008; Patel *et al.*, 2003; Paul *et al.*, 2010; Teng *et al.*, 2010; Vajjha and Das, 2009; Yu *et al.*, 2010). Temperature dependent thermal conductivity of nanofluids is significant for engineering applications of nanofluids because it raises an exciting possibility to develop “smart” nanocoolants that “sense” their thermal environment and tune their heat conduction property to prevent hot spots. In contrast, other research groups (Beck *et al.*, 2010; Timofeeva *et al.*, 2007; Venerus *et al.*, 2006; Yang and Han, 2006; Zhang *et al.*, 2006a; 2006b) measured thermal conductivity of nanofluids and showed no dependence on temperature. Several experimental data of thermal conductivity ratio of Al_2O_3 and CuO nanofluids as a function of temperature are shown in Figure 4.

d. **Size-dependent thermal conductivity**

It has been known that the properties of monodisperse suspensions depend on the particle size (Frens, 1973). However, Chopkar *et al.* (2006) were the first to show experimentally that the effective thermal conductivity of $\text{Al}_{70}\text{Cu}_{30}$ nanofluids strongly depends on the nanoparticle size. This is a significant feature of nanofluids. In addition, their study shows

a nonlinear relationship between the effective thermal conductivity and the particle size in the particle diameter range of 10–80 nm. Their data clearly show steep size dependence in the small particle size range. Size-dependent thermal conductivity of nanofluids also has been observed by Chon *et al.* (2005), and Hong *et al.* (2006). Recently, Kim *et al.* (2007) showed that the thermal conductivity of nanofluids increases linearly with decreasing particle size and stated that no existing empirical or theoretical correlation can explain the linear behavior. Strong size effects in nanofluids are significant in practical applications of nanofluids. In contrast, several research groups have shown that the thermal conductivity of nanofluids increases with increasing particle size (Beck *et al.*, 2009; Chen *et al.*, 2008; Timofeeva *et al.*, 2010).

More recently, Patel *et al.* (2010) measured the thermal conductivity of nanofluids to obtain a comprehensive dataset for parameters such as the nanoparticle volume fraction and size and temperature of nanofluids. Their results reconfirmed that the thermal conductivity of nanofluids displays abnormal enhancement that cannot be predicted by Maxwell model (Maxwell, 1873), strong temperature dependency, and inverse particle size dependency. In Figure 5, some experimental data of thermal conductivity ratio of nanofluids are plotted as a function of particle size.

e. **pH-dependent thermal conductivity**

Xie *et al.* (2002a) and Lee *et al.* (2006) studied the k of nanofluids under varying pH conditions. Xie *et al.* (2002a) were the first to show that the thermal conductivity of Al_2O_3 nanofluids increases gradually as the difference between the pH value of nanofluids and the isoelectric point of Al_2O_3 nanoparticles increases. Lee *et al.* (2006) found that the k of CuO nanofluids increased by a factor of 3 as pH decreased from the point of zero charge (PZC) of 8 to 3, indicating that CuO nanofluids have a strongly pH-dependent k .

f. **Tunable thermal conductivity under external fields**

Philip *et al.* (2007; 2008a) observed that the thermal conductivity of kerosene-based nanofluids containing 6.3 vol.% of magnetite particles has increased up to four times that of the base fluid under an applied magnetic field. Most recently Shima *et al.* (2009) showed that the ratio of thermal conductivity to viscosity can be tuned from 0.725 to 2.35 in magnetically controllable nanofluids containing only 0.078 vol.%. These findings demonstrate that magnetically controllable nanofluids can behave like a multifunctional “smart” material that functions both as a coolant and a damper, offering exciting applications in microfluidic devices, MEMS/NEMS, and other nanotechnology-based miniature devices.

g. **Thermal conductivity of nanofluids containing surface-modified nanoparticles and/or no dispersants**

A few research groups produced nanofluids without any dispersants or with surface-modified nanoparticles (Das *et al.*, 2003a; 2003b; 2003c; Lee *et al.*, 1999; Lee *et al.*, 2008) because the addition of chemical dispersants and stabilizers could adversely influence the properties of nanofluids. Recently, Yu *et al.* (2008) made stable nanofluids by dispersing plasma-treated diamond nanoparticles with no surfactants and showed almost 20% increase in thermal conductivity at 0.15 vol.% of diamond nanoparticles. This work showed the importance of particle surface treatment. This work also illustrated that methods for making nanofluids without using any dispersants are preferred, especially for reference nanofluids. When dispersants and stabilizers are used, their role in altering the microstructure and properties of nanofluids should be studied.

In summary, the unique features of the thermal conductivity of nanofluids, such as anomalously enhanced behavior at low particle concentrations, a nonlinear relationship with

particle volume fraction, and temperature- and size-dependence have been observed in most of the experimental studies carried out over more than 10 years. Nearly all of the anomalous features have been confirmed by multiple groups. However, there are other groups that have observed no anomalous conductivity with their nanofluids. As a result, whether the anomalous features of the k of nanofluids are real or not has become an issue that has sparked controversy in the nanofluids community. Considering the various synthesis methods and process parameter variations and the experimental difficulties in accurately measuring thermal conductivity of nanofluids, it is understandable to have such controversy.

3. **Mechanisms for enhanced heat conduction in nanofluids**

As shown in Figure 1, the classic Maxwell effective medium model (Maxwell, 1873) that assumes the thermal diffusion mechanism underpredicts the magnitude of the thermal conductivity enhancement of most of the nanofluids. Maxwell's model shows that the thermal conductivity of nanofluids depends only on the volume fraction of nanoparticles when the volume fraction is low and the thermal conductivity ratio of nanoparticles to fluid is high. However, the majority of the experimental data described in the previous section show that the thermal conductivity of nanofluids depends on a number of other parameters such as particle size and fluid temperature and acidity. This implies that classical effective medium theories cannot predict some of the new features of the thermal conductivity of nanofluids. Regarding the hypothesis that some fundamental mechanisms that are missing in classical effective medium theories could change the traditional understanding of how heat is conducted, several investigators proposed new concepts and mechanisms behind the thermal conductivity behavior of nanofluids.

The proposed heat conduction mechanisms in nanofluids can be categorized into static mechanisms and dynamic mechanisms. Static mechanisms, which assume that nanoparticles are motionless in nanofluids, include nanolayer, aggregation and percolation, interface thermal resistance, and fractal geometry. Dynamic mechanisms, which are based on the assumption of randomly moving nanoparticles in nanofluids, include Brownian motion and nanoconvection. These mechanisms are developed on a microscopic level.

a. **Microscopic static mechanisms**

Yu *et al.* (2000) showed experimentally the existence of an ordered layer of liquid molecules at the solid-liquid interface that had been predicted for years (Henderson and van Swol, 1984). This nanolayer structure was introduced by Keblinski *et al.* (2002) and Yu and Choi (2003) as the first static mechanism to explain the enhanced thermal conductivity of nanofluids. Figure 6 shows the basic concept of nanolayer. Keblinski *et al.* (2002) estimated the upper limit for the thermal conductivity enhancement with nanolayer effect by assuming that the thermal conductivity of the liquid nanolayer is the same as that of the solid nanoparticle. Yu and Choi (2003) proposed the concept that a nanolayer acts as a thermal bridge between a nanoparticle and a bulk liquid. Based on this new mechanism of a thermal bridge nanolayer, Yu and Choi developed a renovated Maxwell model for the effective thermal conductivity of nanofluids containing spherical nanoparticles with an ordered nanolayer. They extended the concept of the thermal bridge nanolayer to nonspherical particles and renovated the Hamilton-Crosser model (Yu and Choi, 2004).

Clustering or aggregation is an inherent property of nanoparticles whether they are in liquid or dry powder form due to van der Waals forces. Keblinski *et al.* (2002) conceptualized clustering of nanoparticle as a mechanism of enhanced k of nanofluids, assuming that clustered

nanoparticles provide local percolation-like paths for rapid heat transport and increase the effective nanoparticle volume fraction. Wang *et al.* (2003) developed a fractal model for predicting the k of nanofluids containing nanoparticle clusters. Prasher *et al.* (2006a; 2006b) studied the effects of aggregation on the k of nanofluids and showed that the aggregation time constant decreases rapidly with decreasing nanoparticle size and that the k enhancement increases with increasing level of aggregation, leveling off after the optimum level of aggregation is reached. However, Xuan *et al.* (2003) simulated Brownian motion and aggregation of nanoparticles and showed that nanoparticle aggregation reduces the k of nanofluids because the random motion of aggregates is slower than that of a single nanoparticle.

b. **Microscopic dynamic mechanisms**

Effective medium theories assume that particles are stationary in a fluid. Thus, effective medium theories with the microscopic static mechanisms described above cannot explain the k behavior such as temperature- and particle-size-dependence. A suspension of nano-sized particles is different from that of micro- or millimeter-sized particles in that the latter are static and the former are dynamic; nanoparticles are constantly in random motion, even if the bulk fluid is stationary. So it is expected that there will be a fundamental difference in the mechanisms of heat transport in nanofluids due to their dynamic effects.

There are two kinds of Brownian motion in nanofluids: collision between Brownian nanoparticles and convection induced by Brownian nanoparticles. Figure 7 shows the basic concept of Brownian-particle-induced convection.

Collision between nanoparticles due to Brownian motion of nanoparticles is the first dynamic mechanism studied for enhanced k of nanofluids. However, Wang *et al.* (1999) and Keblinski *et al.* (2002) have shown that the k enhancement due to collision between Brownian

nanoparticles is negligible because Brownian nanoparticle diffusion is much slower than thermal diffusion.

Realizing that nanoparticle diffusion has little effect on the k of nanofluids because it is orders of magnitude slower than thermal diffusion, Jang and Choi (2004) proposed the hypothesis that Brownian nanoparticles induce convection at the nanoscale level and that Brownian-motion-induced nanoconvection is a key mechanism to explain the temperature- and size-dependent thermal conductivity of nanofluids. Jang and Choi model (Jang and Choi, 2004) captures both the temperature- and size-dependent features of the thermal conductivity of nanofluids whereas EMT-based models fail to capture any features. Koo and Kleinstreuer (2004) extended the concept of nanoconvection to include the effects of fluids dragged by a pair of nanoparticles and mixing. Prasher *et al.* (2005) extended the concept of nanoconvection by considering the effect of Brownian-motion-induced convection from multiple nanoparticles. Patel *et al.* (2005) used nanoconvection induced by Brownian nanoparticles and the specific surface area of nanoparticles in their micro-convection model. Ren *et al.* (2005) considered kinetic-theory-based microconvection and liquid layering in addition to liquid and particle conduction.

However, the nanoconvection mechanism has been questioned. Evans *et al.* (2006) and Vladkov and Barrat (2006), among others, used molecular dynamics simulations (MDS) to show that the contribution of nanoconvection to the thermal conductivity enhancement is negligible. However, Sarkar and Selvam (2007) also used MDS to show that the thermal conductivity enhancement is mostly due to the increased movement of liquid atoms in the presence of nanoparticles. Li and Peterson (2007a) simulated the mixing effect of the base fluid directly adjacent to the nanoparticles and showed that Brownian-motion-induced microconvection and mixing significantly enhance the macroscopic heat transfer in nanofluids. Eapen *et al.* (2007)

showed experimentally that microconvection does not enhance the thermal conductivity of silica and Teflon suspensions. Therefore, the debate over the nanoconvection mechanism will continue until it is resolved experimentally at the nanoscale.

In summary, a number of microscale and macroscale mechanisms have been proposed to explain the magnitude and trend of the thermal conductivity of nanofluids because effective medium theories based on the underlying assumption of diffusive conduction and motionless nanoparticles cannot predict new features of the thermal conductivity of nanofluids. New models based on the proposed heat conduction mechanisms in nanofluids can predict both the magnitude and trend of the thermal conductivity of nanofluids. However, they cannot accurately predict experimental data. The controversy regarding the proposed mechanisms of the thermal conductivity of nanofluids is far from over (Evans *et al.*, 2006; 2007; Kumar and Murthy, 2005; Xue *et al.*, 2004). The controversy comes primarily from a lack of understanding of the scientific basis for the mechanisms of enhanced thermal conductivity of nanofluids (Chandrasekar and Suresh, 2009; Das *et al.*, 2006). Therefore, the proposed concepts and mechanisms behind the thermal conductivity behavior of nanofluids remain to be validated.

C. **Motivation for Systematic Study on Nanofluids**

The lack of an agreement between experimental data from different groups can be due to differences in sample quality, the dependence of thermal conductivity on many factors, and differences in measurement uncertainties, as described in the previous Section. For example, in case of gold (Au) nanofluids, some research groups (Patel *et al.*, 2003; Paul *et al.*, 2010) observed significant enhancement in the k of nanofluids, while other groups (Putnam *et al.*, 2006; Shalkevich *et al.*, 2010) did not, as shown in Figures 8 and 9. Moreover, in the case of

Al₂O₃/water nanofluids, although experiments were performed with similar volume concentration (~4 vol.%), some researchers have discovered that nanofluids have strongly temperature-dependent thermal conductivity (Chon *et al.*, 2005; Das *et al.*, 2003c; Mintsu *et al.*, 2009), while other showed no temperature dependency (Zhang *et al.*, 2006a; 2006b), as shown in Figure 10.

There are several ways to reduce data inconsistencies due to differences in sample quality. It appears that the primary causes of the significant discrepancies in all nanofluid k data are vast differences in quality between samples that are supposedly identical or at least similar in ingredients and concentrations and uncertainty in characterizing nanoparticles including the size, shape, surface properties, and agglomeration of nanoparticles. Since these characteristics are determined in the production process, the first step in investigating the causes of these data discrepancies, as well as in evaluating any physical mechanisms and theoretical models, is to produce nanofluids of high quality in terms of stability and thermal conductivity, containing the same concentrations and ingredients, preferably without any dispersants or stabilizers especially for reference nanofluids, using the same processes for making nanofluids. When dispersants and stabilizers are used, their role in altering the microstructure and properties of nanofluids should be understood. Nanofluids produced in this way for thermal conductivity measurements should then be characterized, including particle size and size distribution, shape, surface properties, and structures such as levels of agglomeration/clustering of nanoparticles.

In addition to the differences in sample quality, another major cause of the large discrepancies in the k data is the fact that the k of nanofluids depends on a great number of parameters, some of which are coupled. Experimental studies have shown that the k of nanofluids is determined by parameters related to (1) nanoparticles—e.g., concentration, size

(Chon *et al.*, 2005; Patel *et al.*, 2003; Xie *et al.*, 2002a), shape (Eastman *et al.*, 2001; Patel *et al.*, 2003; Xie *et al.*, 2002b—for spherical; Choi *et al.*, 2001; Xie *et al.*, 2003—for nonspherical), agglomeration (fractal-like shapes) (Das *et al.*, 2003c; Lee *et al.*, 1999; Lee *et al.*, 2006; Murshed *et al.*, 2005; Xuan and Li, 2000; Xuan *et al.*, 2003), surface charge (Lee, 2007) and thermal conductivity; (2) base fluids—e.g., thermal conductivity and viscosity; (3) temperature (Das *et al.*, 2003c; Li and Peterson, 2006; Patel *et al.*, 2003); (4) the interfacial chemical/physical effect or interaction between the particles and base fluid (Lee *et al.*, 2006; Xie *et al.*, 2003); and others. Therefore, for meaningful comparison between measured data and critical evaluation of models, it is necessary to measure the k of completely characterized nanofluids including the suspension stability as a function of one variable while the others are fixed. However, this is challenging as indicated by Bang and Heo (2009), who have applied axiomatic design theory (Suh, 2001) to the design of nanofluids. Some of the parameters are coupled, and ideas to decouple them are needed.

Another way to reduce data inconsistencies due to differences in sample quality and differences in measurement uncertainties is to conduct round-robin tests using identical test samples and accurate methods and apparatuses for measuring the thermal conductivity of nanofluids. Recently, an international nanofluid property benchmark exercise (INPBE) (Buongiorno *et al.*, 2009b) was launched to validate nanofluid thermal conductivity measurement methods and to resolve the large discrepancies in the k data. The main findings of the exercise are that the thermal conductivity enhancement was consistent between various measurement techniques and that the generalized effective medium theory was in agreement with the measured thermal conductivity data, suggesting that no anomalous enhancement of thermal conductivity was achieved in the nanofluids they tested (Buongiorno *et al.*, 2009b). For example, the highest average thermal conductivity ratio of 20% was achieved at 31 vol.% of silica

nanoparticles in water. This is much smaller than the theoretical predictions of the EMT of Maxwell (1873) or Bruggeman (1935). In contrast, Lee *et al.* (2011) produced ethylene glycol-based ZnO nanofluids containing no surfactant by a one-step physical method, conducted round-robin tests on thermal conductivity measurements of three samples of surfactant-free nanofluids, and demonstrated that the measured thermal conductivities are beyond the lower and upper bounds calculated using the models of the Maxwell (1873) and Nan *et al.* (1997), with and without the interfacial thermal resistance. Therefore, it is highly desirable to make high-quality nanofluids with both suspension stability and high conductivity for use as reference nanofluids as a way to resolve issues such as the anomalous k behavior of nanofluids. More systematic experiments with well-dispersed, well-characterized nanofluids (i.e., high-quality nanofluids) and a better understanding of the physics of fluid flow and heat transfer at the nanoscale are needed to establish the fundamental mechanisms of heat conduction in nanofluids. Understanding these mechanisms is essential for the development of models that can accurately predict the k behavior of nanofluids.

D. **Objectives**

The objectives summarized for the present research are as follows: (1) development of the novel synthesis methods to produce aqueous nanofluids with small volume fraction of particles (lower than 1 vol.%) in accordance with the term of ‘nanofluids’ (Choi, 2009); (2) morphological characterization (i.e. particle size and size distribution measurements) of produced nanoparticles by novel synthesis methods; (3) development of custom-made transient hot wire (THW) system to minimize natural convection effects and measurements uncertainty in thermal conductivity measurements, (4) measurements of thermal conductivity of nanofluids

with variation of particle size and temperature, (5) pH and electrical conductivity measurements of produced nanofluids, and (6) investigation of main contributing factors which affect the formation of nanoparticles in novel synthesis method and thermal conductivity enhancement of nanofluids.

1. **Development of novel synthesis methods of nanofluids**

- a. **Gold nanofluids with the novel one-step chemical method**

Gold nanoparticles (GNPs) have generated much interest due to their unique and attractive physical and chemical properties, such as high thermal and electrical conductivity, photothermal effects, tunable size and shape dependent optical properties, chemical stability, biocompatibility and facile functionalization, and are used in a wide range of applications including material science, catalysis, biomedicine, and quantum dots technology (Alivisatos, 2001; Daniel and Astruc, 2004; Niemeyer, 2001; Umar *et al.*, 2012; Wu *et al.*, 2011; 2012). Since the first scientific research on the formation of gold colloids by the reduction of gold trichloride by phosphorus was published by Faraday in 1857 (Faraday, 1857), various methods for the synthesis of colloidal gold have been used, such as chemical methods (Brust *et al.*, 1994; Martin *et al.*, 2010; Perrault and Chan, 2009; Turkevich *et al.*, 1951). The well-known Turkevich method (Frens, 1973; Turkevich *et al.*, 1951) is the simplest way to produce aqueous suspensions of monodispersed GNPs with good stability (Turkevich, 1985). Moreover, reported results show that thermal conductivity of gold nanofluids which produced by Turkevich method enhanced up to 8% (Patel *et al.*, 2003) and 48% (Paul *et al.*, 2010) at very small volume fraction as 2.6×10^{-4} vol.% as shown in Figure 9a.

Sonochemistry has also been used to synthesize colloidal gold since the pioneering work on the formation of GNPs using ultrasonic sound was carried out in 1980 (Baigent and

Müller, 1980). Extensive studies on the sonochemical production of GNPs have been performed to investigate the effects of many synthesis variables on the size of GNPs (Baigent and Müller, 1980; Caruso *et al.*, 2002; Nagata *et al.*, 1996; Okitsu *et al.*, 2001; 2005; Polavarapu and Xu, 2009; Reed *et al.*, 2003; Yeung *et al.*, 1993). These studies show that most GNPs have been synthesized in non-aqueous solutions using a high intensity ultrasonic generator. For example, various alcohols were used as the base fluid, reducing agent, and stabilizer in the greater part of sonochemical works (Baigent and Müller, 1980; Caruso *et al.*, 2002; Nagata *et al.*, 1996; Okitsu *et al.*, 2001; 2005; Yeung *et al.*, 1993). However, with regard to GNPs synthesized in aqueous solutions, there has only been limited research. It has been reported that the rates of the formation of GNPs in pure water were approximately zero without any additives such as surfactants, water-soluble polymers and aliphatic alcohols and ketones under atmospheric conditions, resulting in only a small amount of synthesized GNPs that were unstable and coagulated within several hours (Nagata *et al.*, 1996). Horn or cup-horn type ultrasonic generators were used in previous studies (Baigent and Müller, 1980; Caruso *et al.*, 2002; Nagata *et al.*, 1996; Okitsu *et al.*, 2001; 2005; Reed *et al.*, 2003; Yeung *et al.*, 1993) to apply sufficient ultrasound energy to cause the pyrolysis of fluid molecules. An appropriate ultrasonic energy is required to induce collapsing gas bubbles with high temperature (in excess of 4,000 K) (Flint and Suslick, 1991; Henglein, 1987). It also has been reported that the reduction of gold (III) occurred when using a high intensity ultrasonic generator, but this did not occur when using a conventional ultrasonic bath (Okitsu *et al.*, 2001).

The present study is interested in producing GNPs in water (i.e., aqueous Au nanofluids), not in an organic medium, because GNPs used in biological applications are in water. Hence, it is of practical interest to synthesize aqueous GNPs in a simpler but more

consistent process using a conventional ultrasonic bath instead of a horn or cup-horn type ultrasonic apparatus. The importance of the synthesis of aqueous GNPs is well-summarized by Ji *et al.* (2007) as follows: (1) High-quality gold nanocrystals have been synthesized in non-aqueous solutions under elevated temperatures; (2) however, from a green chemistry standpoint, all non-aqueous synthetic schemes are far from ideal; (3) water may eventually become a plausible medium for the growth of high-quality nanocrystals with various compositions (Pradhan *et al.*, 2007); and (4) success will likely come with systematic and quantitative studies of some carefully chosen aqueous model systems such as aqueous gold nanocrystals synthesized by citrate reduction. In addition, a conventional ultrasonic bath may become a simple apparatus for the production of consistent quality spherical GNPs in aqueous solutions. However, Nagata *et al.* (1996) and Okitsu *et al.* (2001) have shown that it is barely possible to synthesize stable GNPs in pure water using a conventional ultrasonic bath under atmospheric conditions.

Recently, Chen and Wen (2011) proposed a novel ultrasonic-aided method for the synthesis of aqueous gold nanofluids containing both spherical and plate-shaped GNPs and demonstrated that their shape and size were controllable. They synthesized aqueous gold nanofluids containing spherical GNPs by the conventional citrate reduction method, and then placed the gold nanofluids in an ultrasonic bath to study the effect of sonication time on nanoparticle size. They also synthesized aqueous gold nanofluids containing plate-shaped GNPs by citrate reduction of chloroauric acid (HAuCl_4) solutions immersed in an ultrasonic bath at room temperature to study the effect of sonication time on the morphology of the gold materials produced.

