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Application of hybrid sphere/carbon nanotube particles in nanofluids

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Abstract
Previous studies on nanofluids have focused on spherical or long-fibre particles. In this work, a new type of complex nanoparticle—a hybrid sphere/carbon nanotube(CNT) particle, consisting of numerous CNTs attached to an alumina/iron oxide sphere—is proposed for applications in nanofluids. In such hybrid nanoparticles, heat is expected to transport rapidly from one CNT to another through the centre sphere and thus leading to less thermal contact resistance between CNTs when compared to simple CNTs dispersed in fluids. CNTs have an extremely high thermal conductivity, but thermal resistance between the CNTs and the fluid has limited their performance in nanofluids. The proposed hybrid sphere/CNT particles are synthesized by spray pyrolysis followed by catalytic growth of CNTs. The spheres are about 70 nm in diameter on average, and the attached CNTs have a length up to 2 μm. These hybrid nanoparticles are dispersed to poly-alpha-olefin with sonication and a small amount of surfactants to form stable nanofluids. The thermal conductivity of the fluids has been measured by a 3ω-wire method over a temperature range 10–90 °C. The results indicate that the effective thermal conductivity of the fluids is increased by about 21% at room temperature for particle volume fractions of 0.2%.

Nanofluids, which consist of nanoparticles suspended in liquids, show particular promise for enhancing thermal properties of heat transfer fluids and are a strong candidate for the next generation of liquid coolants [1–11]. The approach to enhance the thermal conductivity of heat transfer fluids by adding highly conductive particles began more than a century ago when Maxwell first theoretically proposed this technique [12]. Early-stage studies have been confined to millimetre-or micrometre-sized solid particles dispersed in fluids. In the past decade, suspensions of nanometre-sized solid particles, known as nanofluids, have been extensively investigated. Unusually high thermal conductivity enhancement had been experimentally reported in various nanofluid systems by different groups around the world [3–6, 11, 13]. To date, all published studies on nanofluids have focused on spherical or long-fibre (e.g. nanotubes) particles. The effectiveness of particle morphologies on heat transfer in nanofluids has been far less investigated.

In this paper, a new type of complex nanoparticle—hybrid sphere/carbon nanotube (CNT)—has been developed for promoting heat transport in fluids. Such hybrid nanoparticles are expected to reduce thermal contact resistance between CNTs by providing a thermal path through the central spheres. These hybrid sphere/CNT particles are synthesized by spray pyrolysis followed by catalytic growth of CNTs. The thermal conductivity of nanofluids containing the hybrid nanoparticles dispersed in poly-alpha-olefin (PAO) is measured by the 3ω-wire method from 10 to 90 °C. The Brownian

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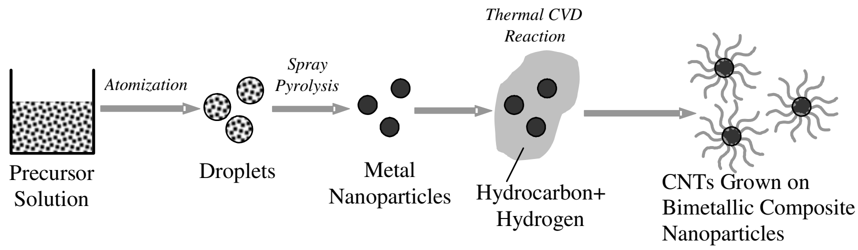

Figure 1. Schematic of gas phase growth pathways of CNTs grown on metal oxide nanoparticles. The precursor solution was prepared with 3 wt% $Fe(NO)_3 + Al(NO)_3$ solution with the $Fe(NO)_3$:$Al(NO)_3$ ratio of = 1:1 for hybrid sphere/CNT particles.

