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Synthesis and characterization of cerium oxide based nanofluids: An efficient coolant in heat transport applications

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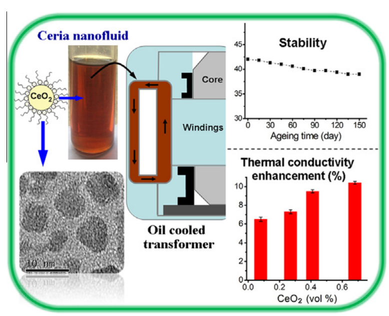
HIGHLIGHTS

- A facile one pot method allows preparation of surface modified ceria nanoparticles.
- The nanoparticles were dispersible in conventional and highly hydrophobic solvents.
- Ceria-oil nanofluids exhibited a long term stability > five months.
- A maximum TC enhancement of 14.6% was achieved with 0.7 vol% nanoparticles.

GRAPHICAL ABSTRACT

A simple one pot method produced surface modified ceria nanoparticles based nanofluids in transformer oil possessing long term stability and appreciable enhancement in thermal conductivity.



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ABSTRACT

Monodispersed oleic acid capped ceria nanoparticles were prepared by a facile one-step strategy involving thermal decomposition of a cerium oleate complex in an organic solvent with high boiling point. The nanocrystals synthesized by this relatively faster and inexpensive route have been optimized and were characterized by X-ray, infrared spectroscopy, dynamic light scattering and transmission electron microscopy. The surface-capped ceria nanoparticles exhibited excellent dispersity in conventional organic solvents and were utilized for the preparation of transformer oil based nanofluids. The suitability of the nanofluids thus obtained as heat transfer fluid was evaluated by measuring the stability of nanofluids, thermal conductivity, viscosity and particle size. The effect of particle loading and temperature on the thermal conductivity of the oil based nanofluids was studied. Oil-based nanofluids containing ceria nanoparticles showed shear-thinning behavior and produced ~14.6% enhancement in thermal conductivity at 50 °C with 0.7 vol% solid loading.

1. Introduction

The idea of overcoming the poor heat transfer properties of conventional coolants such as water, ethylene glycol and transformer oils by dispersing nanoparticulate solids of inherent higher thermal conductivity in it was developed by Dr. Choi of Argonne National Laboratory, US in 1995 [1]. Because of their unprecedented, intriguing properties nanofluids possess potential applications in areas like transportation [2], electronics [3], medical [4], food, and manufacturing of many types [5]. Enormous enhancements in thermal conductivity (TC), long-term suspension stability, and prevention of clogging in microchannels are some among these properties [6]. Nanofluid based heat transport technology is primarily aimed

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at enhancement in thermal properties of fluids and an increase in TC of a heat transferring fluid would eventually result in downsizing the heat transfer systems, lowering of capital costs, and improving the energy conversion efficiencies [7].

Heat transport driven failures are quite often in high voltage power transformers. Dielectric oils in these transformers provide efficient cooling extending its life [8]. These transformer oils require excellent nanoparticle (NP) dispersion, high heat conduction, with simultaneous electrical insulation. Nanofluids with suspension stability for over months are not yet been reported. Philip et al. investigated the temperature dependence of thermal conductivity in non aqueous magnetic nanofluids [9]. Alumina being a insulating ceramic oxide, has a fairly high thermal conductivity (33 $Wm^{-1} k^{-1}$) and has been tested as a candidate in heat transport applications by several researchers [8,10,11]. Choi et al. prepared transformer oil (TO) based nanofluids of Al_2O_3 and AIN by a simple ball milling process [8]. A TC enhancement of 40% in pump oil was reported by Xie et al. with dispersion of 60 nm alumina NPs (5 vol%) where as 1 vol% of 20 nm alumina NPs enhanced the TC of TO by 14% [11]. Stearic acid modified spherical MoS_2 NPs in the size range of 50–100 nm were utilized by Li et al. for preparing oil based nanofluids and reported a TC enhancement of ~18% with 1 wt% NP loading at 40 °C [12]. Motivated by their high inherent TC, metallic NPs such as Cu and Ag were also tested as coolants [13–15]. Xuan et al. observed a 6% enhancement with 100 nm sized Cu NPs in TO and Kole et al. reported ~24% increase in thermal conductivity with 2 vol% Cu NPs dispersed in gear oil [13,14]. However, such nanofluids may cause arcing in high voltage transformer applications. Though most of these oil based nanofluids offer a reasonable enhancement in TC, they lack in the long term stability. In spite of the fact that cerium oxide (commonly called as ceria) NPs have been well explored for applications in areas such as catalysis [16], chemical–mechanical polishing [17], in SOFC's [18,19] etc., limited attempts have been made in fabricating ceria nanofluids [20,21]. A versatile method was developed by Kim et al. for continuous synthesis of surface modified cerium oxide nanoparticles [20]. Unlike metallic counterparts, ceramic (metal oxide) nanoparticles have significantly higher chemical stability over longer periods and are not susceptible to surface oxidation. These promising features together with low electrical conductivity make ceria a suitable candidate in high voltage transformer applications [22].