In this work, only a conventional ultrasonic bath was used without a heater or magnetic stirrer under atmospheric conditions to examine the feasibility of forming aqueous gold

nanofluid by sodium citrate reduction. Although ultrasonication was used in this study and in Chen and Wen (2011), its effect is quite different. Since gold nanofluids with spherical-shaped GNPs were produced in the presence of ultrasonication, it is possible to see the effects of sonication on the formation of spherical-shaped GNPs in the present study. In contrast, such effects were essentially non-existent in the investigation of Chen and Wen (2011) because they sonicated aqueous spherical-shaped GNPs that had been formed and grown in the absence of ultrasonication. The work also examines the effects of ultrasonic energy on the size and morphology of GNPs and discusses a proposed scheme for understanding the role of ultrasonic energy in the formation and growth of spherical GNPs in an ultrasonic bath. The present study shows for the first time that aqueous gold nanofluids with spherical GNPs can be produced by sodium citrate reduction in a conventional ultrasonic bath without any additional heater or magnetic stirrer. This single-step synthesis of aqueous gold nanofluids using a conventional ultrasonic bath allows us to investigate the effects of sonication time and ultrasonic energy on the formation and growth of GNPs.

b. **Alumina nanofluids with the novel two-step method**

Ceramic nanofluids were the first type of nanofluids investigated by the Argonne National Laboratory research group (Eastman *et al.*, 1997). The most common ceramic nanoparticles used by many researchers in their thermal conductivity experiments (Chon *et al.*, 2005; Das *et al.*, 2003c; Lee *et al.*, 1999; 2008; Li and Peterson, 2006; 2007b; Lin *et al.*, 2011; LotfizadehDehkordi *et al.*, 2013; Mintsu *et al.*, 2009; Murshed *et al.*, 2006; 2008; Nine *et al.*, 2012; Patel *et al.*, 2010; Rehman *et al.*, 2012; Schmidt *et al.*, 2008; Teng, 2013; Teng *et al.*, 2010; Timofeeva *et al.*, 2007; Vasheghani *et al.*, 2011; Wang *et al.*, 1999; Xie *et al.*, 2002a; Yang *et al.*, 2012; Yiamsawasd *et al.*, 2012; Zhang *et al.*, 2006a; 2006b) are alumina (Al_2O_3)

particles. As aforementioned in Section B, however, some of drawbacks in current research on thermal conductivity of alumina nanofluids include the lack of agreement between results obtained by different research groups. It can be presumed that the most cause of data discrepancies comes from the quality of synthesized nanofluids. Most of alumina nanofluids were produced by two-step method (Chon *et al.*, 2005; Das *et al.*, 2003c; Lee *et al.*, 1999; 2008; Li and Peterson, 2006; 2007b; LotfizadehDehkordi *et al.*, 2013; Mintsu *et al.*, 2009; Murshed *et al.*, 2008; Nine *et al.*, 2012; Patel *et al.*, 2010; Schmidt *et al.*, 2008; Teng, 2013; Timofeeva *et al.*, 2007; Vasheghani *et al.*, 2011; Wang *et al.*, 1999; Xie *et al.*, 2002a; Yang *et al.*, 2012; Zhang *et al.*, 2006a), generally. In the two-step method, the nanoparticles were produced as a dry powder form, and then dispersed into a fluid to obtain the nanofluids. Thus, the dispersion method can be the key factor to evaluate the quality of nanofluids when using two-step method since it is difficult to prepare stable nanofluids with this method (Yu and Xie, 2012). However, the intrinsic surface properties of nanoparticles when dry powers form should not be overlooked. Dry powders usually have been fabricated by chemical or physical methods (Choi, 2009). Consequently, the surface properties of each dry powder can vary in the fabrication process. For example, TiO_2 (Levchenko *et al.*, 2007; Spencer *et al.*, 2009), SnO_2 (Shi *et al.*, 2012; Spencer *et al.*, 2011), and PdO (Spencer *et al.*, 2012) nanoparticles can be synthesized with varying amounts of water confined on the surface of their nanoparticles depending on the fabrication method. Furthermore, the thermal properties of each oxide nanoparticle were different (Levchenko *et al.*, 2007; Shi *et al.*, 2012; Spencer *et al.*, 2009; 2011, 2012). This implies that the surface properties of particles can be varied according to the synthesis method even in case of having the same particle size. However, most research groups missed the intrinsic surface properties of nanoparticles in the investigation of particle size effects on the k of nanofluids.

Chon *et al.* (2005), Timofeeva *et al.* (2007), and Beck *et al.* (2009) investigated the particle size effects on the k of alumina nanofluids, to name a few. They all used different nanoparticles to compare the effects of particle size on the enhancement of thermal conductivity. It can be presumed that the inconsistencies and/or contradictions of their results maybe come from the passing over of intrinsic surface properties of nanoparticles. Thus, the modified two-step method of alumina nanofluids is suggested in the present study, to minimize the differences of intrinsic surface properties of nanoparticles when preparing the different-sized nanofluids.

Centrifugation generally used to separate particles from the mixture in many industrial and academic fields. Centrifugation was occasionally used to evaluate the stability of nanofluids. Li and Kaner (2005) synthesized aqueous polyaniline nanofiber colloids and used centrifugation to evaluate the stability of the colloids. Singh and Raykar (2008) also applied centrifugation to examine the stability of silver nanofluids prepared by the microwave synthesis method. Centrifugation is only used to estimate the stability of already produced nanofluids in aforementioned previous researches (Li and Kaner, 2005; Singh and Raykar, 2008).

Remained particles in supernatant liquid after centrifugation can have better stability since they overcome the exerted centrifugal force. This implies that the supernate resulting from the centrifugation can be also nanofluid since the supernate still contains particles. Thus, centrifugation is used in the production method of nanofluids with the two-step method in the present study. The present study shows for the first time that three alumina nanofluids, which have three different sizes of alumina nanoparticles, were produced by using one identical-sized alumina nanoparticles without any dispersants and surfactants. This modified synthesis method of producing three different sizes of alumina nanoparticles from single sized nanoparticles can minimize the difference of dispersibility to the base fluid compared to the method of purchasing

three different sizes of alumina nanoparticles due to possible variation of intrinsic surface characteristics from different manufacturing process.

2. **Development of modified transient hot wire (THW) system**

Transient hot wire (THW) method is very widely used technique for measuring thermal conductivity of nanofluids. The main advantage of this method is elimination of convective contributions on the measurement results because the experiment is performed within only few seconds before acceleration of fluid is started by buoyancy forces (*Wakeham et al.*, 1991). Another advantage is the THW method is very fast relative to steady-state method (*Lee et al.*, 1999). However, many uncertain parameters should be considered before measuring thermal conductivity of nanofluids for obtaining reliable data. Thus, in the present study, the modified transient hot wire (THW) system was designed and manufactured in-house considering effect of the tilting angle of the wire (*Giaretto et al.*, 2007; Lee and Jang, 2012) to minimize measurement error, especially due to natural convection.

TABLE I**ADVANTAGES AND DISADVANTAGES OF NANOFLUIDS SYNTHESIS METHODS USED TO DATE**

	Advantages	Disadvantages
One-step physical method	– Good to increase stability of nanofluids – Good to prevent oxidation of metallic particles – Good to reduce particle agglomeration	– Difficult to scale-up (due to high cost and long production time) – Hard to measure particle concentration
One-step chemical method	– Capable of changing particle size and shape – Capable of producing metallic nanoparticles – Relatively easier synthesis procedure than one-step physical method	– Occurrences of particle agglomeration and settlement at high temperature – No data for chemical residue effects on properties of nanofluids (due to remanent reactants) – Hard to synthesize nanofluids with high particle concentration (due to agglomeration) – Incapable of mass production
Two-step method	– Simple production procedure – Easy to control the particle concentration – Scaled up production to commercial quantities	– Easy agglomeration without surfactants – Easy agglomeration in the dried powder status – Almost impossible to produce metallic nanofluids (due to oxidation and agglomeration)

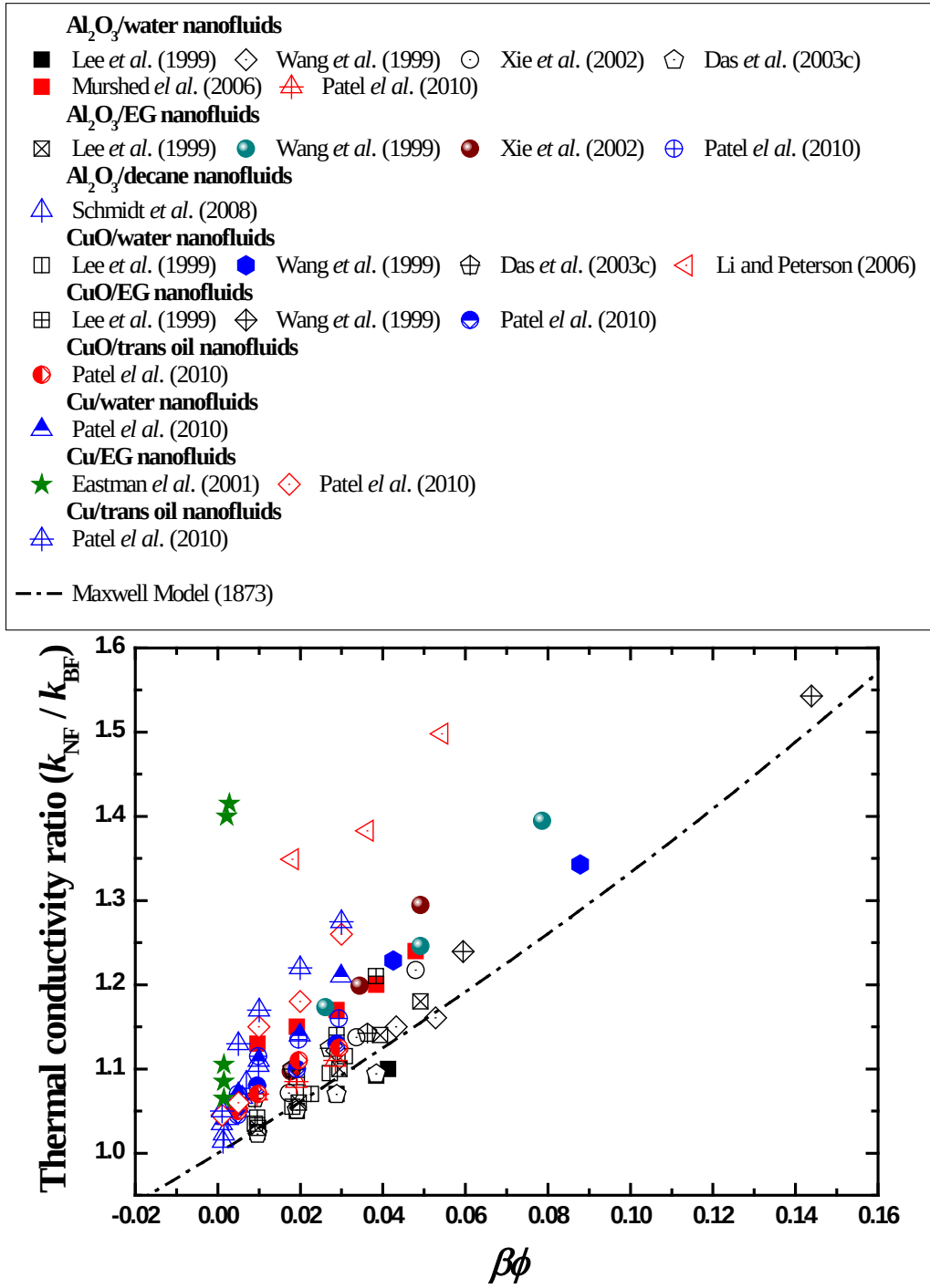
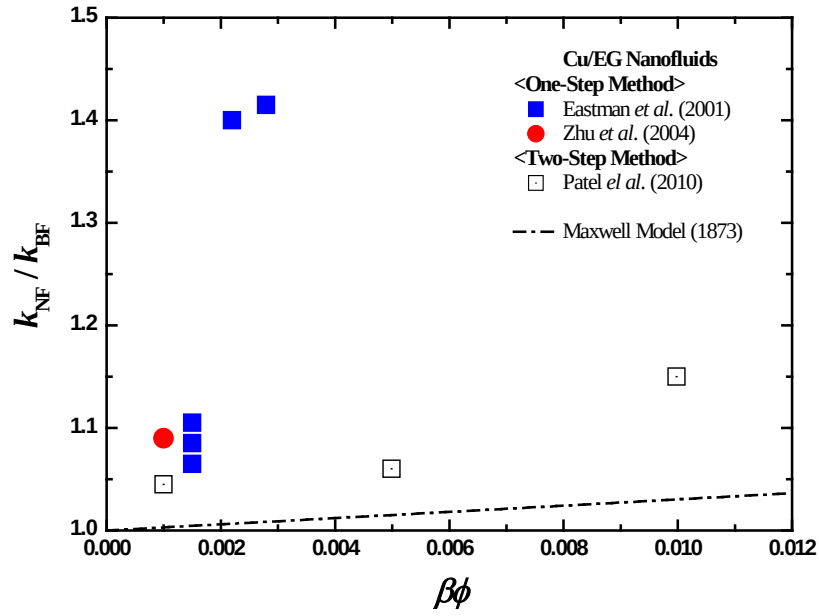
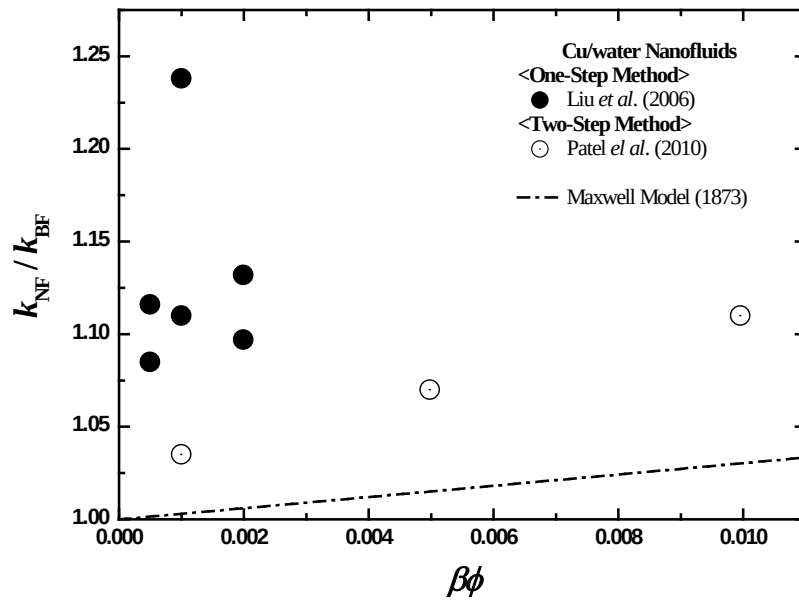


Figure 1. Experimental data on the ratio of thermal conductivity of nanofluids to that of the base fluid as a function of $\beta\phi$, where $\beta \equiv [k_p - k_{BF}]/[k_p + 2k_{BF}]$ and ϕ is the volume fraction of nanoparticles.



(a) Experimental results of thermal conductivity ratio of Cu/EG nanofluids.



(b) Experimental results of thermal conductivity ratio of Cu/water nanofluids.

Figure 2. Comparison of the thermal conductivity ratio for nanofluids produced using one-step and two-step processes.

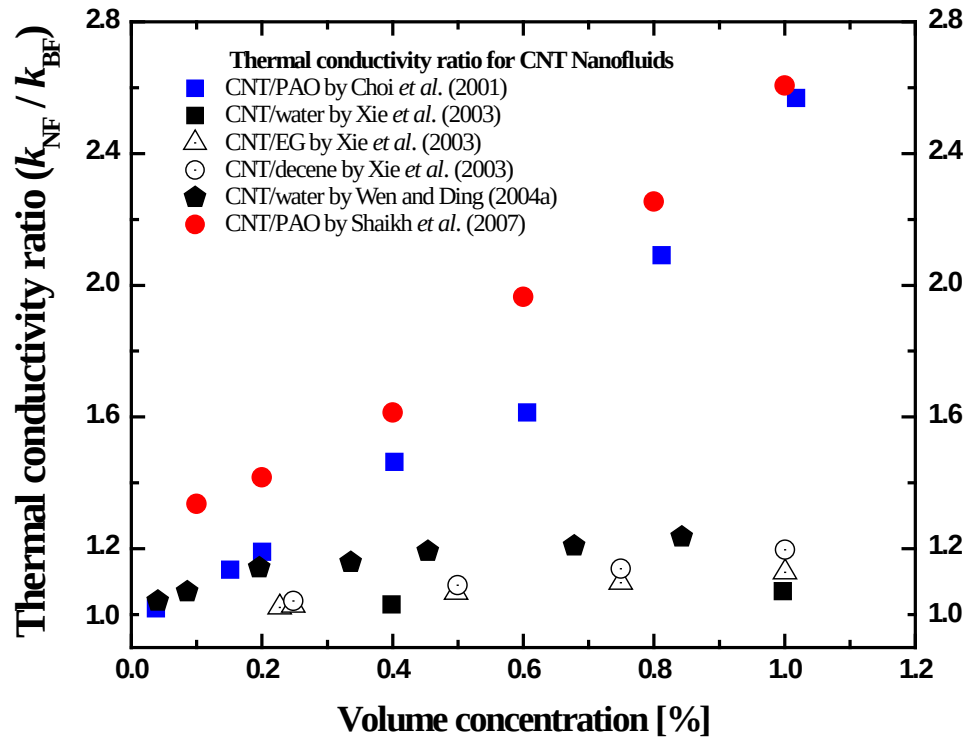
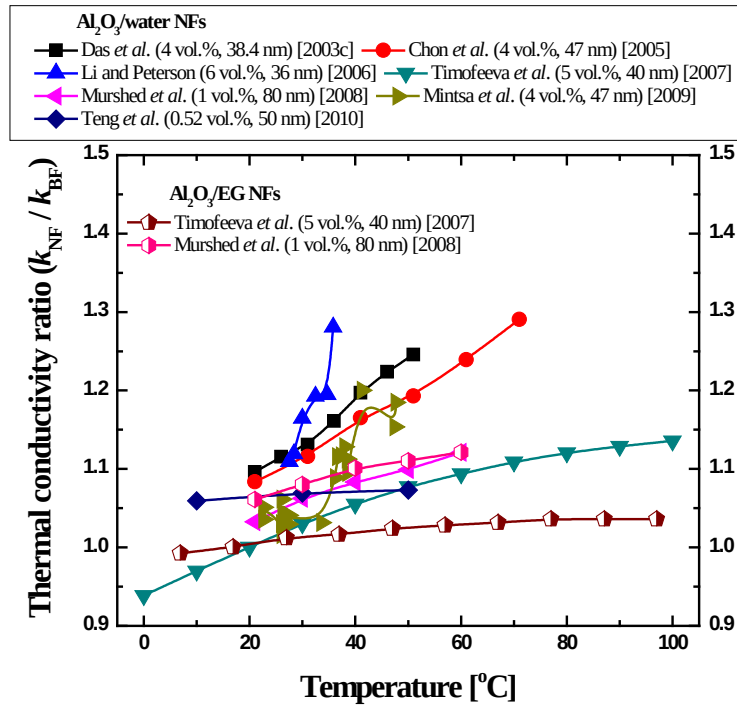
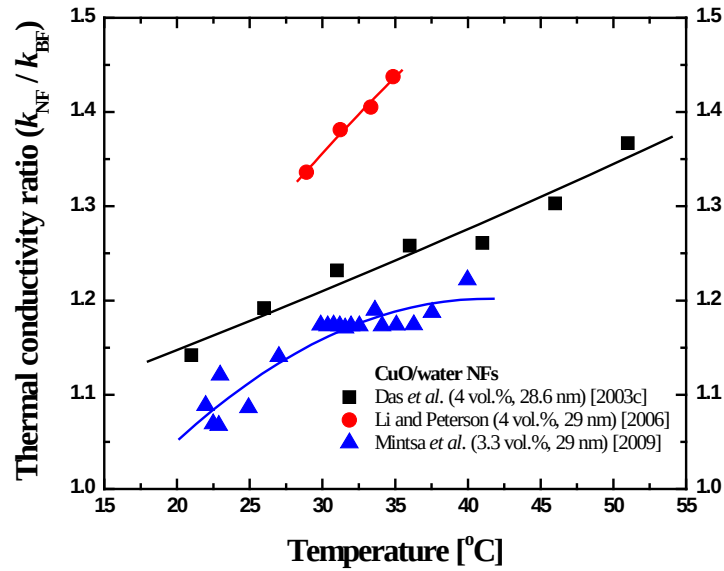


Figure 3. Comparison of the thermal conductivity ratio for CNT nanofluids produced by four groups. Shaikh *et al.* [Shaikh *et al.*, 2007] independently confirmed the magnitude of enhancements and nonlinear trend in the thermal conductivity of the CNT/PAO oil nanofluids Choi *et al.* [Choi *et al.*, 2001] reported six years ago.

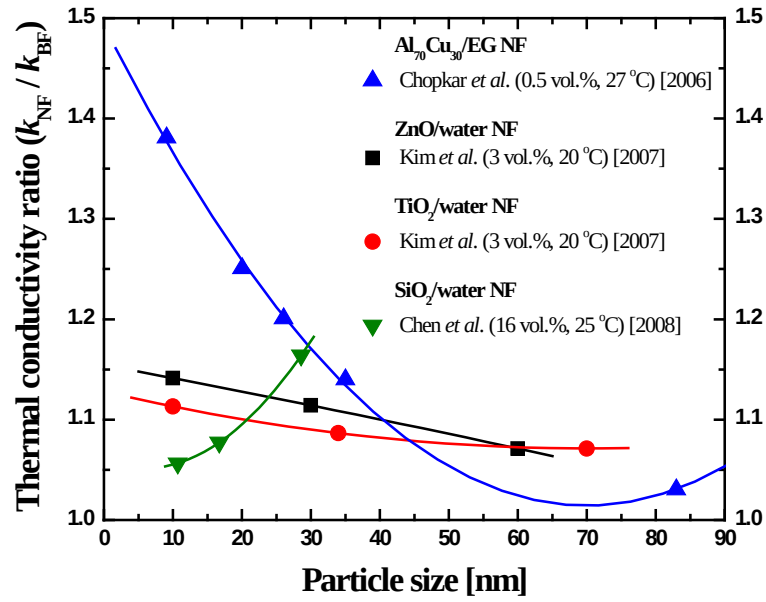


(a) Experimental results of thermal conductivity ratio of Al₂O₃ nanofluids.

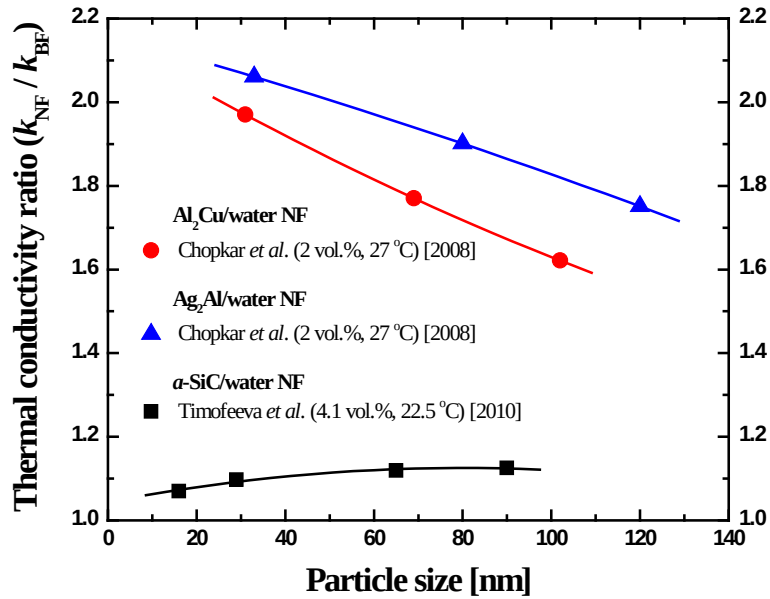


(b) Experimental results of thermal conductivity ratio of CuO nanofluids.