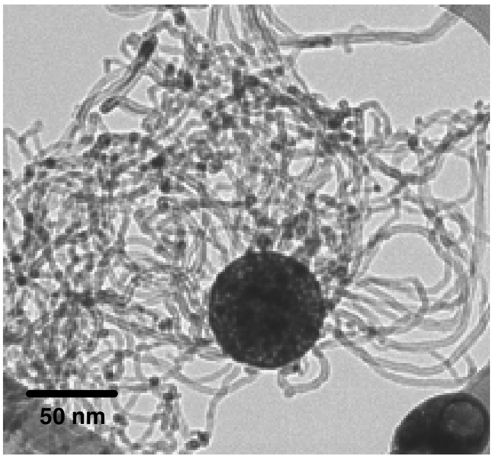

Figure 2. TEM image of a sample hybrid sphere/CNT particle produced by the aerosol method. The central spheres are polydisperse with a broad size range from 10 to 300 nm, having a geometric mean diameter of 70 nm. Image taken by a JEOL 2010 high-resolution transmission electron microscope (HRTEM).

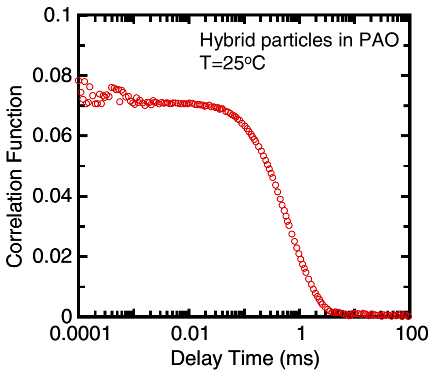

Figure 3. Correlation function of the scattered light versus delay time for the nanofluid consisting of hybrid sphere/CNT particles dispersed in poly-alpha-olefin (PAO). Measurements taken by a Photocor-Complex DLS instrument.

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mobility/diffusivity of these particles in nanofluids is also examined.

The hybrid sphere/CNT nanoparticles are grown in the aerosol phase by an on-the-fly process where spherical nanoparticles are prepared by spray pyrolysis, followed by CNT catalytic growth at the surface of the spherical nanoparticles [14–16]. Figure 1 shows a schematic of the synthesis process. The synthesis involved preparing an aqueous precursor solution of $Fe(NO_3)_3$ and $Al(NO_3)_3$ with a mixing ratio 1:1 at a total concentration of 3 wt%. The bimetallic composite nanoparticles of iron and aluminium are formed from thermal decomposition of aerosol droplets generated by a nebulizer in nitrogen carrier gas. These bimetallic aerosol particles pass through a silica-gel dryer to remove water and then mix with hydrogen gas at the entrance of a tube furnace (at ~1000 °C) for pyrolytic conversion of the metal nitrate to the crystalline oxide nanoparticles. The spherical, oxide nanoparticles are introduced into a second tube furnace (residence time ~3 s) and catalytically react with acetylene and hydrogen at 750 °C, which leads to the CNT growth at their surfaces. The hybrid sphere/CNT particles are collected on a membrane filter. The detailed structure of a hybrid sphere/CNT particle is illustrated in figure 2. It can be seen that numerous CNTs are connected through the spherical, alumina/iron oxide composite nanoparticle. The central spheres are polydisperse with a broad size ranging from 10 nm to 300 nm, having a geometric mean diameter of 70 nm. The attached CNTs have a length up to 2 μm and a relatively uniform diameter of ~10 nm. The CNTs are composed of ~5 walls and a hollow core. The mass fraction of each component in these hybrid sphere/CNT particles is as follows: CNT = ~3 wt%, alumina = ~32 wt%, iron oxide = ~65 wt%. The collected hybrid sphere/CNT particles are dispersed to PAO oil with sonication. A small amount of surfactant (about 1.5 wt%), Span-80, is used to form stable, uniform nanofluids. No significant enhancement in thermal conductivity was observed in the PAO oil with the same amount of Span-80.