One of the critical issues which limit the widespread use of nanofluids is its poor stability against sedimentation [23]. In order to reduce their enhanced surface energy due to high surface area to volume ratio, NPs tend to cluster and form extended structures which in turn cause clogging of channels in the heat-transfer systems and a consequent decrease of the thermal conductivity. Steric stabilization with the employment of amphiphilic surfactants on the NP surfaces is the most widely used technique for preparing stable NP dispersions [17,24,25]. Oleic acid (OA) surfactant is well known to effectively stabilize dispersions of various metals, semiconductors, and metal oxide nanocrystals. The presence of a carboxylic group chemisorbed onto the NP surfaces isolates the particles and prevents both grain growth, and later, ripening. The hydrophobic tail of the surfactant extends out of the NP surface into the nonpolar solvents and stabilizes the particles in hydrophobic environments producing stable colloidal suspension [17].

Recent reports suggest that synthesis via an organic route may be preferable to aqueous methods for the preparation of stable nanofluids in apolar solvents, due to the greater control of particle size and polydispersity [26]. Numerous methods such as hydrothermal [27], alcothermal [28,29], thermal decomposition [30], and aqueous precipitation [16,17] have previously been reported for the synthesis of organophilic CeO_2 nanoparticles with good control of size. Among these, hydrothermal and alcothermal methods require high pressure and/or temperature equipment which involves additional costs, safety measures and processing time. Although aqueous precipitation methods are simple, greener and inexpensive, they require multiple processing steps. Solvothermal decomposition of an organic precursor on the other hand is a facile, one step method to synthesize monodispersed nanoparticles with narrow size distribution [26].

Though the fabrication methods of surface modified ceria NPs and their dispersions in few solvents have been well documented, to the best of our knowledge, there is no report in the open literature on the evaluation of oil based CeO_2 fluids for heat transport applications. We report here the synthesis and characterization of a remarkably stable, highly thermo-conductive nanofluids using ceria NPs in transformer oil. Surface modified ceria NPs were prepared by the thermal decomposition of a cerium oleate precursor in diphenyl ether in the presence of oleic acid as the capping agent. Stable oil-based nanofluids with varying ceria content were prepared by dispersing these capped ceria NP's in transformer oil. The corresponding thermal conductivity and rheological tests were performed and the dependence of TC on the concentration and temperature has been evaluated. The nanofluids demonstrated higher thermal conductivity than the basefluid (oil). An attempt is also made to propose the mechanism of thermal conductivity enhancements in the prepared nanofluids.

2. Experimental

2.1. Materials and methods

Cerium nitrate hexahydrate [$Ce(NO_3)_3{\cdot}6H_2O$, 99.9%] was procured from Indian Rare Earth Ltd., India. Oleic acid (90%) and oleyl amine (70%) were supplied by Alfa Aesaer, India and Sigma–Aldrich respectively. Sodium hydroxide, ethanol and cyclohexane were procured from Merck, India and were of analytical reagent grade. All the chemicals utilized in this study were used as received without further purification. Double distilled water was used for preparation of all aqueous solutions. Sodium oleate was prepared by adding NaOH solution (0.0270 mol) drop-wise to oleic acid (0.0270 mol) in a 100 mL beaker. The resultant viscous solution was mixed well by magnetic stirring and sodium oleate was precipitated by adding excess ethanol. The precipitate was filtered and dried at room temperature.

2.2. Preparation of cerium-oleate

Cerium nitrate hexahydrate (24.2 mmol) and Na-oleate (72.6 mmol) were dissolved in a solution consisting of 100 mL ethanol, 100 mL H_2O and 200 mL cyclohexane. The mixture was heated at 80 °C for 4 h and the organic phase was collected and washed three times with 30 mL water. The remaining cyclohexane was evaporated slowly at 80 °C leaving a solid yellow residue as shown in Fig. 1.

2.3. Synthesis of CeO_2 nanocrystals

In a typical synthesis, 24.2 mmol of the freshly synthesized cerium oleate was dissolved in 150 mL diphenyl ether in a round bottom flask. About 72.6 mmol portions each of OA and oleylamine were added to the above RB flask and the reaction mixture was refluxed at ~265 °C for 1–4 h. The product obtained after 1, 2 and 4 h reflux time are denoted as CeDPE1, CeDPE2 and CeDPE4. As the reaction proceeded, the solution became slightly turbid and brown in color. The reaction mixture was cooled naturally to room temperature. To this ~20 mL acetone was added to precipitate the OA coated CeO_2 nanoparticles. The precipitate was washed thoroughly with acetone and was dried. The capped nanoparticles