Figure 4. Comparison of the thermal conductivity ratio for nanofluids as a function of temperature.

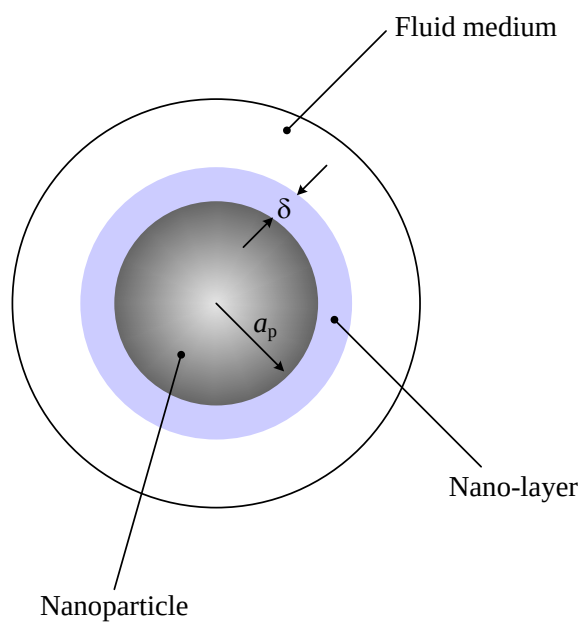


(a) Published experimental results of k ratio of nanofluids through 2006 to 2008.

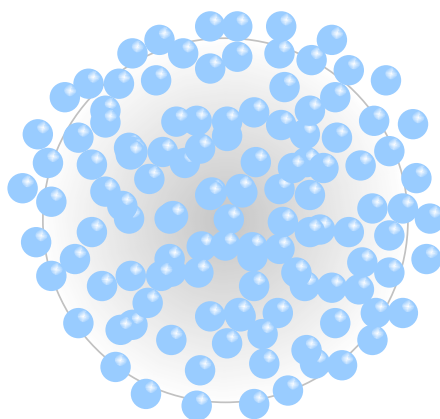


(b) Published experimental results of k ratio of nanofluids through 2008 to 2010.

Figure 5. Comparison of the thermal conductivity ratio for nanofluids as a function of particle size.



(a) Schematic of nanolayer



(b) Nanolayer

Figure 6. Single spherical nanoparticle with nanolayer (or interfacial layer) in the base fluid.

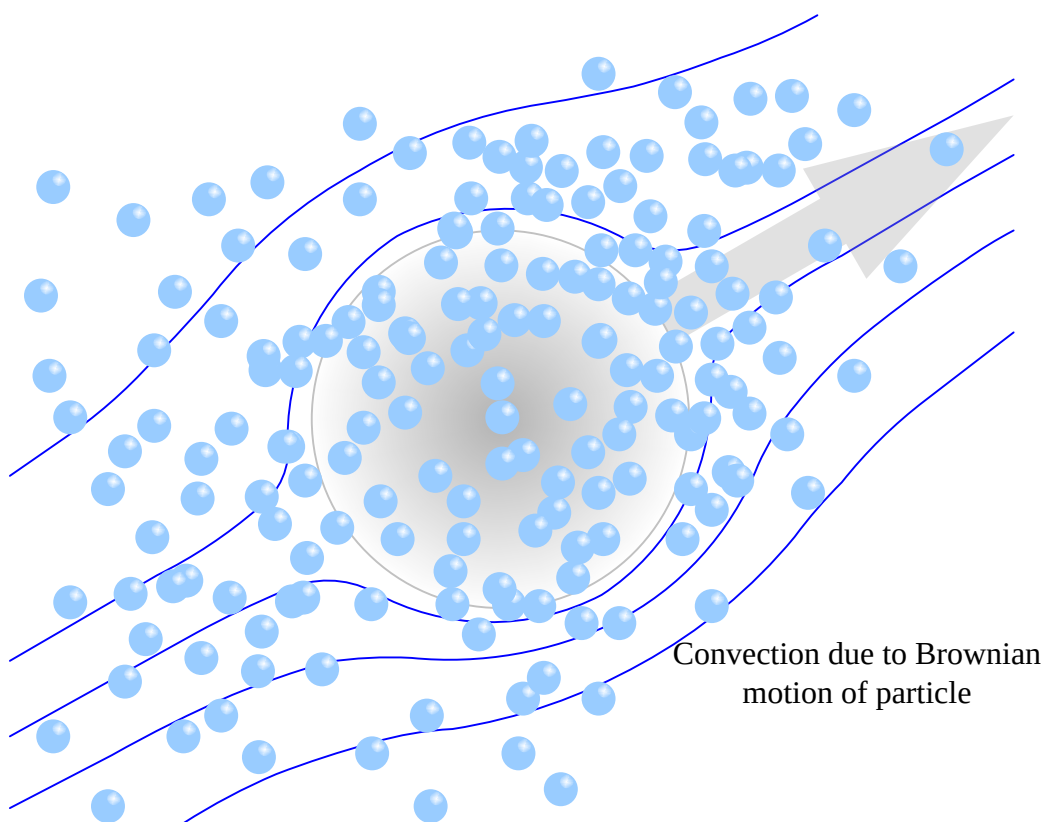


Figure 7. Microscale convection effect due to the Brownian motion of the particle.

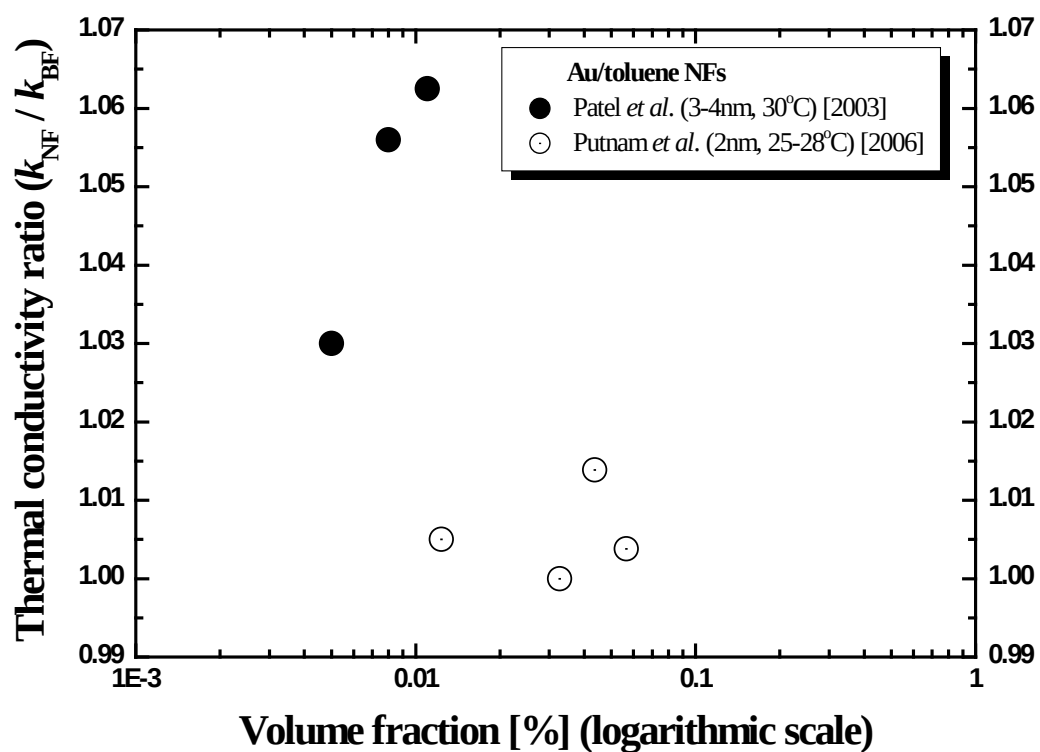
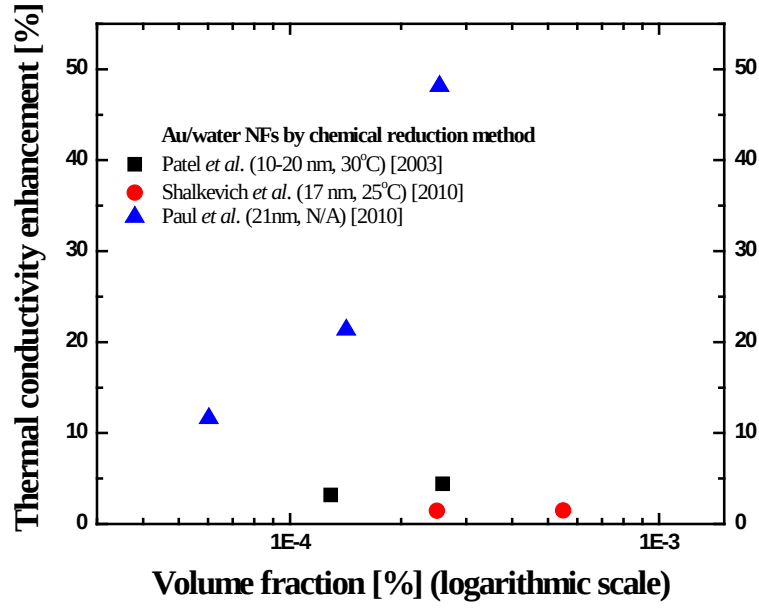
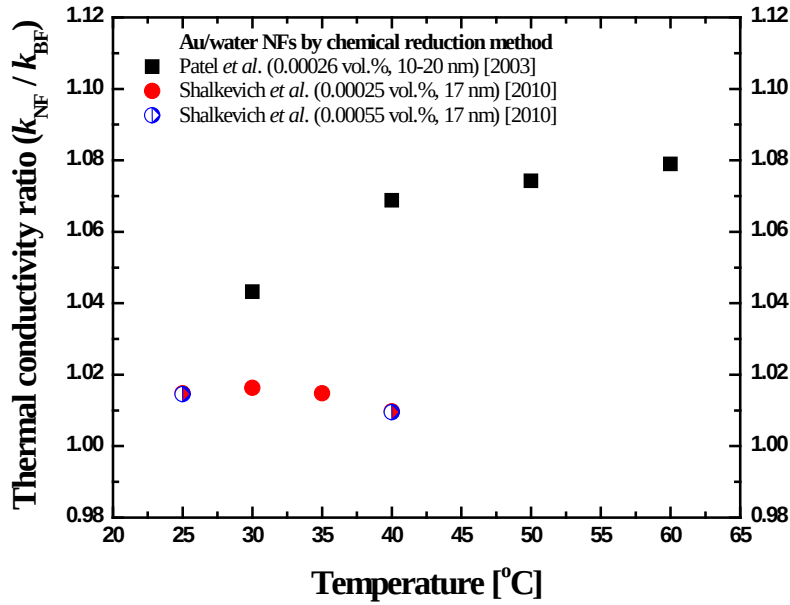


Figure 8. Experimental data of thermal conductivity enhancement of gold (Au) nanoparticles suspended in toluene as a function of volume fraction (logarithmic scale).



(a) Experimental results of k enhancement as a function of volume fraction (logarithmic scale).



(b) Experimental results of thermal conductivity ratio as a function of temperature.

Figure 9. Comparison of the thermal conductivity ratio for Au/water nanofluids.

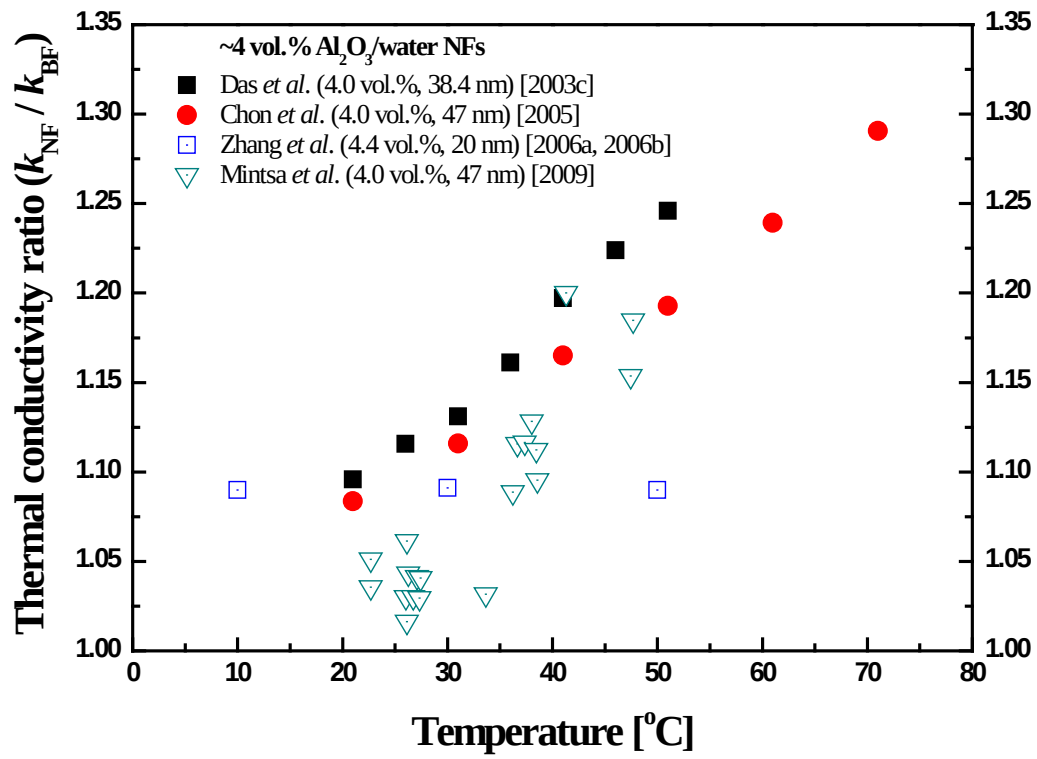


Figure 10. Comparison of the thermal conductivity ratio for Al_2O_3 /water nanofluids with similar volume fraction (~4 vol.%) as a function of temperature.

II. EXPERIMENTAL METHODS

A. Production of Gold Nanofluids Using an Ultrasonic Bath

1. Gold nanofluids production as a function of sonication time

Two separate but identical aqueous chloroauric acid (HAuCl_4) solutions were prepared by adding HAuCl_4 (Sigma-Aldrich Corporation, St. Louis, MO, USA) to two conical flasks filled with 200 ml HPLC (high-performance liquid chromatography) grade water (J.T. Baker Chemical Company, Phillipsburg, NJ, USA). The HAuCl_4 concentration was set to 0.25 mM (Huang *et al.*, 2006; Ji *et al.*, 2007; Paul *et al.*, 2010). A conventional ultrasonic bath (VWR Aquasonic 150 T, 40 kHz, 135 W, VWR International, LLC, Radnor, PA, USA) was filled with 4.5 L of water at 80 °C. Due to ultrasonication the temperature of the water was slightly raised and maintained at 80 °C to 85 °C during the synthesis of the gold nanofluids in order to produce gold nanoparticles (GNPs) of the smallest possible size using the citrate reduction method (Turkevich *et al.*, 1951). The two flasks containing identical aqueous HAuCl_4 solutions were immersed in the ultrasonic bath for 10 min to stir and heat up the solutions. The flasks were capped during sonication to prevent the loss of solution due to evaporation. After 10 min of sonication, sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) was added to the two aqueous HAuCl_4 solutions. The molar ratio between HAuCl_4 and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ was set as 1:3.5 to synthesize the smallest GNPs (Ji *et al.*, 2007). The molar ratio between HAuCl_4 and sodium citrate is an important factor that affects the size and morphology of synthesized GNPs. The effects of molar ratio between HAuCl_4 and sodium citrate on the size and morphology of GNPs are presented elsewhere (Frens, 1973; Ji *et al.*, 2007). The traditional molar ratio between HAuCl_4 and sodium citrate to produce approximately 20 nm-sized GNPs with the conventional citrate reduction (CR) method is almost

1:3.5 as stated in (Frens, 1973; Ji *et al.*, 2007), and many research groups have successfully reproduced approximately 20 nm-sized GNPs with the conventional CR method at almost 1:3.5 ratio (Frens, 1973; Ji *et al.*, 2007; Paul *et al.*, 2010). To investigate the effects of sonication energy on the size of gold particles produced, one of the mixtures was sonicated for 30 min after adding $C_6H_5Na_3O_7$, and the other mixture was sonicated for an additional 60 min, as shown in Figure 11.

2. **Gold nanofluids production as a function of reaction temperature**

Size of GNPs can be dependent on the reaction temperature when using the citrate reduction method (Turkevich *et al.*, 1951). Thus, in the present study, five cases of gold nanofluids at different reaction temperature were considered to investigate effects of reaction temperature on the morphology and properties of produced gold particles. Each aqueous $HAuCl_4$ solution was immersed in water solvent and subjected to ultrasonic energy (SUC-350H, 40 kHz, 300 W, SHIN IL ULTRASONIC CO., Seoul, South Korea) for 10 min to mix the solutions and raise their temperature. Flasks were capped during sonication to prevent loss of solutions due to evaporation. Sodium citrate ($C_6H_5Na_3O_7$) was added to aqueous $HAuCl_4$ solutions after 10 min of sonication. The sonication time to produce gold nanofluids was fixed at 15 min. The different reaction temperatures of the five gold nanofluids were 30 °C, 50 °C, 60 °C, 70 °C and 80 °C. The produced gold nanofluids were cooled at room temperature (~25 °C).

B. **Production of Alumina Nanofluids Using the Modified Two-Step Method**

The alumina nanoparticles were purchased from Alfa Aesar (Ward Hill, MA, USA, 99.5% purity and nominal powder size is 40–50 nm) and HPLC grade water was obtained from J.T. Baker (Phillipsburg, NJ, USA). We prepared three different-sized alumina/water nanofluids

by using centrifugal force. In the first step, dry alumina nanoparticles were dispersed in water at room temperature. The volume concentration of particles was set to 6 vol.%. Then, the 6 vol.% alumina nanofluid was immersed in the ultrasonic bath (40 kHz and 300W) for 5 hours to form a stable suspension (Lee *et al.*, 2008). After sonication, half of the sonicated 6 vol.% alumina nanofluid was centrifuged with 7155 RCF (relative centrifugal force) for 30 min and then the supernate of centrifuged alumina nanofluid was decanted. This nanofluid is named as AN1 in the present study. The measured volume concentration of AN1 was 0.51 vol.%. The other half of the sonicated 6 vol.% alumina nanofluid was centrifuged with 2795 RCF for 30 min and the supernate of centrifuged alumina nanofluid was also decanted. Then, HPLC grade water was added to this decanted nanofluid to adjust the volume fraction to 0.51 vol.%. This alumina nanofluid is named AN2. 0.51 vol.% alumina/water nanofluid without centrifugal force was also prepared: Alumina nanoparticles were dispersed in water (0.51 vol.%), then this suspension was immersed in the ultrasonic bath (40 kHz and 300W) for 5 hours. This nanofluid is called AN3. All three alumina nanofluids were produced without any surfactants and dispersants. Figure 12 shows the schematic of alumina/water nanofluids preparation procedure by the modified two-step method with centrifugal force.

C. **Morphological Characterization of Nanoparticles in Produced Nanofluids**

The particle size distribution and mean particle size in aqueous gold and alumina nanofluids were measured with the dynamic light scattering (DLS) technique using a Zetasizer Nano S90 system (Malvern Instruments). Since the dynamic light scattering (DLS) technique requires extremely dilute suspensions (~ 0.01 vol.% to ~ 0.28 vol.% for alumina nanofluids), three dilute aqueous alumina nanofluids at a fixed concentration of 0.05 vol.% were made and

measured at 25 °C by DLS. Transmission electron microscope (TEM) images of the nanoparticles were also taken by JEOL JEM-2100 F TEM and JEOL JEM-2010 (JEOL Ltd., Tokyo, Japan) to study the dispersed form and particle size distribution of nanoparticles.

D. **Transient Hot Wire (THW) System**

The transient hot wire system was designed and manufactured in-house to measure the effective thermal conductivity of aqueous gold and alumina nanofluids considering the effect of the tilting angle of the wire (Giaretto *et al.*, 2007; Lee and Jang, 2012) to minimize measurement error, especially due to natural convection. Platinum was used as the material of the hot wire, since it has higher thermal conductivity compared to nichrome and tantalum, also used as hot wires. The diameter of hot wire is one of the most significant factors in the THW system. A 50 μm diameter platinum wire has been adopted for the present application among many commercially available sizes, since smaller wire diameters are considered to be too fragile for cleaning and handling of nanofluid samples. Metallic nanofluids are electrically conductive, thus employing a bare wire could lead to indeterminate results in the experimental measurements. Some of the problems pointed by Nagasaka and Nagashima (1981) in the application of the general transient hot-wire method to electrically conducting liquids are: (1) current flows through the liquid, causing the heat generation by the wire to become unclear; (2) polarization arising on the surface of the wire; (3) distortion of the small output voltage signal owing to influence of the conducting metallic cell. In order to surmount these possible errors, the bare metal wire should be coated using electrically insulating material. Thus, Teflon was employed as an insulating material, since it has high resistance to chemical reactions, corrosion and stress-cracking at elevated temperatures. Consequently, a 50 μm diameter platinum wire with a Teflon insulation

coating of 25 μm thickness (i.e., total 100 μm hot wire), manufactured by A-M Systems, Inc., has been used as the hot wire. Soldered spots are also insulated by silicon after soldering to avoid electrical disturbances. The wire tension can be maintained and adjusted by the top side of a tension spring and both side of supporters. The XYZ linear translation stage employed to adjust the wire tilting angles aimed to reduce the natural convection effects. Single hot wire with high aspect ratio (wire length-to-diameter ratio of 3600) was used in this study as a sensor to minimize conduction loss at the end of the wire instead of a two-wire compensation system (Eastman *et al.*, 2001) which is used to eliminate axial conduction at both ends of the wire. The wire length is 177 mm, the resistance at 0 $^{\circ}\text{C}$ is 7.9 Ω (this value is experimentally determined and compensated; described in the next section). A 490 mL Pyrex cylinder with inner diameter of 50 mm and length of 250 mm was used as the nanofluids container. The schematic of the custom-made transient hot wire apparatus is shown in Figure 13.