In these hybrid sphere/CNT particles, the attached CNTs should expect an additional drag force to reduce the mobility motion of the centre spheres. The Brownian motion of the hybrid particles has been examined in the prepared PAO-based nanofluids using a Photocor Complex-DLS instrument at room temperature [17]. The autocorrelation function of the scattered light is plotted in figure 3. The Brownian diffusivity of the hybrid particles is found to be 1.74×10^{-9} cm^2 s^{-1}, which is slightly smaller than that for a simple spherical particle. This implies that the attached CNTs have only a minimal effect on the overall Brownian mobility of the hybrid particles. The central sphere might promote heat transfer in fluids through two ways:

(1) acting as the Brownian particles,
(2) providing a rapid thermal path between CNTs.

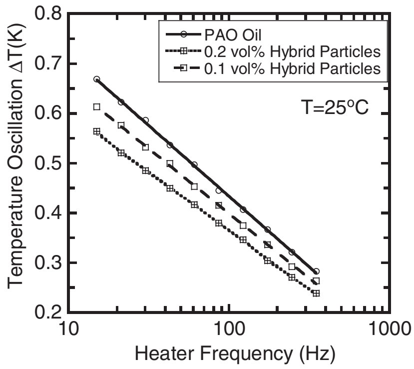

Figure 4. Measured amplitude of the temperature oscillation versus frequency of the electric drive current in the metal wire immersed in poly-alpha-olefin (PAO) with and without hybrid sphere/CNT particles. The test temperature is 25 °C.

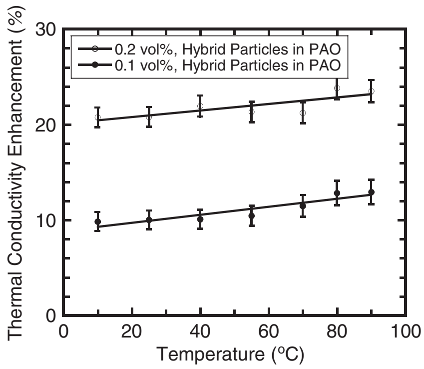

Figure 5. Temperature dependence of the thermal conductivity enhancement in the nanofluids with hybrid sphere/CNT particles at 0.1 and 0.2 vol% concentrations. Thermal conductivity enhancement in the nanofluids is normalized by the thermal conductivity of the base fluids at each specified temperature. Linear fits to the data are shown as a guide to the eye.

The fluid thermal conductivity has been measured with the 3ω-wire method [10, 11, 18]. The 3ω-wire method is a combination of the well developed hot wire method [19] and the 3ω method [20–22]. In the 3ω-wire method, an insulated metal wire is immersed into the liquid sample, acting as both a heater and a thermometer. A sinusoidal current at frequency ω is passed through the metal wire, and then a heat wave at frequency 2ω is generated in the liquid. The 2ω temperature rise of the wire can be deduced by the voltage component at frequency 3ω. The liquid thermal conductivity can be obtained from the slope of the straight lines, because the thermal conductivity of the liquid, k, is inversely proportional to the slope of the 2ω temperature rise of the wire as a function of the driven frequency ω. The test cell is placed inside a circulating thermal bath to control the temperature of the sample nanofluids. Calibration experiments were performed for hydrocarbon (oil), fluorocarbon and water at atmospheric pressure. Literature values were reproduced with an error of $<1\%$.