1. **Thermal conductivity measurements method**

The working equation of transient hot wire method for thermal conductivity measurement is given by

$$k = \frac{q}{4\pi} \frac{d(\ln t)}{d(\Delta T)} \quad (2-1)$$

where k , q , t , and T are the effective thermal conductivity, input power per unit length, time, and temperature, respectively. Temperature-rise (ΔT) is determined by measuring resistance change of platinum hot wire rather than direct measurement of temperature to obtain slight change of temperature rise value accurately. The converting equation of resistance-change to temperature-rise is given by Bentley's equation (Bentley, 1984)

$$R_w = R_0 [1 + \alpha (T_w - T_0)] \quad \text{or} \quad \Delta R_w = \alpha R_0 (\Delta T) \quad (2-2)$$

where R_w , R_0 , α , T_w , and T_0 are the resistance of the wire, resistance of the wire at 0 °C, temperature coefficient, temperature of the wire, and $T_0 = 0$ °C. The temperature coefficient of resistance of platinum wire (α) is 0.0039092 [1/°C] from the provider (A-M Systems, Inc., USA). As shown in Figure 14, the resistance change of platinum wire is determined by converting the voltage change of points A and B using Wheatstone bridge's resistance balance equation

$$\Delta R_w = \frac{(R_1 + R_2)(R_3 + R_w) \frac{\Delta V}{V_0}}{R_2 - (R_1 + R_2) \frac{\Delta V}{V_0}} \quad (2-3)$$

where R_1 , R_2 , R_3 , and V_0 are the resistance of resistor 1, resistance of potentiometer, resistance of resistor 3, and input voltage, respectively. The input power per unit length (q) is determined by Ohm's law as

$$q = \frac{R_w}{L_w} \left(\frac{V_0}{R_3 + R_w} \right)^2 \quad (2-4)$$

where L_w is the length of the wire. Therefore, the final form of working equation for thermal conductivity is

$$k = \frac{1}{4\pi} \frac{R_w}{L_w} \left(\frac{V_0}{R_3 + R_w} \right) \frac{d(\ln t)}{d(\Delta T)} \quad (2-5)$$

In the Wheatstone bridge, R_w indicates the resistance of the platinum hot wire, R_1 and R_3 are precision resistors (Precision resistor company, Inc., U.S.A, tolerance <0.1%) with 1 kΩ and 5 Ω respectively, and R_2 is a 1.111 kΩ potentiometer (IET labs, Inc., HARS-X series,

accuracy <0.01%). These resistances are measured by a digital multimeter (Fluke-289, accuracy 0.05%) and voltage difference is measured by data acquisition (Agilent 34970A, accuracy 0.004%, sampling time 0.04sec). Input voltage is supplied by DC power supply (Agilent E3631A, accuracy 0.1%). Upon switching the DC power supply, the Wheatstone bridge initiates the voltage change in the hot wire, and this varying voltage and total input voltage over time are recorded by the analog-to-digital (A/D) converter with resolution of 3 μ V at a sampling rate of 25 Hz. From this measured voltage variation and Ohm's law applied to the electric circuit shown in Figure 14, the resistance change of the wire and the varying current through the hot wire can be calculated. The temperature variation of the wire can be calculated by the temperature-resistance relationship of the platinum wire. In addition, a constant temperature chamber was used to reduce thermal disturbances due to variations in room temperature.

2. **Calibration procedure of transient hot wire system**

The transient hot wire method has a lot of uncertainties (Healy *et al.*, 1976) due to different conditions between ideal and real boundaries. In the actual measurement system, more complex problems exist: First of all, it is hard to obtain directly the resistance value of platinum hot wire at 0 °C by using multimeter due to many difficulties such as connection between platinum hot wire and measurement probe; also precision errors from the length of hot wire and variation of ambient temperature. A second issue is the decision on the operating time. Since the actual measurement system could be affected by tilting or tensing the wire, the operating time is more restricted than theoretical and numerical results. Thus, the calibration procedure is presented to validate the custom-made apparatus. In order to verify and calibrate our thermal conductivity measurement device, measurements are performed using water and varying the temperature from 10 °C to 80 °C. The flow chart of calibration procedure is introduced in

Figure 15. In the first step, the experiments are repeated over 10 times at each temperature, then, the thermal conductivity and the proper operating time section is determined from the measurement data. It is noticeable that higher apparent thermal conductivity than reference value is observed at the later time section because natural convection rapidly occurred due to their relatively small viscosity. Thus, the suitable operating time section should be selected by considering the natural convection effect.

A correlation coefficient (r^2) should be monitored simultaneously. The importance of correlation coefficient is explained by following the working equation for thermal conductivity

$$k = \frac{q}{4\pi} \frac{d(\ln t)}{d(\Delta T)} = \frac{q}{4\pi} \frac{1}{S} \quad (2-6)$$

where S is the inverse slope between natural logarithmic time ($\ln t$) and variation of temperature (ΔT). Since q (input power per unit length) is nearly constant, the slope is the only variable for determining thermal conductivity. Thus, it can be found that the quality of slope is very significant to determine the validity of experimental data—in other words, the decision on the reliability of the experimental data can be made by observing the linearity of slope in the suitable operating time section through the linear regression analysis as

$$r^2 = \frac{\left[n \left(\sum_{i=1}^n (\Delta T)_i (\ln t)_i \right) - \left(\sum_{i=1}^n (\ln t)_i \right) \left(\sum_{i=1}^n (\Delta T)_i \right) \right]^2}{\left[n \left(\sum_{i=1}^n (\ln t)_i^2 \right) - \left(\sum_{i=1}^n (\ln t)_i \right)^2 \right] \left[n \left(\sum_{i=1}^n (\Delta T)_i^2 \right) - \left(\sum_{i=1}^n (\Delta T)_i \right)^2 \right]} \quad (2-7)$$

Generally, the correlation coefficient of unity means that two variables are perfectly in linear relation. The value of correlation coefficient is very sensitive in the transient hot wire method due to unexpected perturbations, such as flow instability of sample fluid and electrical

disturbances. Thus, in the present study, the proper operating time section is determined by fulfillment of two prerequisite conditions of deviation <1.5% and correlation coefficient (r^2) > 0.9998.

E. Uncertainty Analysis of Thermal Conductivity Measurements

The govern equation of THW is described in Equation (2-1) (Carslaw and Jaeger, 1959). Thus, the relative uncertainty of thermal conductivity can be expressed as (Richard and Donald, 2006)

$$u_k = \sqrt{\left(\frac{\partial k}{\partial q} u_q\right)^2 + \left(\frac{\partial k}{\partial \Delta T} u_{\Delta T}\right)^2} \quad (2-8)$$

Equation (2-8) can be expressed as

$$u_k = \sqrt{\left(\frac{1}{4\pi} \frac{d(\ln t)}{d\Delta T} u_q\right)^2 + \left(\frac{q}{4\pi} d(\ln t) \left(-\frac{1}{(d\Delta T)^2}\right) u_{\Delta T}\right)^2} = \sqrt{\left(k \frac{u_q}{q}\right)^2 + \left(k \frac{u_{\Delta T}}{\Delta T}\right)^2} \quad (2-9)$$

Therefore, the relative uncertainty of thermal conductivity can be written as

$$\frac{u_k}{k} = \sqrt{\left(\frac{u_q}{q}\right)^2 + \left(\frac{u_{\Delta T}}{\Delta T}\right)^2} \quad (2-10)$$

The input power, q , can be obtained by Wheatstone bridge's resistance relationship as follows

$$q = \frac{(R_{w,0} + \Delta R_w)}{L_w} \left[\frac{V_0}{R_3 + (R_{w,0} + \Delta R_w)} \right]^2 \quad (2-11)$$

where the V_0 , L_w , $R_{w,0}$, ΔR_w , and R_3 are input voltage, length of hot wire, hot wire resistance at 0 °C, variation of hot wire resistance, and fixed resistance in the Wheatstone bridge, respectively as shown in Figure 14.

The uncertainty of input power can be written as

$$u_q = \sqrt{\left(\frac{\partial q}{\partial L_w} u_{L_w}\right)^2 + \left(\frac{\partial q}{\partial V_0} u_{V_0}\right)^2 + \left(\frac{\partial q}{\partial R_3} u_{R_3}\right)^2 + \left(\frac{\partial q}{\partial \Delta R_w} u_{\Delta R_w}\right)^2} \quad (2-12)$$

and

$$\left(\frac{u_q}{q}\right) = \sqrt{\left(\frac{u_{L_w}}{L_w}\right)^2 + \left(2 \frac{u_{V_0}}{V_0}\right)^2 + \left(2 \frac{u_{R_3}}{R_3 + (R_{w,0} + \Delta R_w)}\right)^2 + \left(\left(\frac{1}{R_w} - \frac{2}{R_3 + (R_{w,0} + \Delta R_w)}\right) u_{R_w}\right)^2} \quad (2-13)$$

The temperature-rise of hot wire (ΔT) can be obtained from the temperature-resistance correlation (Bentley, 1984)

$$R_w = R_{w,0} [1 + \beta(T_2 - T_1)] \quad (2-14)$$

Hence, the temperature-rise can be described as resistance terms

$$d\Delta T = d\left(\frac{\Delta R_w}{\beta R_{w,0}}\right) \quad (2-15)$$

where β is the temperature coefficient. Then,

$$\left(\frac{u_{\Delta T}}{\Delta T}\right) = \sqrt{\left(\frac{u_{\Delta R_w}}{\Delta R_w}\right)^2} \quad (2-16)$$

In Equation (2-16), ΔR_w can be also obtained by Wheatstone bridge's relationship as follows

$$\Delta R_w = \frac{(R_1 + R_2)(R_3 + R_{w,0})(\Delta V / V_0)}{R_2 - (R_1 + R_2)(\Delta V / V_0)} \quad (2-17)$$

The uncertainty form can be expressed as

$$u_{\Delta R_w} = \left[\left(\frac{\partial \Delta R_w}{\partial R_1} u_{R_1} \right)^2 + \left(\frac{\partial \Delta R_w}{\partial R_2} u_{R_2} \right)^2 + \left(\frac{\partial \Delta R_w}{\partial R_3} u_{R_3} \right)^2 + \left(\frac{\partial \Delta R_w}{\partial \Delta V} u_{\Delta V} \right)^2 + \left(\frac{\partial \Delta R_w}{\partial V_0} u_{V_0} \right)^2 \right]^{1/2} \quad (2-18)$$

Therefore, the uncertainty of ΔR_w can be written as

$$\begin{aligned} \left(\frac{u_{\Delta T}}{\Delta T} \right) = \frac{u_{\Delta R_w}}{\Delta R_w} = & \left[\left(\left(\frac{1}{(R_1 + R_2)} + \frac{(\Delta V / V_0)}{R_2 - (R_1 + R_2)(\Delta V / V_0)} \right) u_{R_1} \right)^2 \right. \\ & + \left(\left(\frac{1}{(R_1 + R_2)} - \frac{(1 - (\Delta V / V_0))}{R_2 - (R_1 + R_2)(\Delta V / V_0)} \right) u_{R_2} \right)^2 + \left(\frac{u_{R_3}}{R_3 + R_{w,0}} \right)^2 \\ & + \left(\left(\frac{1}{\Delta V} + \frac{(R_1 + R_2)(1/V_0)}{R_2 - (R_1 + R_2)(\Delta V / V_0)} \right) u_{\Delta V} \right)^2 \\ & \left. + \left(\left(\frac{1}{V_0} + \frac{(R_1 + R_2)((\Delta V / V_0^2))}{R_2 - (R_1 + R_2)(\Delta V / V_0)} \right) u_{V_0} \right)^2 \right]^{1/2} \end{aligned} \quad (2-19)$$

The error due to variation of measured temperature from thermocouple's accuracy is

$$u_{k_{ref}} = \frac{k_{ref}(T + 1 \text{ } ^\circ\text{C}) - k_{ref}(T - 1 \text{ } ^\circ\text{C})}{2} \quad (2-20)$$

where the subscript *ref* denotes the reference value.

Finally, relative uncertainty of transient hot wire method can be written as

$$\frac{u_k}{k} = \sqrt{\left(\frac{u_q}{q} \right)^2 + \left(\frac{u_{\Delta T}}{\Delta T} \right)^2 + \left(\frac{u_{k_{ref}}}{k_{ref}} \right)^2} \quad (2-21)$$

and

$$\begin{aligned}
\frac{u_k}{k} &= \sqrt{\left(\frac{u_q}{q}\right)^2 + \left(\frac{u_{\Delta T}}{\Delta T}\right)^2 + \left(\frac{u_{k_{ref}}}{k_{ref}}\right)^2} \\
&= \left[\left(\frac{u_{L_w}}{L_w}\right)^2 + \left(2\frac{u_{V_0}}{V_0}\right)^2 + \left(2\frac{u_{R_3}}{R_3 + (R_{w,0} + \Delta R_w)}\right)^2 + \left(\frac{u_{k_{ref}}}{k_{ref}}\right)^2 \right. \\
&\quad + \left. \left(\left(\frac{1}{R_w} - \frac{2}{R_3 + (R_{w,0} + \Delta R_w)}\right)u_{R_w}\right)^2 + \left(\left(\frac{1}{(R_1 + R_2)} + \frac{(\Delta V / V_0)}{R_2 - (R_1 + R_2)(\Delta V / V_0)}\right)u_{R_1}\right)^2 \right. \\
&\quad + \left. \left(\left(\frac{1}{(R_1 + R_2)} - \frac{(1 - (\Delta V / V_0))}{R_2 - (R_1 + R_2)(\Delta V / V_0)}\right)u_{R_2}\right)^2 + \left(\frac{u_{R_3}}{R_3 + R_{w,0}}\right)^2 \right. \\
&\quad + \left. \left(\left(\frac{1}{\Delta V} + \frac{(R_1 + R_2)(1/V_0)}{R_2 - (R_1 + R_2)(\Delta V / V_0)}\right)u_{\Delta V}\right)^2 \right. \\
&\quad + \left. \left(\left(\frac{1}{V_0} + \frac{(R_1 + R_2)((\Delta V / V_0^2))}{R_2 - (R_1 + R_2)(\Delta V / V_0)}\right)u_{V_0}\right)^2 \right]^{1/2}
\end{aligned} \tag{2-22}$$

In case of the relative uncertainty of transient hot wire method, the experimental parameters (R_1 , R_2 , R_3 , R_w , L_w , V_0 , ΔV) are random variables, and experimental data has random variation. When the size of sample is less than 30, the probability distribution follows the t -distribution (Richard and Donald, 2006). The t -distribution with $\lambda = n - 1$ degrees of freedom is

$$t = \frac{\bar{x} - \mu}{\sigma / \sqrt{n}} \tag{2-23}$$

where, $\sigma / \sqrt{n} = P$ is estimated standard error of $\bar{x}$ and

1) Estimate sample mean: $\bar{x} = \frac{1}{n}(x_1 + x_2 + \dots + x_j) = \frac{1}{n} \sum_{j=1}^n x_j$

2) Estimate sample variance: $\sigma^2 = \frac{1}{n-1} \sum_{j=1}^n (x_j - \bar{x})^2$

The $100(1 - \alpha)\%$ confidence interval on μ of t -distribution can be obtained by the following equation

$$\bar{x} - t_{\lambda, \alpha/2} P \leq \mu \leq \bar{x} + t_{\lambda, \alpha/2} P \quad (2-24)$$

Random variation (precision error) of measured data can be determined by Equation (2-24).

Finally, uncertainties with a 95% confidence interval can be obtained by using precision and bias error as

$$u = \left[B^2 + \left(t_{\lambda, 95\%} P_{\text{precision}} \right)^2 \right]^{1/2} \quad (2-25)$$

where u , B , and $t_{\lambda, 95\%} P_{\text{precision}}$ are measurement uncertainty, bias error, and estimate of the precision error in the repeated pressure measurement at 95% confidence. In addition, λ is the degree of freedom and B is expressed by

$$B = \sqrt{u_{\text{accuracy}}^2 + u_{\text{resolution}}^2} \quad (2-26)$$

The accuracy and resolution of each measurement device is shown in Table II.

TABLE II

THE ACCURACY AND RESOLUTION OF EACH MEASUREMENT DEVICE

	Resistance [Ω]	Data acquisition [V]	Power supply [V]	Vernier calipers [mm]	Thermo- couple [$^{\circ}\text{C}$]
					
Product	Fluke-289	Agilent 34970A	Agilent E3631A	Stolz PDIC-201	Omega (TMTSS- 020U-6-120)
Accuracy	0.05 %	0.004 % + 0.004 % (% of reading + % of range)	0.1 %	0.01 mm	1 $^{\circ}\text{C}$
Full scale	$50\Omega / (R_3, R_w)$ $500\Omega / (R_2)$ $5\text{k}\Omega / (R_1)$	0.1 V	6 V	200 mm	From -200 to $350\text{ }^{\circ}\text{C}$
Resolution	0.01 Ω	$3.815 \times 10^{-7} \text{ V}$ (18bits)	0.001 V	0.01 mm	0.1 $^{\circ}\text{C}$

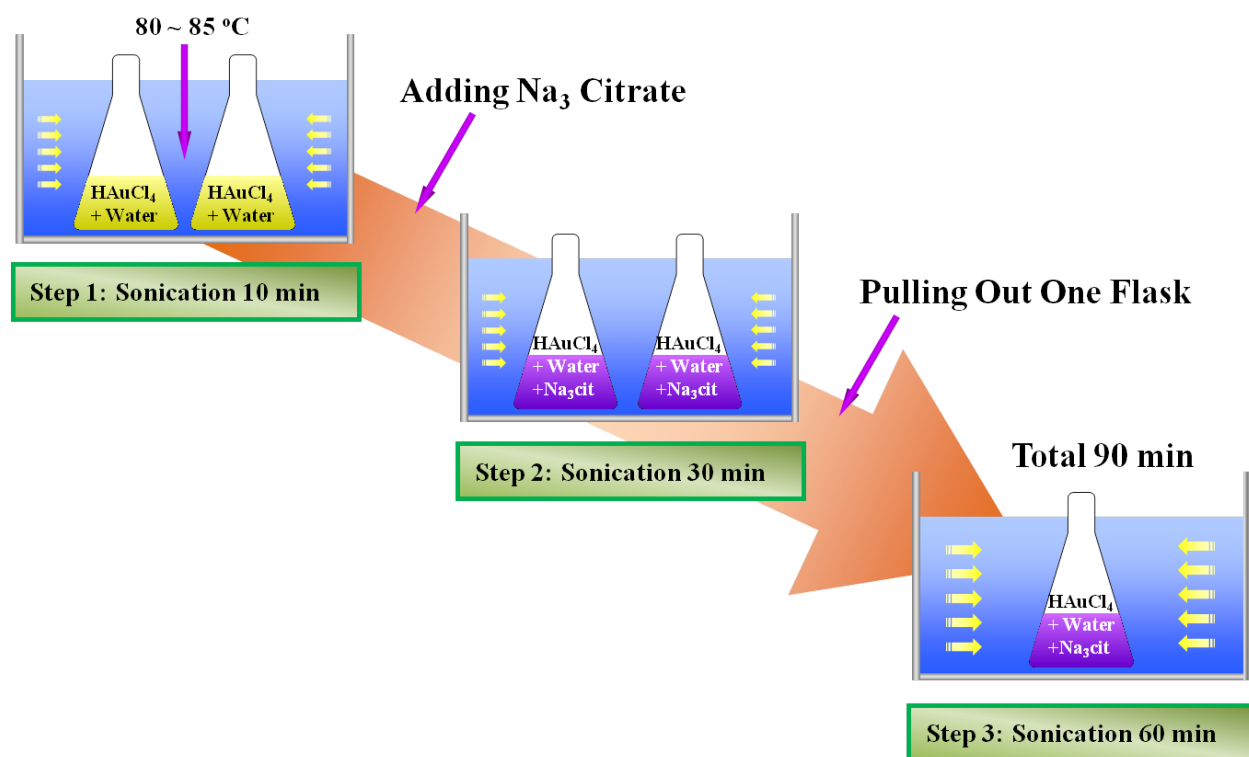


Figure 11. Schematic of aqueous gold nanofluids synthesis procedure by modified citrate reduction method.

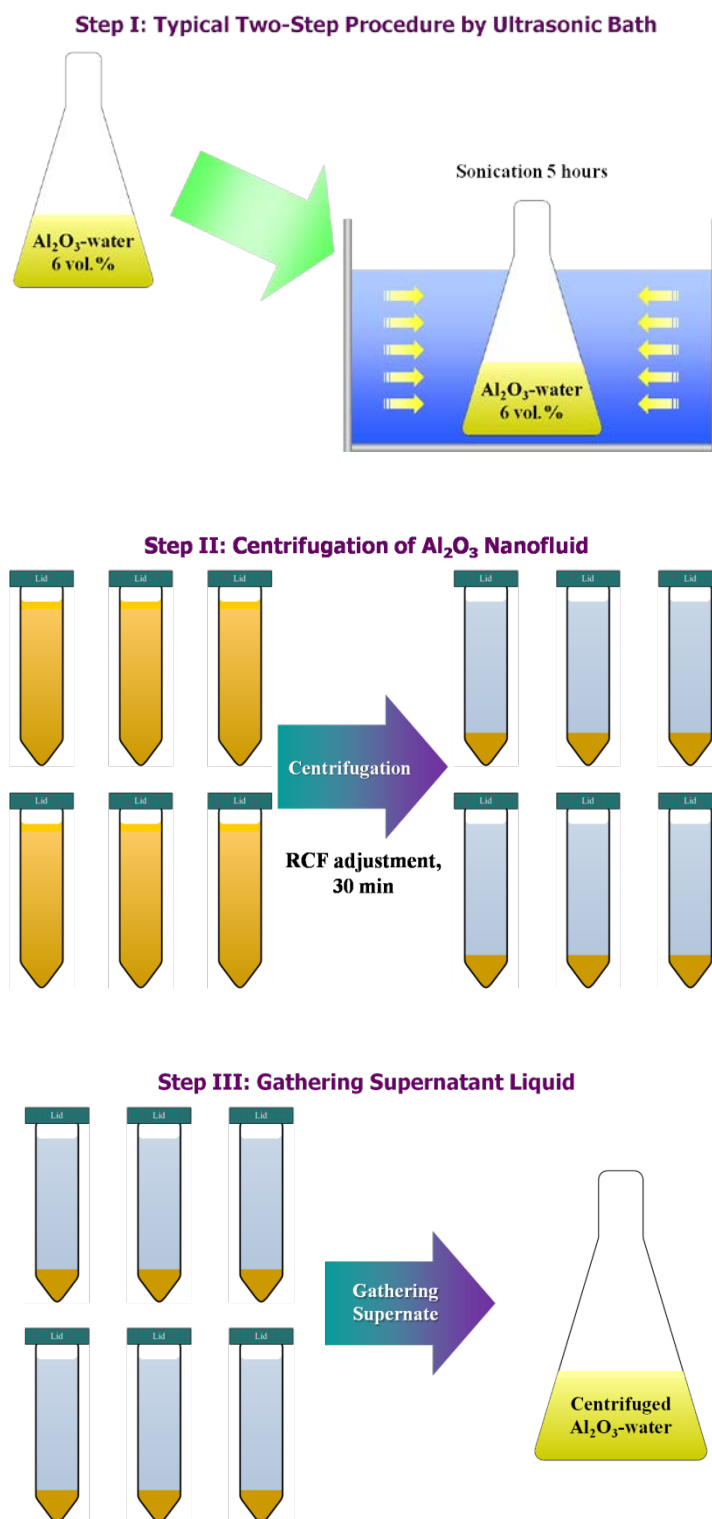


Figure 12. Schematic of alumina/water nanofluids synthesis procedure by modified two-step method with centrifugal force.

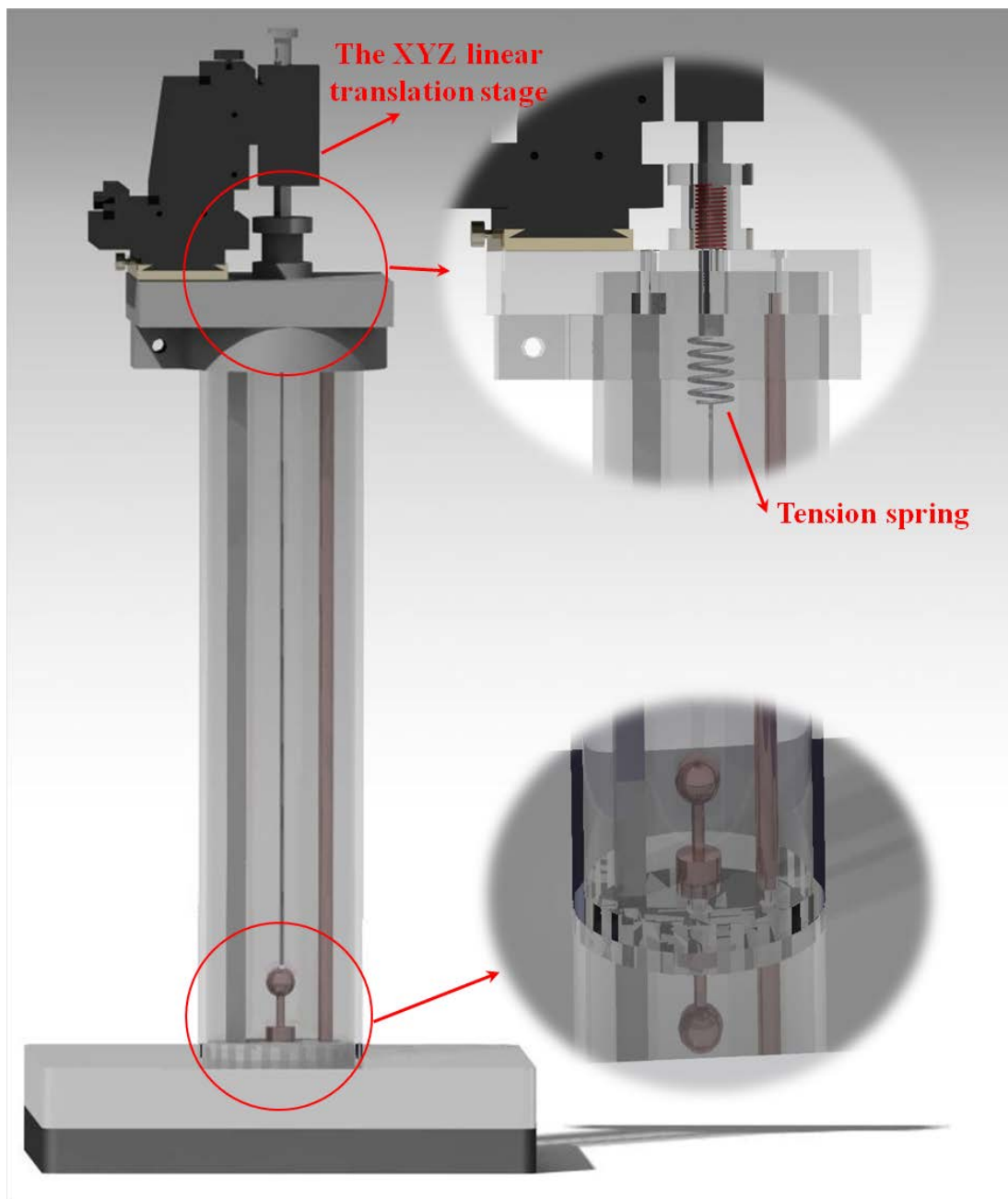


Figure 13. Schematic of the modified transient hot wire apparatus for measuring thermal conductivity of nanofluids.

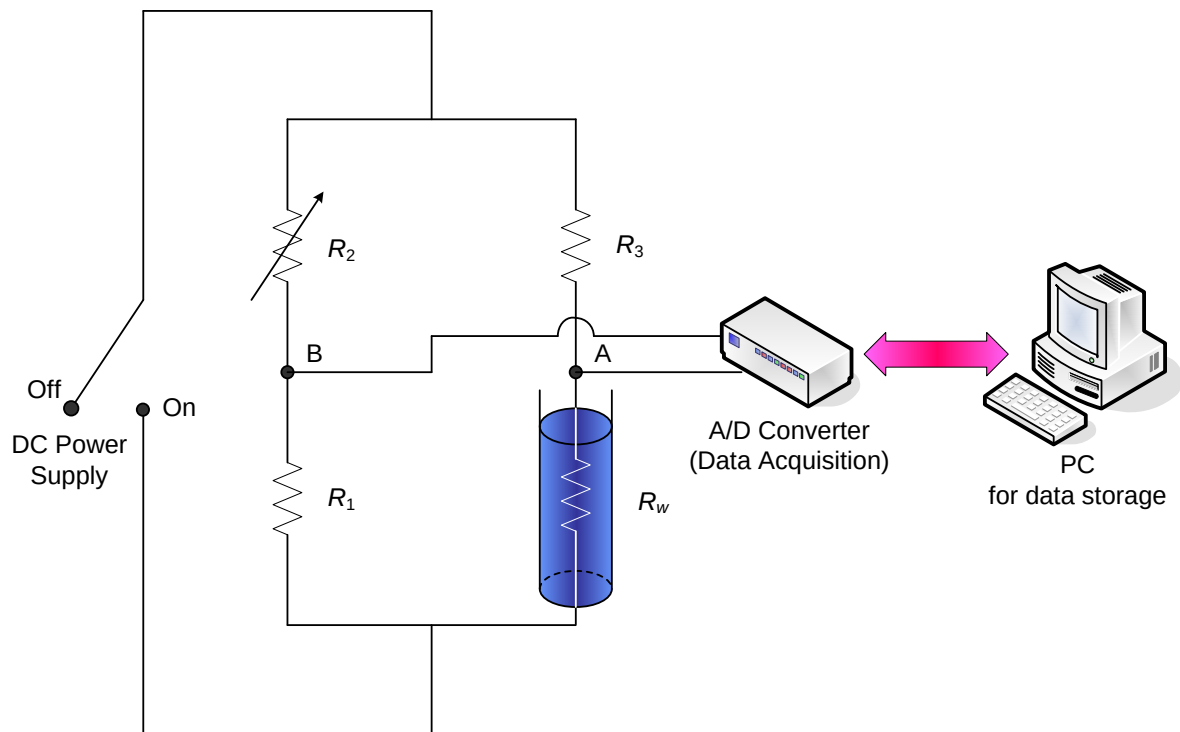


Figure 14. Schematic of the transient hot wire system for measuring thermal conductivity of nanofluid.

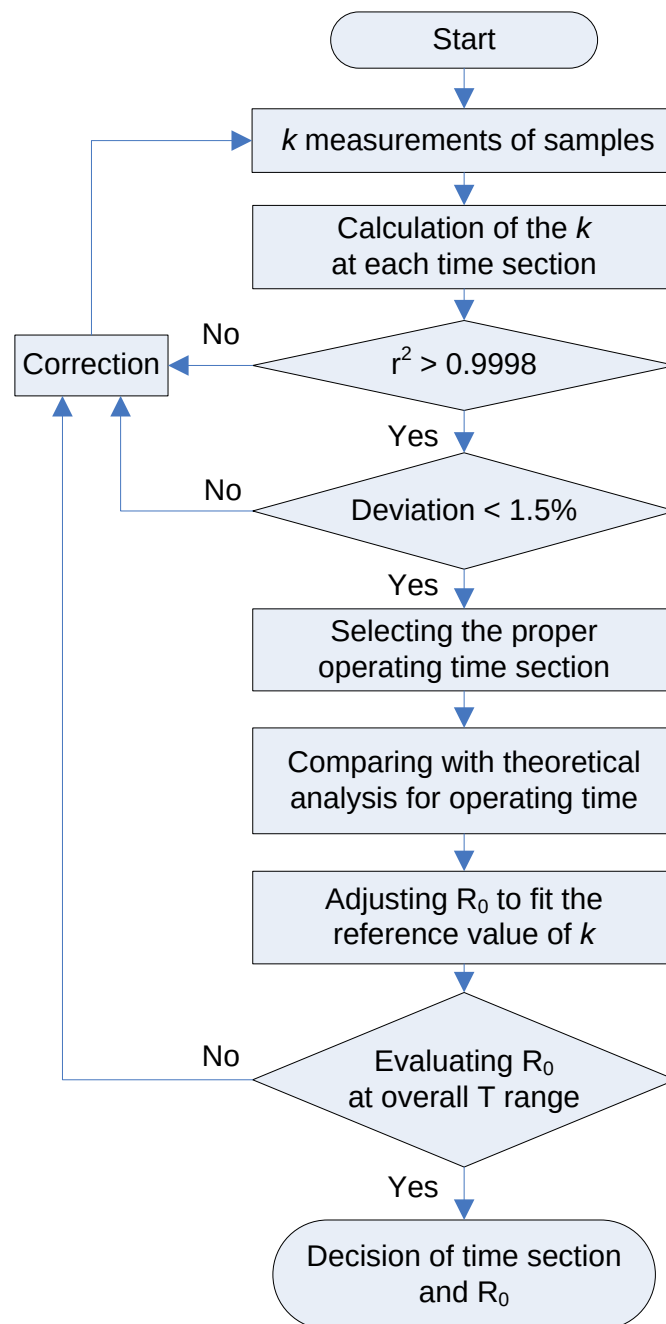


Figure 15. Flow chart of calibration procedure of thermal conductivity measurements.

III. RESULTS AND DISCUSSION

A. Morphology of Nanoparticles in Produced Nanofluids

1. Synthesized gold nanoparticles using an ultrasonic bath

a. Effects of sonication time

The final colors of the suspensions produced were reddish-violet or dark purple as shown in Figure 16. The two suspensions were capped and cooled naturally at room temperature. They still remained stable with little or no agglomeration after 2 months of storage. As shown in Figure 16 the ultraviolet (UV)-visible absorption spectrum of the two final products demonstrated the existence of spherical shape GNPs because the absorption peak was centered between 520 and 540 nm (Ji *et al.*, 2007). The plasmon band of 243 kJ (30 min with 135 W ultrasonic power) sonicated gold nanofluid is narrower than the 729 kJ (90 min with 135 W ultrasonic power) sonicated one. This implies that the GNP size distribution of the 30 min-sonicated solution is more uniform than the 90 min-sonicated solution (Polavarapu and Xu, 2009).

TEM images of these GNPs are shown in Figure 17. The TEM samples were prepared by Formvar stabilized with carbon-coated copper TEM grids and dried in air for 12 h about 2 months after the nanofluid synthesis. The particle size of the 243 kJ (30 min with 135 W ultrasonic power) sonicated solution was roughly 20 nm (21.7 ± 2.5 nm, average diameter $\pm$ standard deviation) and the size distribution was highly monodispersed, while the particle size and distribution of the 729 kJ (90 min with 135 W ultrasonic power) sonicated solution were broad (20 to 50 nm, 37.2 ± 12.4 nm) and polydispersed.

Figure 18 shows the effect of ultrasonic energy (sonication time $\times$ ultrasonic power) on the size of GNPs when using a conventional ultrasonic bath with fixed ultrasonic power and frequency (135 W and 300 W, 40 kHz). We can see that the size of nanoparticles is critically dependent on the ultrasonic energy or sonication time at a given power. GNPs were not formed when the two aqueous HAuCl_4 solutions were initially sonicated with 36 kJ of ultrasonic energy from the bath-type ultrasonic generator. However, spherical GNPs with a diameter of 20 nm (19.6 ± 1.0 nm, average diameter $\pm$ standard deviation) were successfully synthesized when the ultrasonic energy was increased to 91.5 kJ. The nanoparticle size was observed to slowly grow with increasing ultrasonic energy up to 270 kJ, and the size distribution was highly monodispersed. The nanoparticle size rapidly grows to nearly 50 nm (37.2 ± 12.4 nm) with higher energy beyond 540 kJ, and polydispersity also increases with increasing ultrasonic energy. As discussed in the next paragraph, particle-particle fusion is one possible reason for the size increase with increasing sonication time. The error bars in Figure 18 correspond to the standard deviation of the average size of GNPs. Since Chen and Wen (2011) presented their data as a function of sonication time from 0 to 45 min, their data (open blue diamonds) are reproduced in the inset for comparison with the results of the present study (solid red circles). As shown in the inset, Chen and Wen (2011) produced spherical GNPs with diameters of approximately 20 nm. Their results seem to be consistent with the results obtained in this study. However, we see an interesting difference in the size of nanoparticles during the first 2 min of sonication time due to the different synthesis procedures. As mentioned in the introduction, Chen and Wen (2011) studied the effect of sonication time on nanoparticle size using aqueous gold nanofluids that were first synthesized by the conventional citrate reduction method and then placed in an ultrasonic bath. Therefore, the size of their GNPs was 20 nm at the start (0 min) of sonication. In contrast,

in the present study because we sonicated the aqueous HAuCl_4 solutions that were immersed in the ultrasonic bath, we were not able to find aqueous spherical GNPs of 20 nm synthesized after 2 min of sonication time.

A possible reaction mechanism to explain the reduction of HAuCl_4 by sodium citrate was postulated by Ojea-Jiménez *et al.* (2010) and is repeated here for the sake of completeness. Figure 19 shows the postulated chemical reduction mechanism for the formation of GNPs. Initially, HAuCl_4 is reduced to Au(I), and this process would involve two steps: (1) a fast ligand exchange with the citrate anion to form an intermediate complex, which remains unaffected by isotope effects, and (2) an equilibrium to give a ring closure, followed by a slow and rate-determining step involving a concerted decarboxylation and reduction of HAuCl_4 species. The citrate anion is expected to coordinate equatorially substituting a planar Cl^- ligand and forming the corresponding complex $[\text{AuCl}_3(\text{C}_6\text{H}_5\text{O}_7)^{-2}]^-$ (The first step). Deprotonation of the alcohol group and coordination of the alcohol oxygen axially to HAuCl_4 to give a pentacoordinated intermediate complex would take place as a rapid equilibrium, which would be followed by the axial complex disintegrating into products in the rate-limiting step (The second step). The resulting Au(I) species can finally form a multimolecular complex with the dicarboxyacetone molecules present in solution, which play an important role in the disproportionation of aurous species and the subsequent formation of Au (0) atoms (The third step).

To investigate the role of ultrasonic energy on size, a hypothesis is proposed based on observations and experimental data as shown in Figure 20. Recent studies on the growth mechanism of GNPs have shown that wire-like gold nanoclusters exist on the formation process by extensive nanowire network (Ji *et al.*, 2007; Pei *et al.*, 2004; Pong *et al.*, 2007). In particular, for a low $\text{HAuCl}_4/\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ ratio below 1:3.5, the tendency is towards an extremely fast

reaction rate, and consequently, the aggregation of primary particles to the wire-shaped nanoclusters occurs (Ji *et al.*, 2007). This aggregation by the nanowire network lasts longer as the concentration of sodium citrate decreases. It can be assumed that ultrasonic energy can physically break the chain-like structure of the gold nanowires. As shown in Figure 21, ultrasonic energy prevented or minimized the randomly self-assembled wire-shaped formation and extensive network of nanowires. This physical effect can expedite sphere-shaped GNPs with Oswald ripening or intra-particle ripening (Ji *et al.*, 2007); hence, well-dispersed and monodispersed GNPs can be induced. Moreover, finally formed GNPs can be further dispersed by ultrasonic energy. However, the excess of ultrasonic energy can lead to particle-particle fusion (Radziuk *et al.*, 2010) and this can cause a polydispersed state. Thus, suitable ultrasonic energy is the primary parameter to determine particle size and its distribution, as well as the morphology of the nanoparticles. In other words, there is an appropriate and optimal sonication time which contributes to the tunable size of GNPs.

b. **Effects of reaction temperature**

Table III shows the measurement results of DLS data of five gold nanofluids that were produced with different ambient temperatures in a conventional ultrasonic bath. The gold nanofluid which was produced at 70 °C has the smallest particle size of 40 nm, while the particle size of gold nanofluid which was produced at 50 °C was almost 50 nm. Moreover, ‘Count Rate’ analyzed by the measurement apparatus, i.e. concentration of gold nanofluid which was produced at 50 °C is almost half compared to other gold nanofluids. This can be caused by agglomeration of gold nanoparticles. Thus, reaction temperature contributes to the tunable size of GNPs.

2. **Synthesized alumina nanoparticles using the modified two-step method**

Figure 22 shows the mean particle size of decanted alumina nanoparticles, i.e., nanoparticles which remained in supernates, as a function of RCF when centrifugation was applied. Mean particle diameter was measured by DLS. According to expectations, the particle size of decanted nanofluids decreases with increasing applied RCF, as shown in Figure 22 since small particles would settle even at large RCF condition. Figure 23a shows the particle size distribution and agglomerated particle size in aqueous alumina nanofluids, as obtained by DLS. Alumina nanoparticle from AN1 has the mean diameter of $d_{AN1} = 71.57$ nm. The mean diameters of AN2 and AN3 are $d_{AN2} = 114.5$ nm and $d_{AN3} = 136.8$ nm, respectively. TEM images of the alumina nanoparticles are shown in Figure 23b, 23c and 23d. The TEM samples were prepared by Formvar stabilized with carbon-copper TEM grids and dried in air for 15 hours. As shown by the TEM images, the size distributions of three alumina nanofluids are not monodispersed; the ranges of size distribution of AN1, AN2, and AN3 are 3–27 nm, 10–76 nm and 10–111 nm, respectively. However, it can be clearly shown that there is difference in particle size among the three alumina nanofluids.

B. pH and Electrical Conductivity of Gold Nanofluids

1. Effects of sonication time

Figure 24 shows the pH measurement results and Figure 25 presents electrical conductivity measurement results of produced gold nanofluids as a function of applied sonication time. The uncertainties of pH and electrical conductivity measurements are within 2%. The pH and electrical conductivities were measured from 10 °C to 30 °C using constant temperature chamber. The pH of gold nanofluids varied with changing sonication time as shown in Figure 24. Measured pH values were distributed from 5.2 to 6.1 and the pH of 30 min sonicated gold

nanofluid is the lowest. Measured electrical conductivities also varied with sonication time, as shown in Figure 25.

2. **Effects of reaction temperature**

Figure 26 shows the pH measurement results and Figure 27 shows electrical conductivity measurement results of produced gold nanofluids as function of different reaction temperature. The uncertainties of pH and electrical conductivity measurements are also within 2%. The pH and electrical conductivities were measured from 10 °C to 30 °C using constant temperature chamber. The pH values of gold nanofluids also varied with reaction temperature as shown in Figure 26. Measured pH values were distributed from 4.9 to 5.8 and the pH of gold nanofluid which was produced at 50 °C reaction temperature is the lowest. Measured electrical conductivities also varied with reaction temperature, as shown in Figure 27.

Previous reported data shows the size dependency of gold nanoparticles and properties change by pH variation (Bartczak and Kanaras, 2010; Ji *et al.*, 2007). However, there are no data on properties such as pH and electrical conductivity variations of gold nanofluids, which were produced by sonication method. Thus, there is need to investigate the characteristics of pH and electrical conductivity of gold nanofluids produced by sonication method experimentally and analytically.

C. **Effective Thermal Conductivity of Nanofluids**

1. **Calibration with the base fluid**

The base fluid used in this study as the suspending liquid is water. To validate the accuracy of the transient hot wire system for measuring thermal conductivity, calibration experiments were performed in the temperature range of 10 °C to 80 °C at atmosphere pressure.

The calibration experimental data showed good agreement with thermal conductivities of reference data (Incropera and Dewit, 2002). The calibration data in Figure 28 and Figure 29 show that for a given temperature, repeatability and accuracy of the transient hot wire system are excellent, providing a measurement uncertainty of the thermal conductivity within 1.5%.

2. **Thermal conductivity of gold nanofluids**

Figure 30 shows the thermal conductivity ratio of produced gold nanofluids to base fluid (HPLC grade water). The measurements range is from 10 °C to 30 °C. The thermal conductivities of gold nanofluids are measured by the custom-made transient hot wire system. Uncertainty of the measurements is less than $\pm 1.5\%$ from the uncertainty analysis. As shown in Figure 30, most of results are distributed in $\pm 1.5\%$ enhancements to the thermal conductivity of the base fluid. This means there are no enhancements of thermal conductivities of gold nanofluids to their base fluid at very small volume fraction ($\sim 2.0 \times 10^{-4}$ vol.%) and experimental results are consistent with previous published data (Shalkevich *et al.*, 2010). However, there is no thermal conductivity measurements data of gold nanofluids produced by chemical reduction method with high volume fraction of particles because gold nanoparticles agglomerate and settle at large concentrations, as reported from Patel *et al.* (2003). Thus, we need to investigate the methodology of water-based gold nanofluids with high concentration.

3. **Thermal conductivity of alumina nanofluids**

Figure 31 shows thermal conductivity ratio, defined as k_{NF}/k_{BF} , where k_{NF} and k_{BF} are thermal conductivity of the alumina nanofluids and the base fluid, respectively, as a function of temperature. The experimental data were compared with the prediction of the Maxwell model (Maxwell, 1873). The relative uncertainties of thermal conductivity were less than 1.5%. The thermal conductivity ratio of the three different alumina nanofluids increases

with increasing temperature. However, the rate of increment in thermal conductivity was different. For the AN1, the thermal conductivity increases sharply with increasing temperature compared to other two alumina nanofluids with a maximum increment of about 4.7% from the prediction of the Maxwell model at 80 °C. On the other hand, the thermal conductivity enhancement of the AN2 is smaller in the overall temperature range compared to the AN1 with a maximum increment of about 0.85% from the prediction of the Maxwell model at 80 °C. Moreover, in case of the AN3, the thermal conductivity enhancement is even lower than the prediction of the Maxwell in the overall temperature range.

The different increment in the thermal conductivity of water-based alumina nanofluids can be explained by the viewpoint of different particle size and size distribution. The effect of particle size on the thermal conductivity of nanofluids can be observed in Figure 32, which shows the thermal conductivity ratio of alumina nanofluids as a function of mean particle diameter. Thus, as shown in Figure 23 and Figure 32, it is clear that the particle size can affect the thermal conductivity of alumina nanofluids although the size distribution is not monodispersed; the thermal conductivity of alumina nanofluids increases with decreasing particle size.