The raw experimental data in the thermal conductivity measurement for the PAO oils, with and without hybrid sphere/CNT particles, are shown in figure 4. The slope of the 2ω temperature oscillation curves will yield the thermal conductivity of the liquids. The curves representing the nanofluids are less steep, indicating a higher conductivity than that of the pure PAO oil. In the nanofluids with 0.1 and 0.2 vol% nanoparticles, the conductivity enhancement has been measured over a temperature range of 10 to 90 °C and the data are plotted in figure 5. The conductivity enhancement of the nanofluids is normalized to thermal conductivity of the base fluid at each specified temperature. The thermal conductivity of the pure PAO is experimentally found to be 0.1434 W m^{-1} K^{-1} at 25 °C, which is in good agreement with literature data [4]. The hybrid sphere/CNT particles are found to increase the thermal conductivity of PAO by about 21% at room temperature for volume fractions of only 0.2%. The increase in thermal conductivity is reduced approximately by half after the fluid is diluted from volume fractions of 0.2% to 0.1%. It can be also seen in figure 5 that the conductivity enhancement increases with increasing temperature, about 20.5% at 10 °C and 23.6% at 90 °C for 0.2 vol%. It has been reported that the conductivity enhancement in nanofluids increases very rapidly with temperature, approximately going as T^{α} (where $\alpha > 1$), in the moderate temperature range, if the particle Brownian motion plays a dominant role for the enhanced heat transfer in nanofluids [5, 10, 23]. The measured conductivity enhancement of the nanofluids with hybrid nanoparticles, however, shows a weaker temperature dependence—approximately linearly proportional to temperature. This implies that the diffusive heat conduction along the highly conductive CNTs must be primarily responsible for the enhancement in the effective thermal conductivity in the fluids containing hybrid nanoparticles. This is also consistent with the analysis in [10], which suggests that the dominant mechanism in thermal conductivity enhancement in nanofluids strongly depends on the particle aspect ratio, and the effects of the Brownian motion could be predominant for spherical nanoparticle-based nanofluids while the diffusive heat conduction mechanism will gradually take over the dominance as the particle aspect ratio increases. In [10], it was experimentally observed that thermal conductivity enhancement decreases with increasing temperature in nanofluids with Bi3Te2 nanorods.

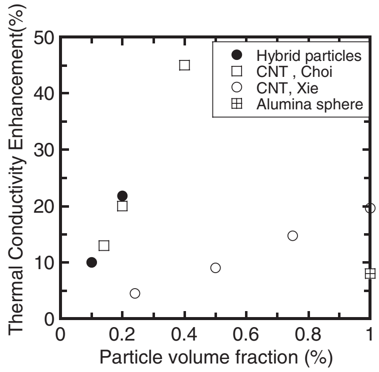

Figure 6. Performance comparison of particles with different morphologies, e.g. spheres, carbon nanotubes (CNTs) and hybrid sphere/CNT particles (urchin-like), in nanofluids. Alumina spheres in water are reported by Masuda *et al* [1], CNTs in PAO by Choi *et al* [4] and CNTs in decene by Xie *et al* [13].

It is interesting to compare the performance of different particle morphologies, e.g. spheres, CNTs and the hybrid sphere/CNT particles, in fluids. Figure 6 lists the values of the enhancement in the effective thermal conductivity for alumina spheres (13 nm diameter) in water, CNTs in PAO, CNTs in decene and our hybrid sphere/CNT particles in PAO. The x axis in figure 6 represents the volume fraction of particles dispersed in the fluids. For nanofluids with the hybrid sphere/CNT particles, the volume fraction includes the contribution from both the centre spheres and the attached CNTs. It can be seen in figure 6 that the hybrid sphere/CNT particles can provide a conductivity enhancement much higher than those for simple spheres, and even slightly higher than those for simple CNTs, when compared at the same volume fraction of particles. It should be noted that mass fraction of CNTs in the hybrid sphere/CNT particles is very small, approximately 3 wt%, while the centre spheres occupy about 97 wt%.

In summary, the hybrid sphere/CNT nanoparticles have been synthesized with a spray pyrolysis method for enhancing thermal transport in heat transfer fluids. Such hybrid nanoparticles are expected to reduce significantly the thermal contact resistance between the CNTs by providing a thermal path through the centre spheres. The hybrid sphere/CNT particles have been shown to increase the thermal conductivity of the PAO oil by about 21% for volume fractions of only 0.2% at room temperature, a much higher enhancement in thermal conductivity as compared to simple spheres at the same particle loadings. The hybrid sphere/CNT particles could also find other applications such as in magnetic fluids and polymer composites.

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