The large enhancement was observed at the high temperature region than the low temperature region in aqueous alumina nanofluids (Figure 31) and this result suggests that there are other effects which play an important role on thermal conductivity enhancement beyond the conventional effective medium theory (EMT). Present experimental data show the particle size and temperature dependence in thermal conductivity enhancement and cannot be explained by the classical effective medium theory (EMT) model, such as the Maxwell model (Maxwell, 1873). Hasselman and Johnson (1987) derived an expression for the effective thermal

conductivity of composites taking into account the thermal barrier resistance at the interface between the materials and the relations for insertion shapes for spherical, cylindrical and flat plate for low concentration of dispersions. The resulting expression for spherical particles can be arranged as

$$\frac{k_{\text{NF}}}{k_{\text{BF}}} = \left[\frac{k_p(1+2\alpha) + 2k_{\text{BF}} + 2\phi(k_p(1-\alpha) - k_{\text{BF}})}{k_p(1+2\alpha) + 2k_{\text{BF}} - \phi(k_p(1-\alpha) - k_{\text{BF}})} \right] \quad (3-1)$$

where k_{NF} , k_{BF} , k_p , and ϕ are thermal conductivity of the nanofluids, thermal conductivity of the base fluid, thermal conductivity of the particle and volume fraction of the nanoparticle within the base fluid, respectively. In Equation (3-1), α denotes a dimensionless parameter defined as $\alpha = a_K / a_p$, where a_K is the so-called Kapitza radius and a_p is the radius of nanoparticle. Kapitza radius a_K defined as $a_K = R_b k_{\text{BF}}$, where R_b is the Kapitza resistance (thermal boundary resistance). The contribution of the thermal boundary resistance on effective thermal conductivity was evaluated using the Hasselman and Johnson (H-J) model (Hasselman and Johnson, 1987) by assuming all the particles are spherical and particle sizes are within 10–140 nm based on the DLS and TEM results, and R_b is assumed to be $R_b \approx 0.77 \times 10^{-8} \text{ Km}^2\text{W}^{-1}$ for water (Wilson *et al.*, 2002). Figure 33 shows the predictions of the H-J model (Hasselman and Johnson, 1987) along with the experimental data as a function of the temperature. According to the H-J model assuming particle sizes are within 10–140 nm, the prediction values can be regarded as the upper bound of the thermal conductivity enhancement when the mean particle diameter (d_p) is 140 nm, while the lower bound is calculated with $d_p = 10$ nm. This trend is contradictory to the present experimental result since thermal conductivity enhancement increases with decreasing the particle size. Moreover, in case of the AN1, the thermal conductivity enhancement is above the upper bound in the overall temperature range. Hence, the

H–J model cannot explain the size effect on the thermal conductivity enhancement in present experimental data and we confirmed that thermal boundary resistance does not have significant influence on the thermal conductivity of the effective medium as pointed out elsewhere (Eapen *et al.*, 2007; Gao *et al.*, 2009).

We also estimated the effect of Brownian motion on effective thermal conductivity using the Brownian model (BM) (Prasher *et al.*, 2005). Prasher *et al.* (2005) considered three possible mechanisms of thermal energy transfer in nanofluids: (1) translational Brownian motion; (2) the existence of an interparticle potential; (3) convection in the liquid due to the Brownian movement of the particles. They performed an order-of-magnitude analysis on these three possible mechanisms and deduced that local convection due to the Brownian movement of the nanoparticles is the only mechanism that could explain the anomalous enhancement of thermal conductivity. Their semi-empirical model, i.e., Brownian model (BM) can be written as

$$\frac{k_{\text{NF}}}{k_{\text{BF}}} = \left(1 + A \text{Re}^m \text{Pr}^{0.333} \phi\right) \left[\frac{k_p + 2k_{\text{BF}} + 2(k_p - k_{\text{BF}})\phi}{k_p + 2k_{\text{BF}} - (k_p - k_{\text{BF}})\phi} \right] \quad (3-2)$$

where k_{NF} , k_{BF} , k_p , and ϕ are thermal conductivity of the nanofluids, thermal conductivity of the base fluid, thermal conductivity of the particle and volume fraction of the nanoparticle within the base fluid, respectively, In Equation (3-2), A and m are empirical constants. We assumed that the particle sizes are within 10–140 nm and used empirical constant values of $A = 40000$ and $m = 2.5$ as stated in reference (Prasher *et al.*, 2005). Figure 34 shows the predictions of the BM and comparison with the experimental data as a function of the temperature. In case of the prediction by BM, the thermal conductivity of alumina nanofluids reaches the highest value when the mean particle diameter (d_p) is 10 nm and the lower bound shown in Figure 34 is calculated with $d_p =$

140 nm. Although some experimental data are outside the lower bound, the trend of the thermal conductivity enhancement is in accordance with the predictions of the BM. For the experimental data of AN1, the fitting value of BM in Figure 34 using the mean particle size of 30 nm is similar to the experimental data. Thus, it can be presumed that the BM can predict the temperature- and size-dependent thermal conductivity data for alumina nanofluids, suggesting that the Brownian-motion-induced convection from multiple nanoparticles or Brownian motion is the reason for the observed thermal conductivity enhancement and tendency in the present study. However, it should be pointed out that although predictions of the BM show the trend of the experimental results, used mean diameters in the prediction are not to be taken as exact values since BM is the semi-empirical model, i.e., constants A and m can only be determined by experiment. Moreover, mean particle size of 30 nm is not a measurement value, but a fitted value.

The effective medium theory (EMT) models such as the Maxwell model (Maxwell, 1873) and the Hasselman and Johnson (H-J) model (Hasselman and Johnson, 1987) cannot be applied to predict the thermal conductivity enhancement; it can be presumed that the BM (Prasher *et al.*, 2005) can predict the temperature- and size-dependent thermal conductivity data for present alumina nanofluids, however, BM is a semi-empirical model, which requires experimental data as aforementioned. Thus, in the present study, the effect of Brownian motion on effective thermal conductivity estimated using the Brownian velocity of nanoparticles based on the Einstein diffusion theory (Einstein, 1956). The root-mean-square (rms) velocity of the nanoparticles also have been used as the Brownian velocity or convection velocity (Eapen *et al.*, 2007; Koo and Kleinstreuer, 2004; Prasher *et al.*, 2005). However, the order of rms velocity is unreasonable to regard as the Brownian velocity of nanoparticles (Eapen *et al.*, 2007). The Brownian velocity based on the Einstein diffusion theory (Einstein, 1956) is defined as

$$V_{BR} \equiv \frac{K_B T}{3\pi\mu_{BF}d_p l_{BF}} \quad (3-3)$$

where K_B is the Boltzmann constant, defined as 1.3807×10^{-23} J/K, μ_{BF} is the viscosity of the base fluid, d_p is the particle diameter, and l_{BF} is the mean free path of the base fluid and assumed a constant value of 0.17 nm for water (Chon *et al.*, 2005). The Brownian velocity of the nanoparticles is commonly regarded as an important factor when the prediction model is based on Brownian motion (Chon *et al.*, 2005; Jang and Choi, 2004; Koo and Kleinstreuer, 2004; Prasher *et al.*, 2005), which is functions of particle size and temperature. The present experimental data show the temperature- and size-dependency in the thermal conductivity enhancement, thus, it is physically reasonable to use the concept of the Brownian velocity to evaluate the effect of the particle size and temperature on the heat conduction of alumina nanofluids.

Figure 35 shows the comparison of the calculated Brownian velocity of nanoparticles in water using Equation (3-3) with the enhancement ratio of thermal conductivity of alumina nanofluids, defined as $(k_{NF} - k_{BF})/k_{BF}$, as a function of temperature. In calculating the Brownian velocity of nanoparticles, the proportionality constants were used as $Constant \times V_{BR}$. This is intended to examine the tendency comparison of the increment rate of the Brownian velocity with the enhancement ratio of thermal conductivity of nanofluids since the thermal conductivity enhancement in nanofluids may not be only the function of the Brownian velocity. The proportionality constants used for these calculations are 0.56 for AN1, 0.26 for AN2, and 0.21 for AN3. The increment rate of the calculated Brownian velocity is in accordance with the enhancement ratio of the thermal conductivity as shown in Figure 35. Moreover, the fitted proportionality constants for each case decrease with increasing mean particle diameter and this

tendency may suggest that there are other size effects beyond the Brownian velocity on the heat conduction mechanism of nanofluids. Thus, it can be concluded that the Brownian velocity is the key factor of the temperature- and size-dependent thermal conductivity data for alumina nanofluids and it is suggested that the Brownian-motion-induced convection from multiple nanoparticles or Brownian motion is the main reason for the observed thermal conductivity enhancement shown in Figure 35.

TABLE III

DYNAMIC LIGHT SCATTERING RESULTS OF GOLD NANOPARTICLE SIZES AS FUNCTION OF REACTION TEMPERATURE IN A CONVENTIONAL ULTRASONIC BATH

case	Reaction temperature (i.e. T of filled water)	Peak 1 (Diameter/Intensity)	Peak 2 (Diameter/Intensity)
1	30 °C	~ 47nm/67%	~ 1.8nm/33%
2	50 °C	~49nm/65%	~2.3nm/35%
3	60 °C	~42nm/67%	~1.5nm/33%
4	70 °C	~41nm/70%	~1.5nm/30%
5	80 °C	~43nm/72%	~1.6nm/28%

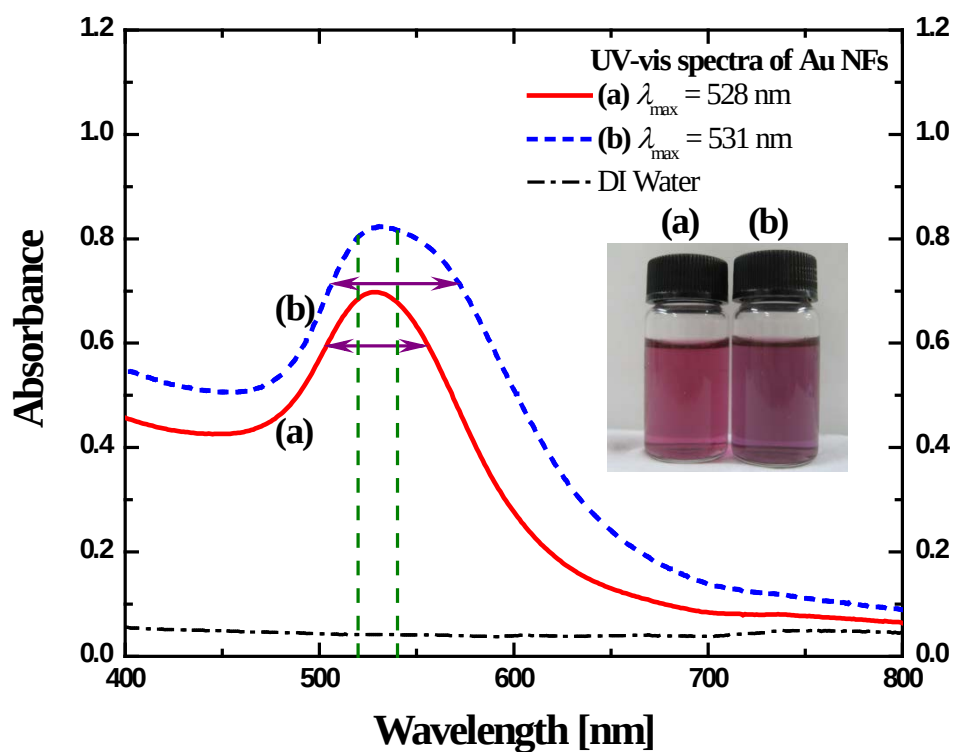


Figure 16. UV-visible spectroscopy of synthesized gold suspensions: (a) gold suspension (maximum absorption peak $\lambda_{\max}$ is 528 nm) prepared with 243 kJ (30 min with 135 W ultrasonic power) of sonication; (b) gold suspension (maximum absorption peak $\lambda_{\max}$ is 531 nm) prepared with 729 kJ (90 min with 135 W ultrasonic power) of sonication.

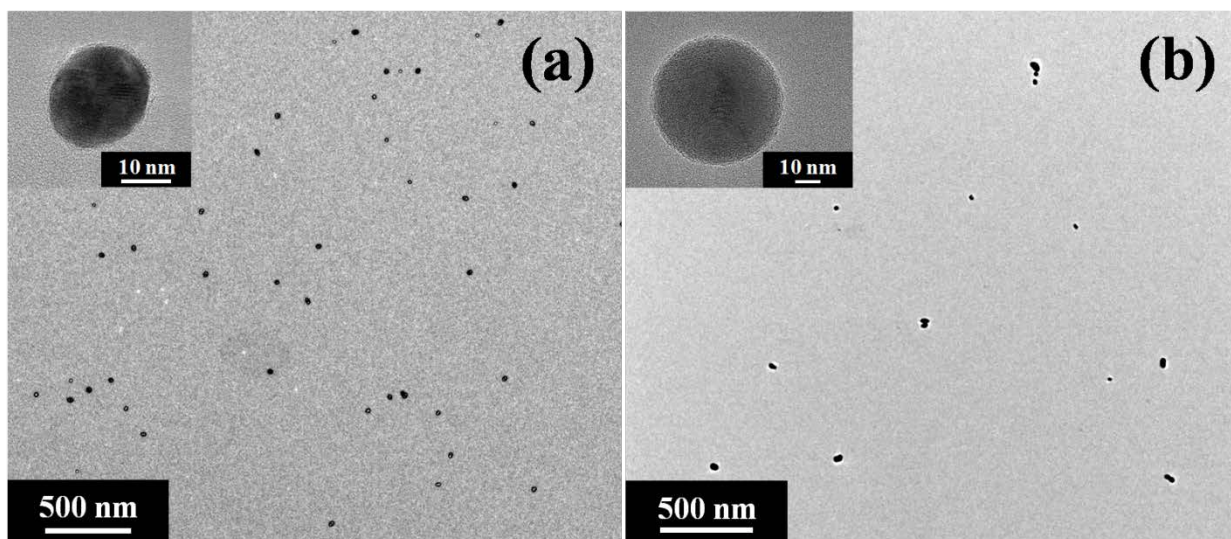


Figure 17. TEM images of synthesized gold nanoparticles: (a) gold nanoparticles (approximately 20 nm) prepared with 243 kJ (30 min with 135 W ultrasonic power) of sonication; (b) gold nanoparticles (20 to 50 nm) prepared with 729 kJ (90 min with 135 W ultrasonic power) of sonication. Initial HAuCl_4 concentration was 0.25 mM and molar ratio between HAuCl_4 and sodium citrate was set at 1:3.5.

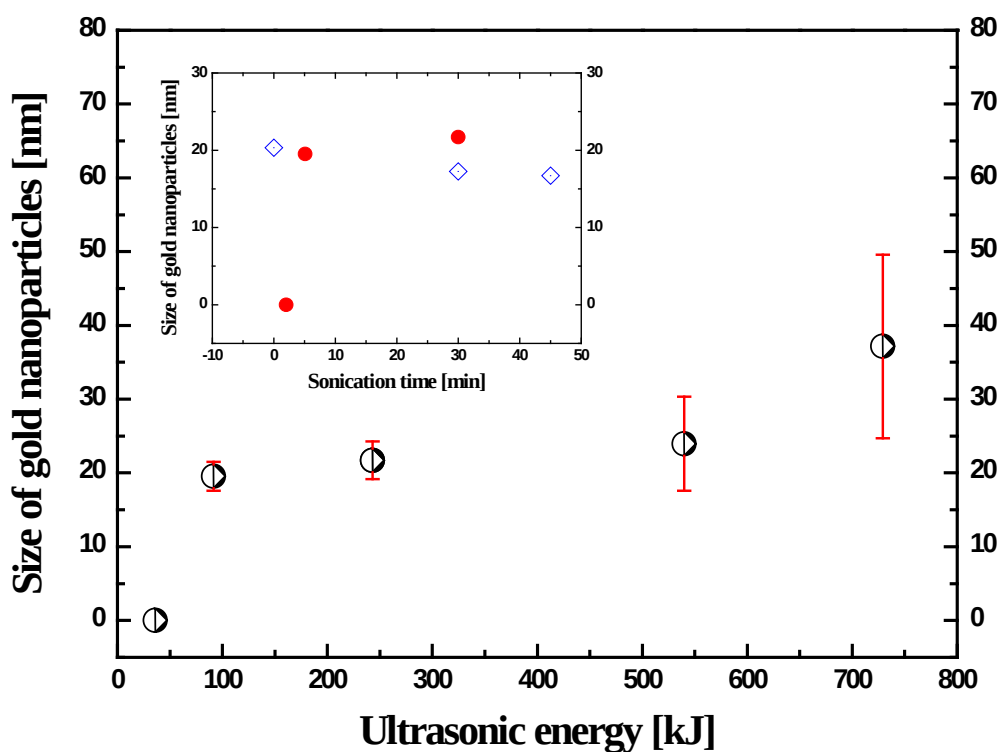


Figure 18. Average size of gold nanoparticles as a function of ultrasonic energy: The error bars correspond to the standard deviation of the average size of gold nanoparticles. Because Chen and Wen (2011) presented their data as a function of sonication time from 0 to 45 minutes, their data (open blue diamonds) are reproduced in the inset for comparison with data from the present study (solid red circles).

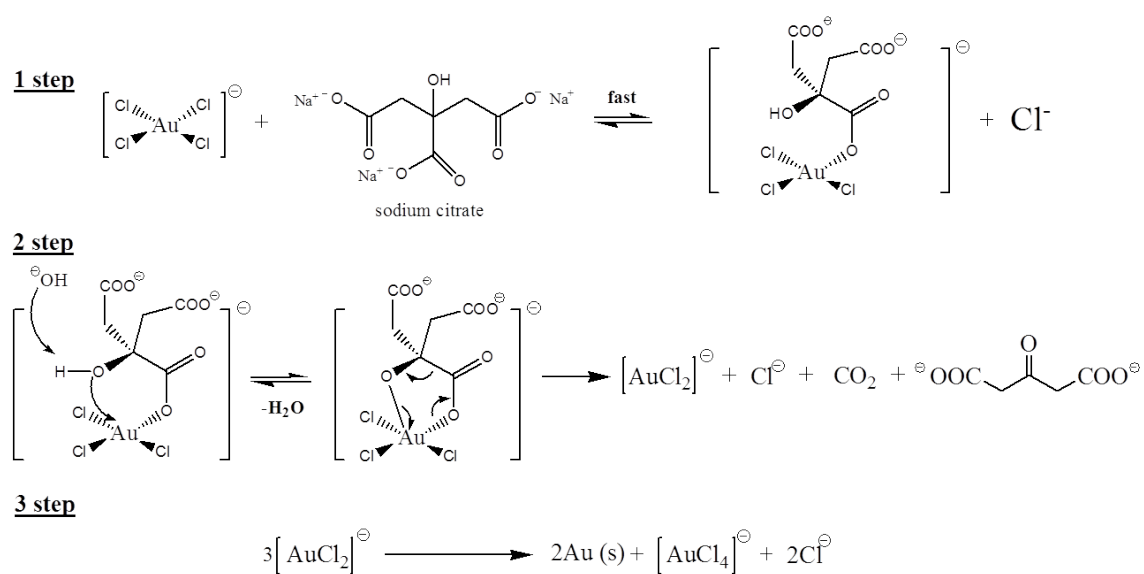


Figure 19. Reduction mechanism of HAuCl_4 by sodium citrate: (a) Ligand exchange reaction, and (b) decarboxylation and reduction of HAuCl_4 species. This mechanism was postulated by Ojea-Jiménez *et al.* (2010).

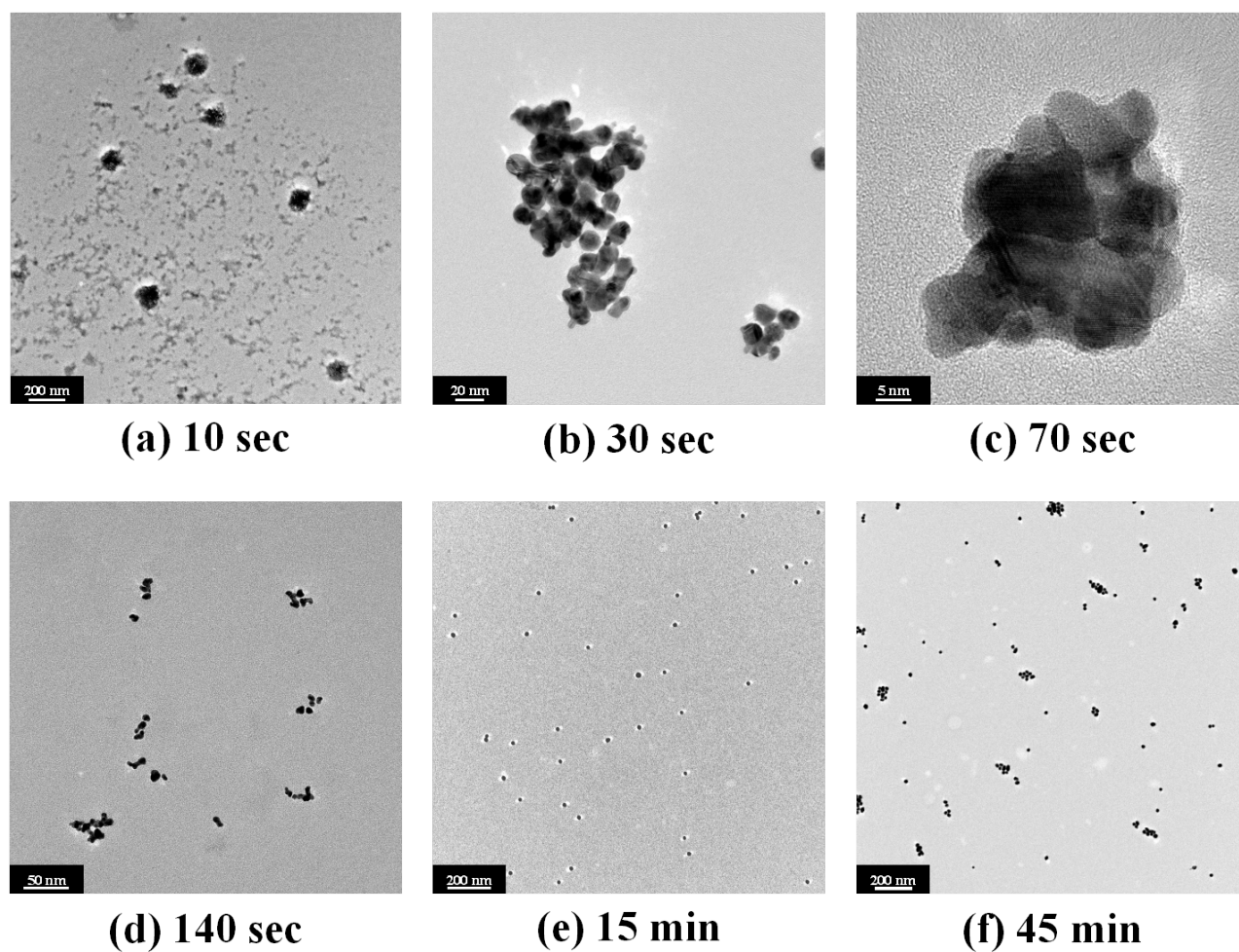


Figure 20. TEM images of gold nanoparticles formed by citrate reduction as function of elapsed time when using a conventional ultrasonic bath (40 kHz, 300 W): (a) after 10 sec, (b) after 30 sec, (c) after 70 sec, (d) after 140 sec, (e) after 15 min; and (f) after 45 min. Initial HAuCl_4 concentration was 0.25 mM, and molar ratio between HAuCl_4 and sodium citrate was set at 1:3.5.

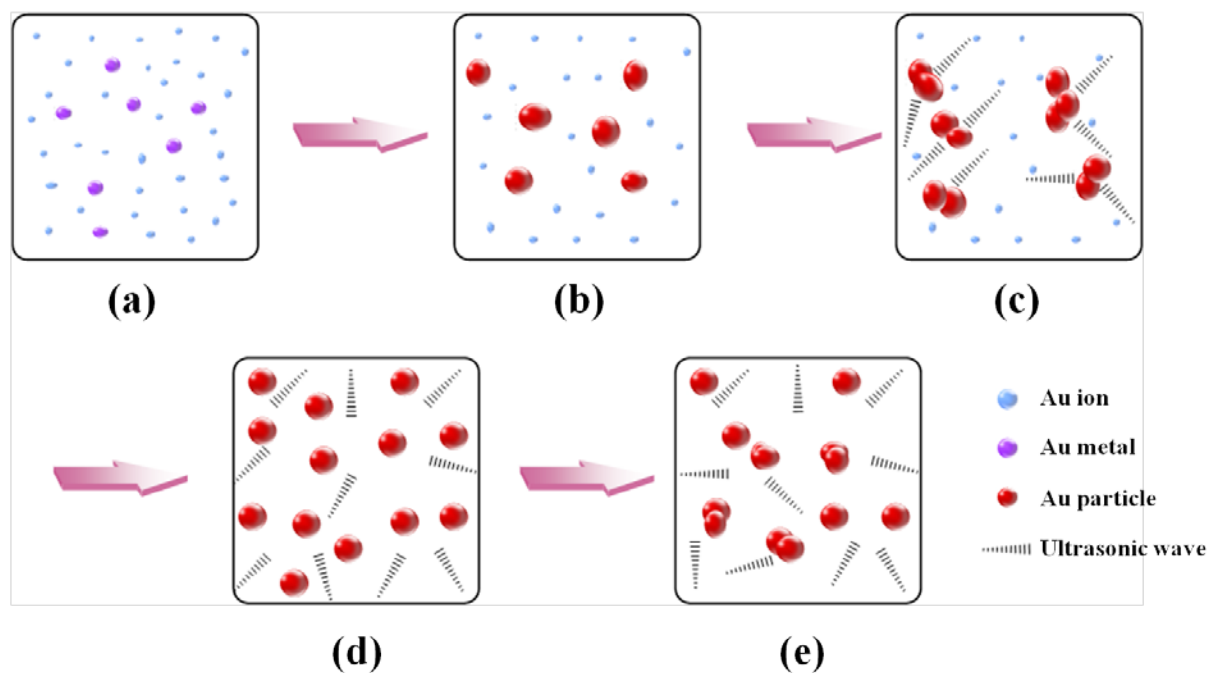


Figure 21. Proposed scheme for understanding the role of ultrasonic energy in the formation of gold nanoparticles: (a) Reduction of gold ions with sonication energy, (b) growth of gold nanoparticles (c) prevention or minimization of wire-shaped gold cluster formation by breaking chain-like nanowires by ultrasonic waves, (d) monodispersed gold nanoparticles by ultrasonic waves with Oswald ripening or intra-particle ripening, and (e) particle-particle fusion induced by excess of ultrasonic energy.

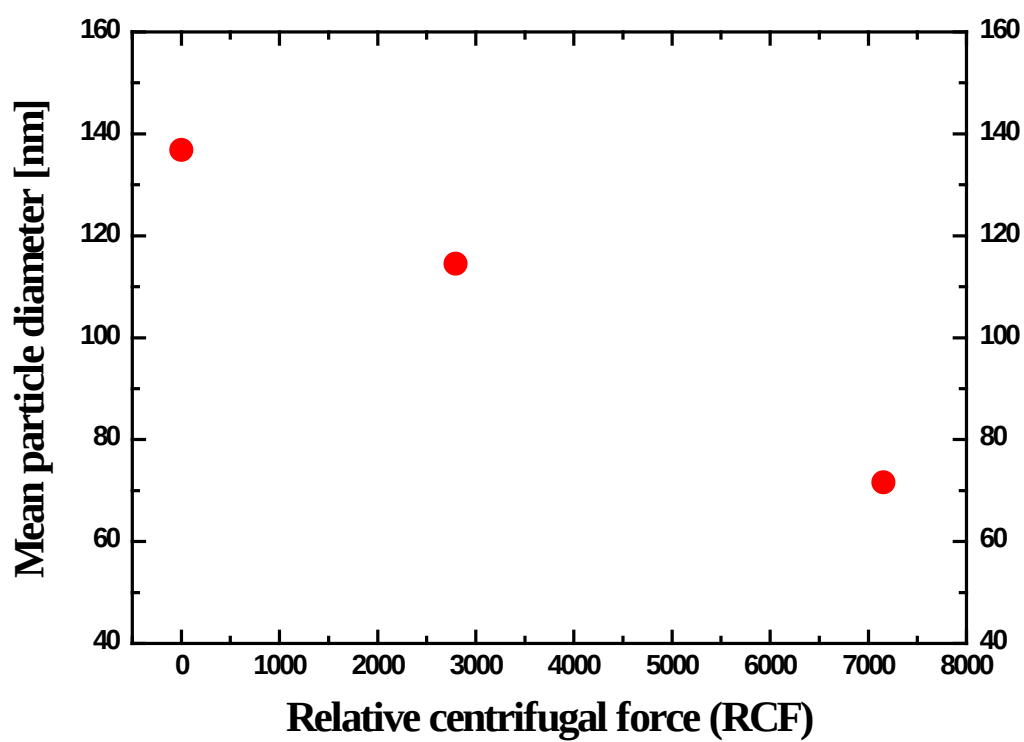


Figure 22. Mean particle diameters of decanted alumina nanoparticles (remained nanoparticles in supernate after centrifugation) as a function of applied relative centrifugal force. Mean particle diameter was measured by dynamic light scattering.

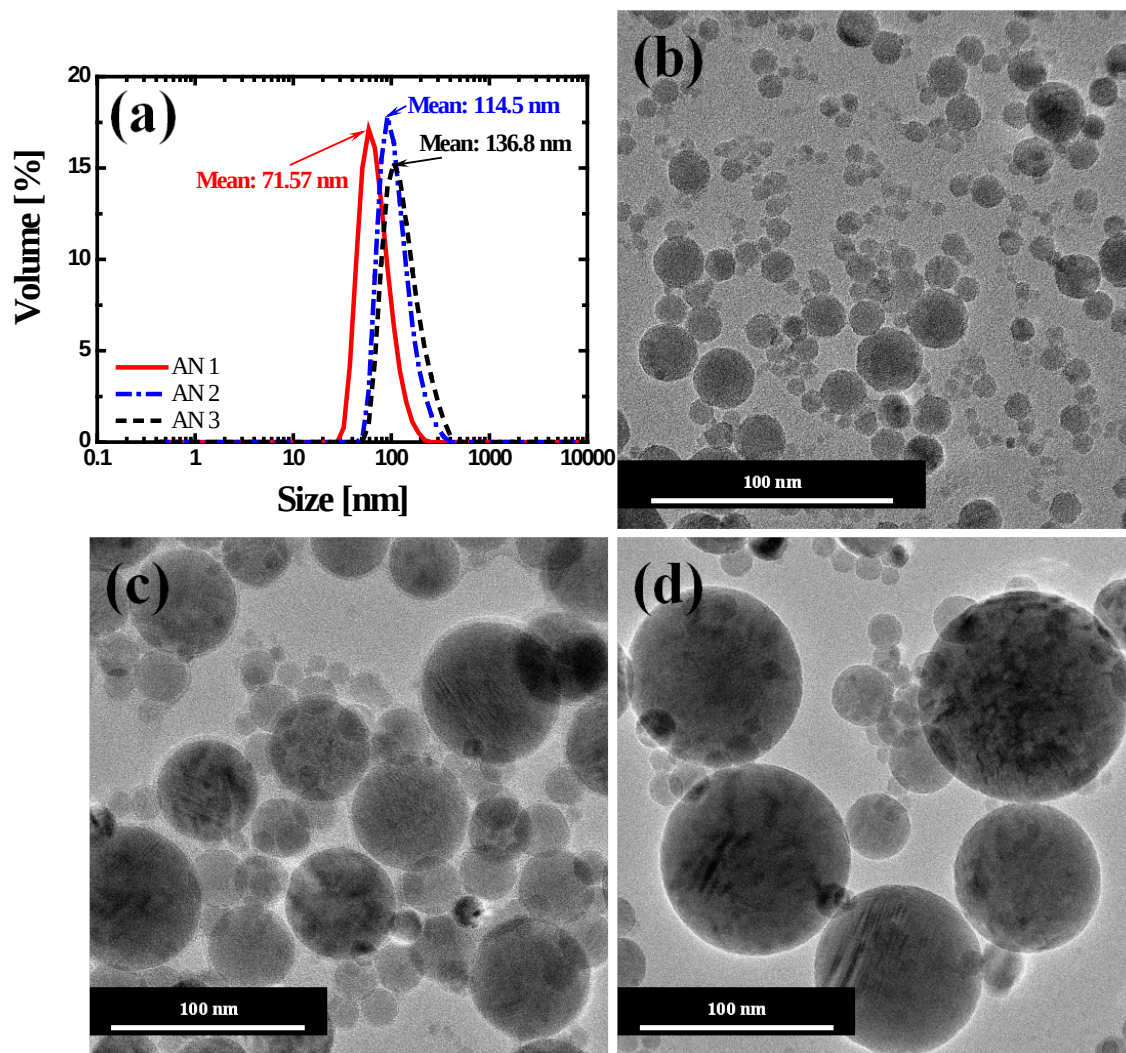


Figure 23. Particle size and particle size distribution of alumina nanofluids: (a) particle size distribution of three alumina nanofluids by the DLS technique. (b) TEM image of AN1, (c) TEM image of AN2, (d) TEM image of AN3.

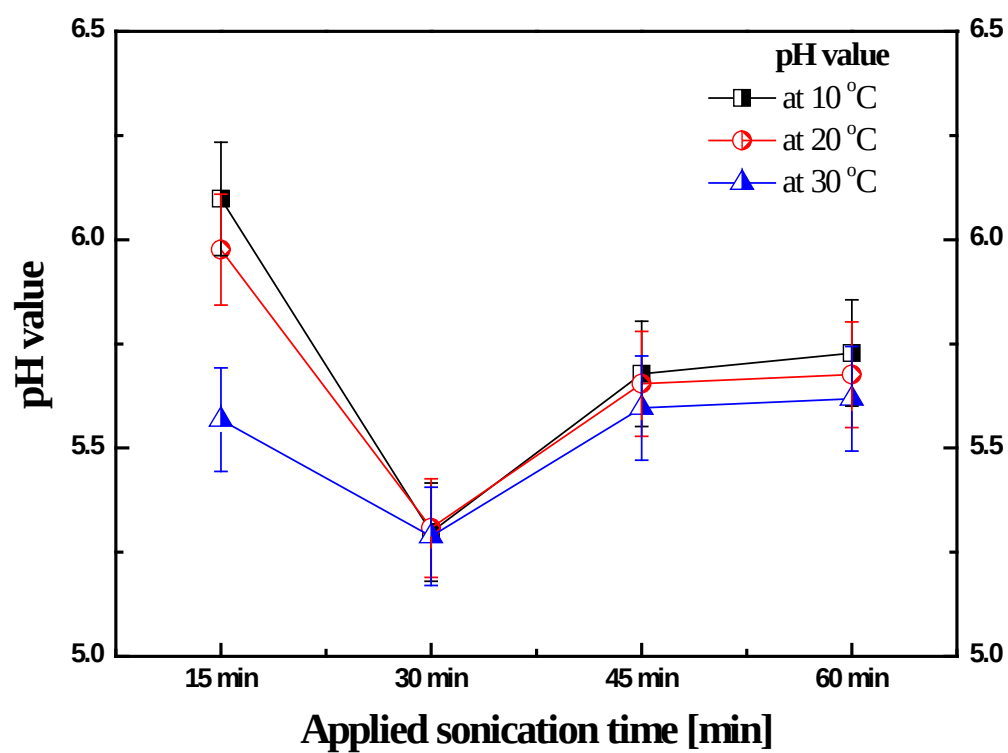


Figure 24. pH data of gold nanofluids as a function of applied sonication time during synthesis: The error bars correspond to the uncertainty ($\pm 2.0\%$).

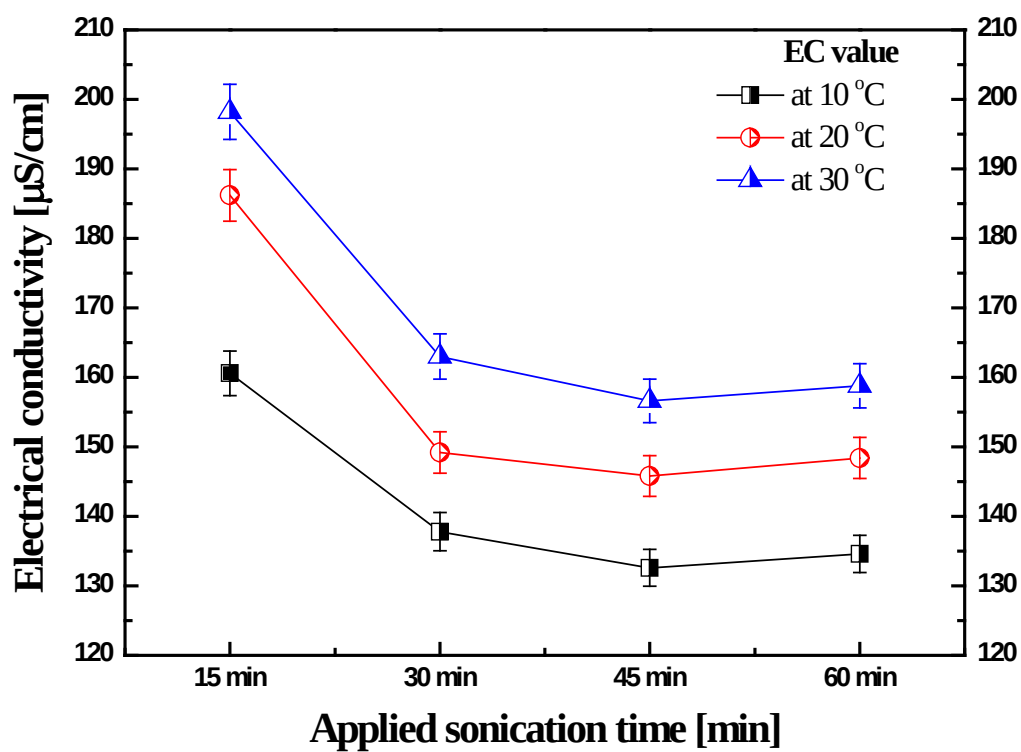


Figure 25. Electrical conductivity (EC) data of gold nanofluids as a function of applied sonication time during synthesis: The error bars correspond to the uncertainty ($\pm 2.0\%$).

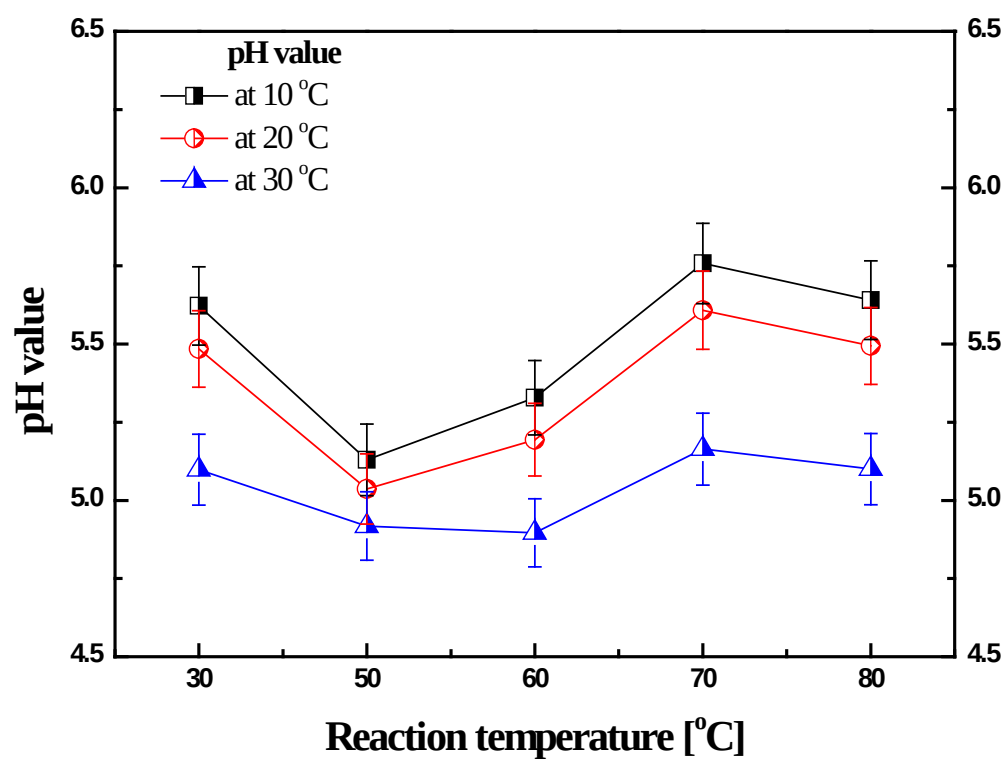


Figure 26. pH data of gold nanofluids as a function of reaction temperature during synthesis: The error bars correspond to the uncertainty ($\pm 2.0\%$).

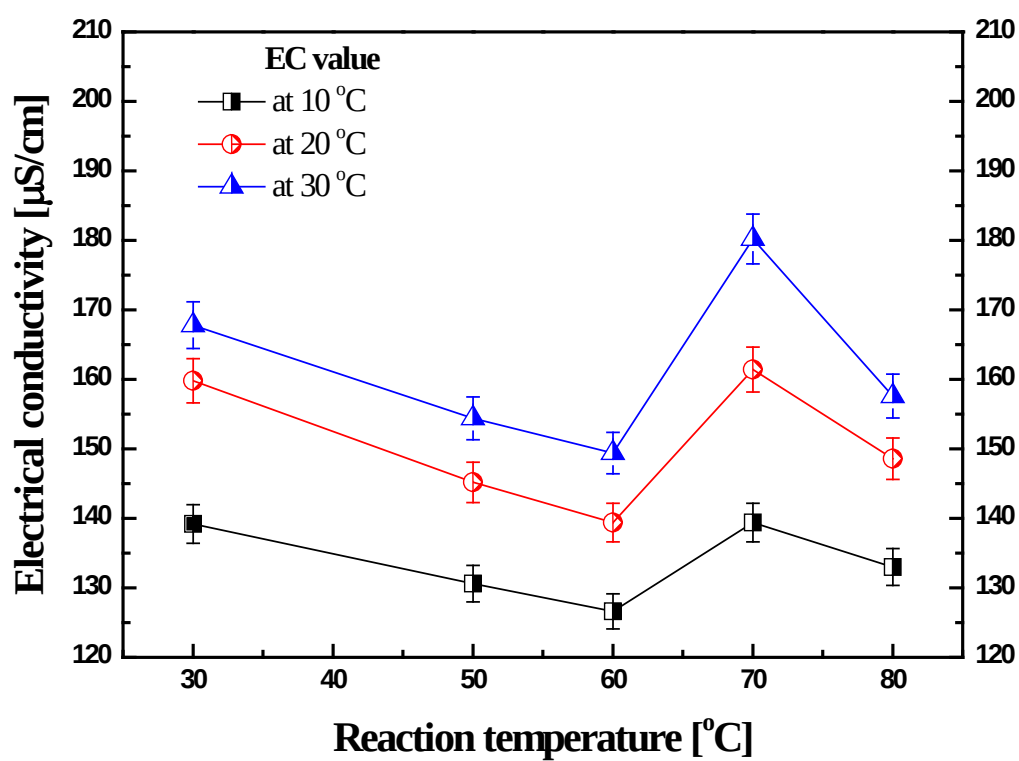


Figure 27. Electrical conductivity (EC) data of gold nanofluids as a function of reaction temperature during synthesis: The error bars correspond to the uncertainty ($\pm 2.0\%$).

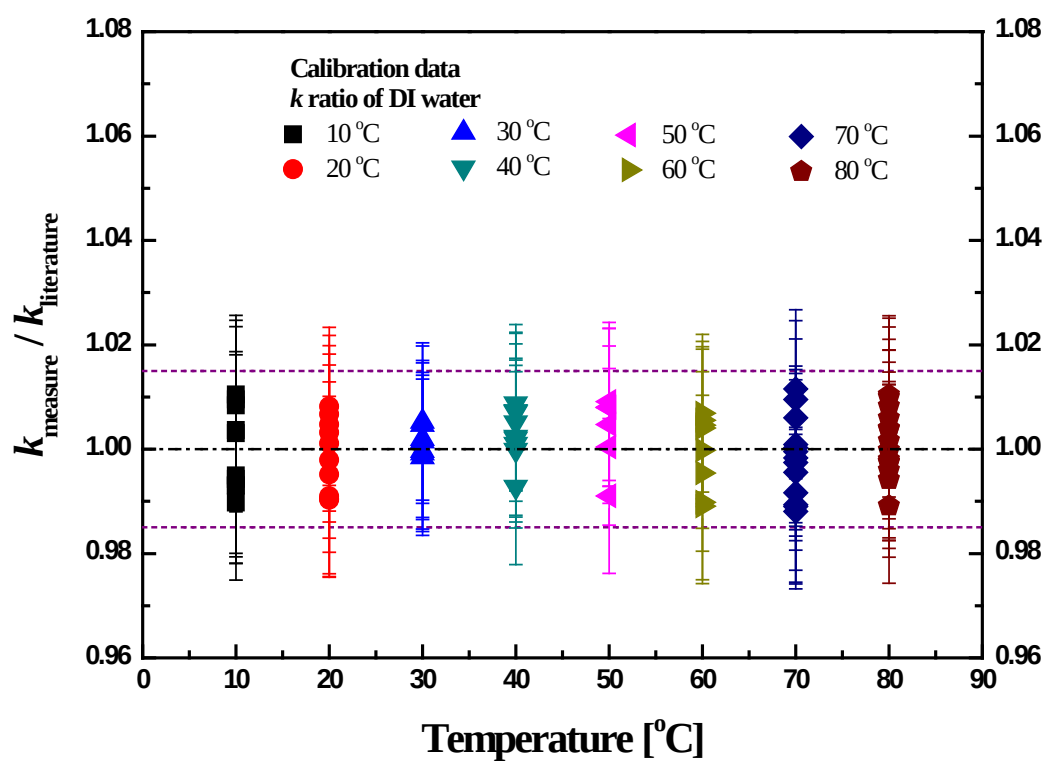


Figure 28. Thermal conductivity ratio (measurement value to literature value) data of HPLC grade water as a function of temperature: The error bars correspond to the uncertainty ($\pm 1.5\%$).

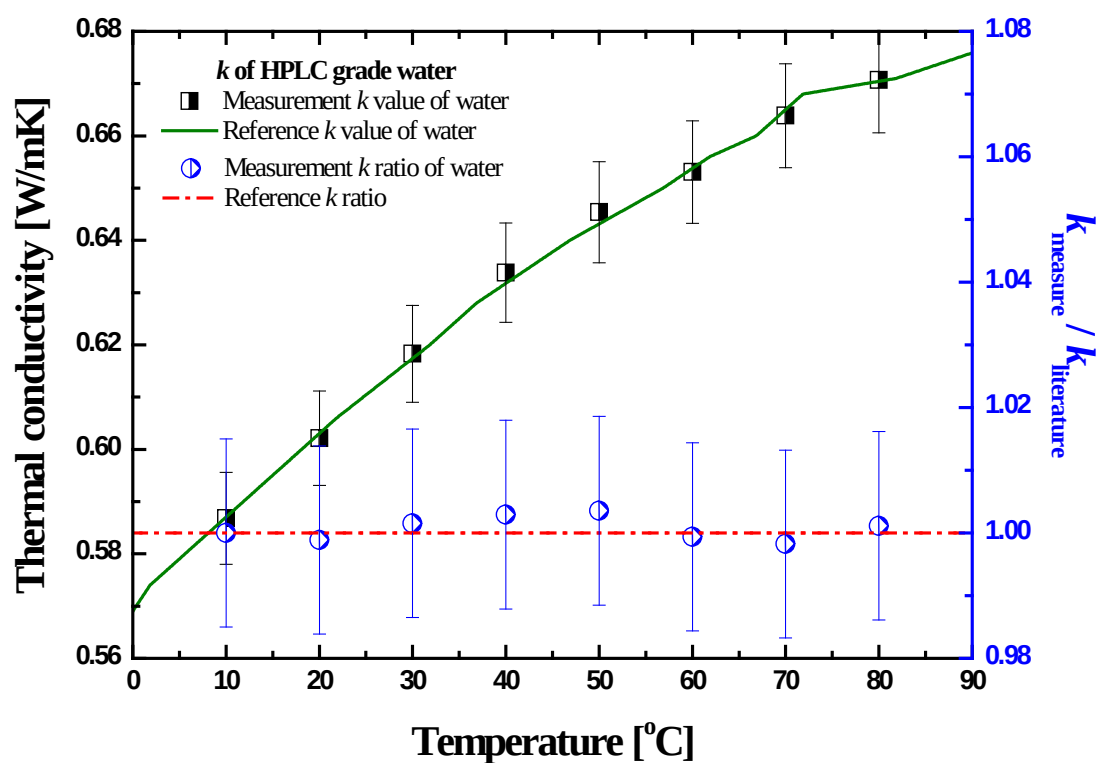


Figure 29. Mean calibration data of thermal conductivity of HPLC grade water as a function of temperature: The error bars correspond to the uncertainty ($\pm 1.5\%$).

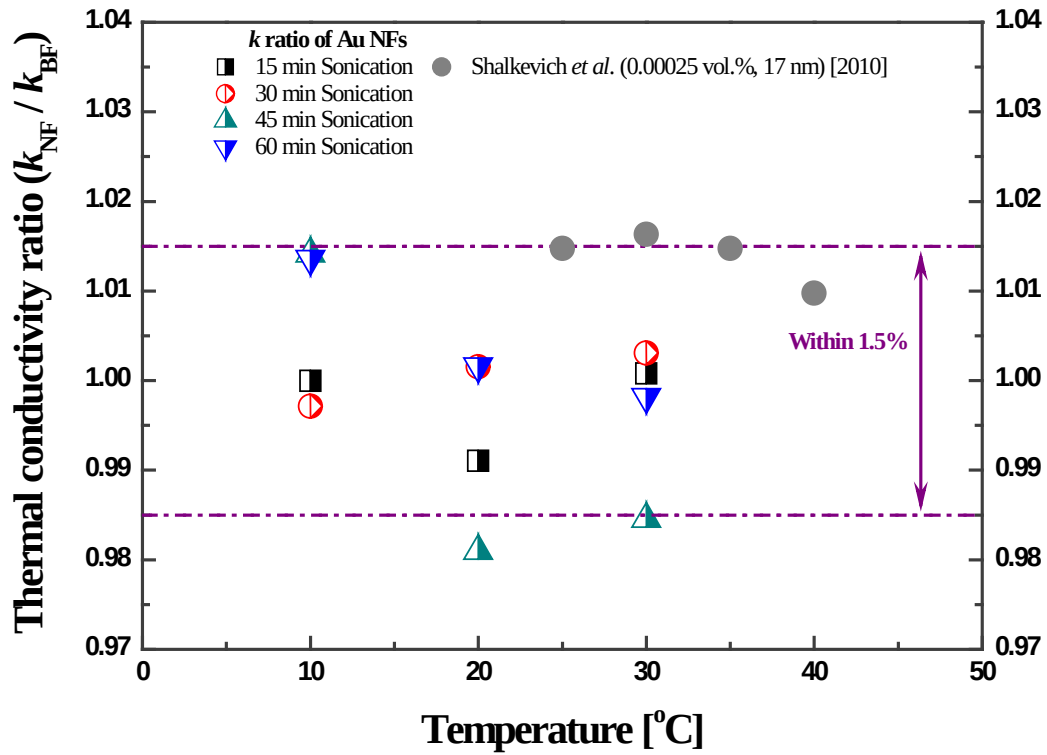


Figure 30. Comparison of the thermal conductivity ratio for aqueous gold nanofluids as a function of temperature: Gold nanofluids produced by using conventional ultrasonic bath with variation of applied sonication time. Experimental results are in accord with Shalkevich *et al.*'s data [Shalkevich *et al.*, 2010] (solid gray circles).

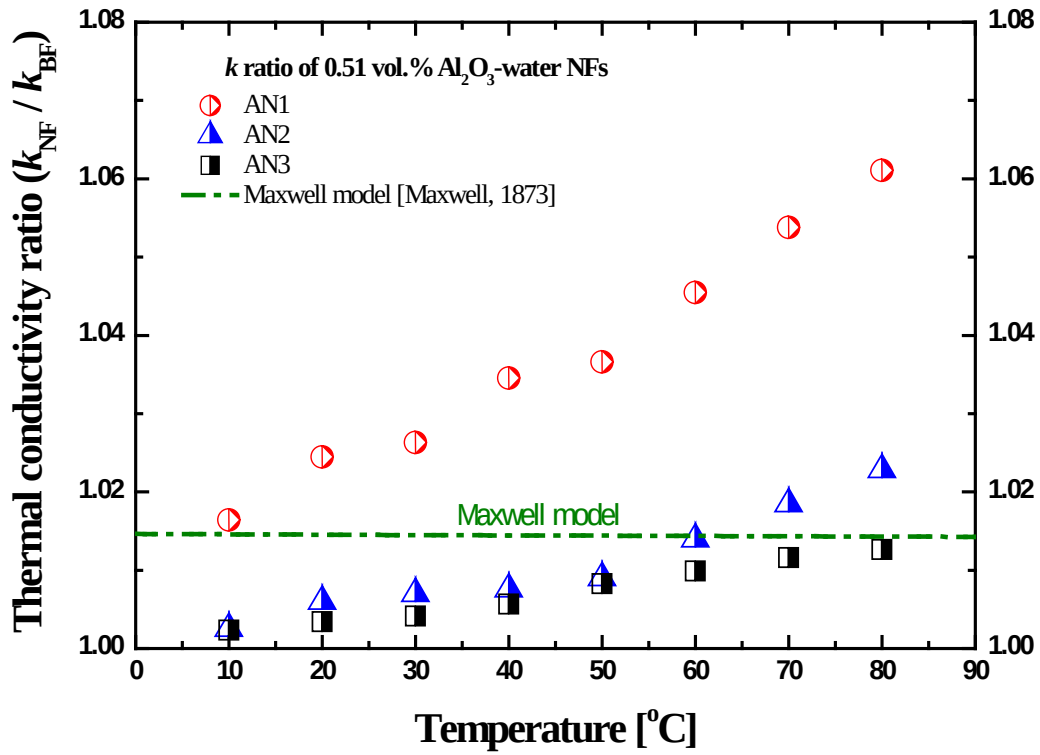


Figure 31. Thermal conductivity ratio (nanofluids to water) of three 0.51 vol.% Al_2O_3 /water nanofluids as a function of temperature. Dots are experimental data, and line is the prediction value from the Maxwell model [Maxwell, 1873] assuming nanoparticles are uniformly distributed in the base fluid.

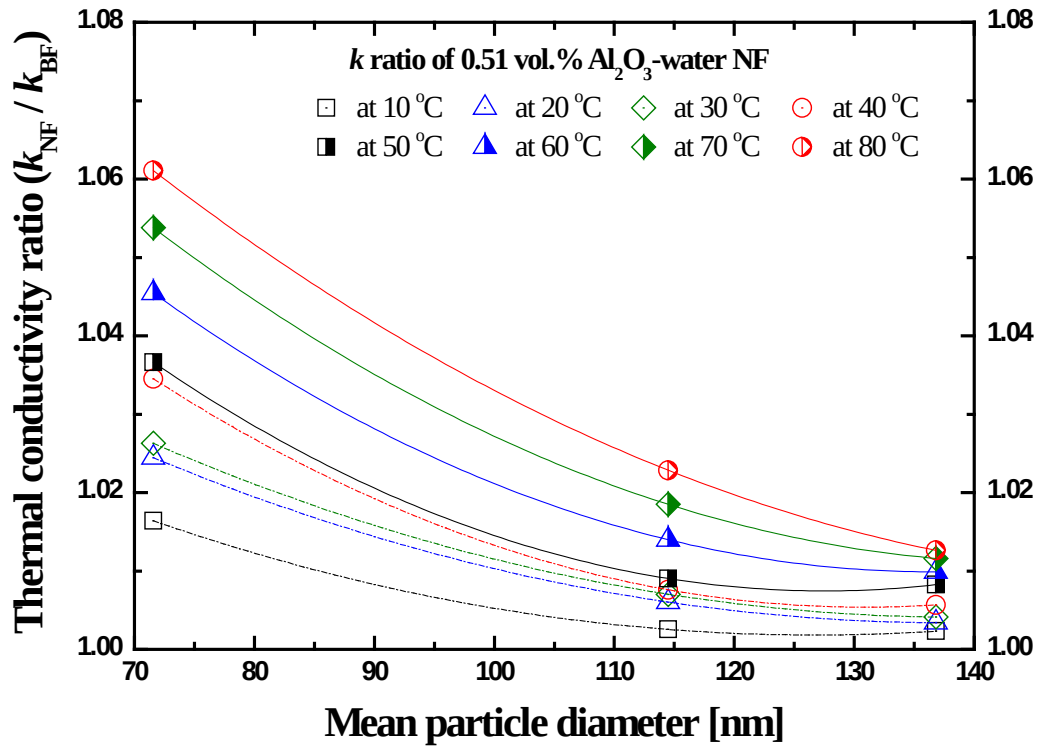


Figure 32. Thermal conductivity ratio (k of nanofluids to that of water) of Al_2O_3 /water nanofluids as a function of mean particle diameter. Dots are experimental data, and line is polynomial fitting values of experimental data.

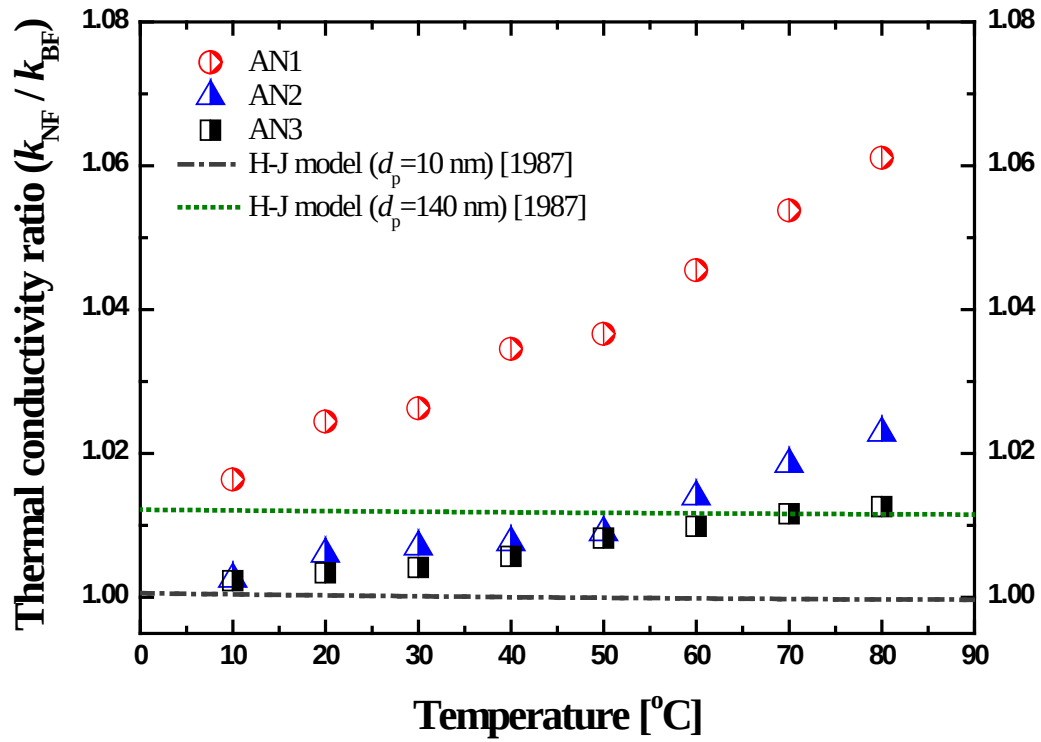


Figure 33. Thermal conductivity experimental data comparison with Hasselman and Johnson (H-J) model [Hasselman and Johnson, 1987] as a function of temperature. The upper bound and the lower bound of the thermal conductivity enhancement were calculated with the mean particle size of 140 nm and 10 nm, respectively.

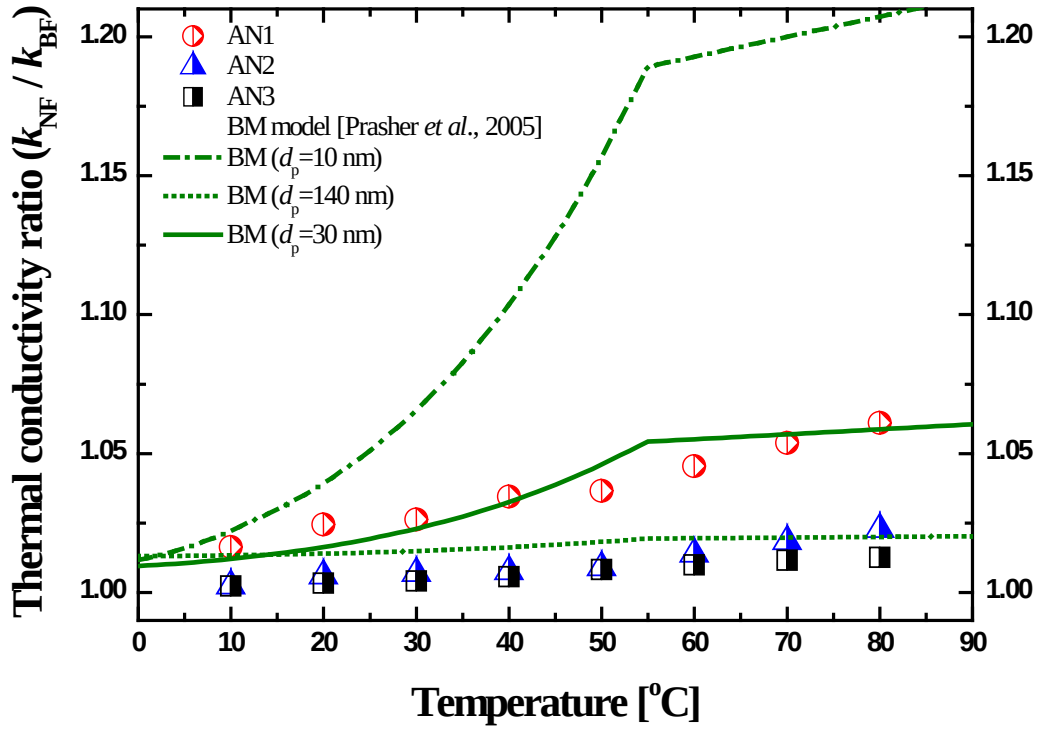


Figure 34. Thermal conductivity experimental data comparison with Brownian model (BM) as a function of temperature. The upper and the lower bounds of the thermal conductivity enhancement are calculated with the mean particle size of 10 nm and 140 nm, respectively. The experimental value is fitted using a mean diameter of 30 nm for the case of AN1.

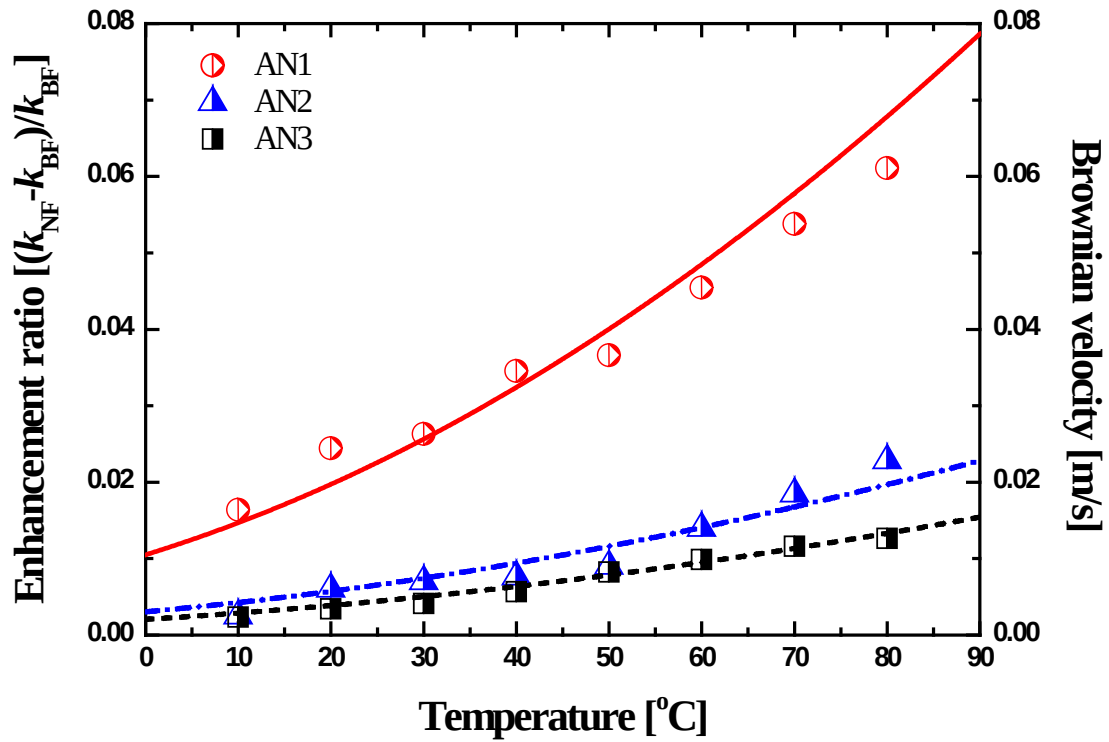


Figure 35. Comparison of the Brownian velocity of nanoparticles in water with the enhancement ratio of thermal conductivity of three aqueous alumina nanofluids as a function of temperature. Dots are experimental data, and lines are the calculated values of the Brownian velocity with proportionality constants which are for (a) AN1: 0.56, (b) AN2: 0.26, and (c) AN3: 0.21.

IV. CONCLUSIONS

Numerous studies have shown that nanofluids have superb physical properties, among which thermal conductivity has been studied most extensively but remains controversial. The lack of an agreement between experimental data from different groups can be due to differences in sample quality, the dependence of thermal conductivity on many factors, and differences in measurement uncertainties. Thus, production methods and thermal conductivity as the transport property of nanofluids are investigated in the present study. The conclusions drawn from the present work are summarized as follows:

(1) Highly monodispersed spherical GNPs were produced by the sodium citrate reduction method using a conventional ultrasonic bath without additional heating or magnetic stirring. It was found that the sonication energy has a significant effect on the particle size and morphology of GNPs for a fixed ultrasonic power and frequency. Thus, this study shows the importance of ultrasonic energy in the ultrasonic-induced production of water-soluble GNPs of tunable sizes (20 to 50 nm) by citrate reduction. Transmission electron microscopy and dynamic light scattering are used to characterize particle size, shape and distribution. A hypothetical scheme for understanding the role of ultrasonic energy on the size of water-soluble GNPs was discussed. The single-step method using a conventional ultrasonic bath developed in this study offers new opportunities to synthesize aqueous suspensions of monodispersed spherical GNPs without magnetic stirring. The use of ultrasonication without any additional heating and stirring devices is both technologically and scientifically important. Since our results successfully demonstrated that ultrasonication alone is very effective in the synthesis of spherical GNPs, we have developed a simplified method to produce spherical GNPs. Furthermore, because this

simplified method involves fewer steps compared to the procedure used by Chen and Wen (2011), it is a highly reproducible method for making gold nanofluids with spherical GNPs of consistent quality. It can, hence, be expected to produce a large volume of consistent quality spherical-shaped GNPs and gold nanofluids.

(2) The effects of nanofluid production methods on the particle morphology and properties of aqueous Au nanofluids are investigated using chemical reduction method with a conventional ultrasonic bath for the first time. The temperature range of measured properties was from 10 to 30 °C. Applied energy to the production of nanofluids and reaction temperature are two main parameters in the production of aqueous gold nanofluids. Experimental results show that pH and electrical conductivity variations are dependent on the production conditions.

(3) Centrifugation is used to produce nanofluids with the two-step method. The present study shows for the first time three alumina nanofluids with different sizes of nanoparticles, that were produced from the same original nanoparticle dispersion by means of centrifugation and without involving any dispersants or surfactants. This modified synthesis method of producing three different sizes of alumina nanoparticles from single-sized nanoparticles can minimize the difference of dispersibility into the base fluid, as compared to the method of acquiring three different sizes of alumina nanoparticles with different intrinsic surface characteristics due to their different manufacturing process.

(4) The transient hot wire system was designed and manufactured in-house to measure the effective thermal conductivity of aqueous gold and alumina nanofluids considering the effect of the tilting angle of the wire to minimize measurement error, especially error due to natural convection. Measured thermal conductivity values of HPLC grade water by using the custom-

made THW system were within 1% of literature values and relative uncertainties of thermal conductivity were less than 1.5%.

(5) The thermal conductivities of gold nanofluids were measured by the custom-made transient hot wire system. Uncertainty of the measurements was less than $\pm 1.5\%$ from the uncertainty analysis. There were no enhancements of thermal conductivities of gold nanofluids with respect to their base fluid at very small volume fraction ($\sim 2.0 \times 10^{-4}$ vol.%) and experimental results are consistent with previous published data (Shalkevich *et al.*, 2010).

(6) Measurements of thermal conductivity of alumina nanofluids were conducted over a temperatures ranging from 10 to 80 °C in order to observe more clearly the corresponding effects. This broad range of 10 to 80 °C is unusual in thermal conductivity measurements of water-based nanofluids. The relative uncertainties of thermal conductivity were less than 1.5%. The thermal conductivity ratio of the three different alumina nanofluids presented similar trends; increases with rising temperature, although the rate of increment in thermal conductivity varied with particle size. The maximum increment in thermal conductivity of alumina nanofluids is about 4.7% from the prediction of the Maxwell model at 80 °C. The experimental results clearly show the size- and temperature-dependency on the thermal conductivity enhancement. Moreover, it is found that the temperature effect depends on the particle size. In other words, there is a coupling dependency on the size of nanoparticles and temperature in heat conduction enhancement of alumina nanofluids. The experimental results were compared to the effective medium theory (EMT) models and the calculated Brownian velocity to evaluate the feasibility of the Brownian motion being the main contributing factor which affects the thermal conductivity enhancement. It can be concluded that the Brownian velocity is the key factor of the temperature- and size-dependent thermal conductivity data for alumina nanofluids and it is suggested that the

Brownian-motion-induced convection from multiple nanoparticles or Brownian motion is the main reason for the observed thermal conductivity enhancement.

V. FUTURE WORK

To clarify and extend the present study, some additional research should be pursued, as follows:

(1) There is need to investigate the pH and electrical conductivity characteristics of gold nanofluids produced by the sonication method experimentally.

(2) Presently, there is no thermal conductivity measurement data of gold nanofluids produced by chemical reduction method with high particle volume loadings, because gold nanoparticles agglomerate and settle at large concentrations; Patel *et al.* (2003). Thus, there is much to be learned by investigating water-based gold nanofluids with high particle concentrations.

(3) More systematic experiments, such as thermal conductivity measurements in the frozen region (where Brownian motion is diminished) are needed to clarify whether Brownian motion is the main reason for the observed, albeit minimal, thermal conductivity enhancement.

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