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Low-cost and high-throughput synthesis of copper nanopowder for nanofluid applications

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HIGHLIGHTS

- Synthesis of highly concentrated (~1.2 M) aqueous copper sol.
- Low-cost production of sodium citrate stabilized re-dispersible copper nanopowder in large scale.
- High-throughput synthesis in a conventional CSTR.
- Formation of stable nanofluids from the Cu nanopowder.

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ABSTRACT

Copper (Cu) is a low cost and efficient filler for nanofluids. However, commercially available copper nanopowders are as costly as silver. A few methods are available for synthesis of copper nanopowder in the lab, but the amount of powder produced per batch is very small, and it is impractical to produce a large volume of nanofluid using these methods. Solution based high concentration synthesis for production of copper nanopowder using batch reactor has been reported in this work. Cost of production is minimal in this method and nanoparticles are separated from the suspension by a controlled flocculation process. The proposed method relies on the higher solubility of cuprammonium complex in an aqueous medium and its chemical reduction using hydrazine hydrate. The colloid has been stabilised using sodium citrate and obtained as sub 50 nm powder re-dispersible in water and ethylene glycol (EG). Continuous synthesis of this product using a Continuous Stirred Tank Reactor (CSTR) has also been demonstrated. The quality of particles from the CSTR is similar to that of the batch method. Stable nanofluids have been prepared by re-dispersing the nanopowder in water and EG. Moderate enhancement (~5%) in thermal conductivity for Cu-EG nanofluids and small enhancement (~2%) for Cu-water nanofluid have been observed with 0.6 vol% of copper loading.

1. Introduction

Heat transfer fluids (HTF) like water, ethylene glycol and engine oils are essential for proper performance of process equipment, automobiles, electronics and power generation systems. However, conventional HTFs show severe limitations in handling large heat flux of modern high-speed devices due to their poor thermal conductivity [1]. Especially in modern optoelectronic devices, heat flux reaches up to 1000 kW/m^2 which is difficult to handle using conventional cooling methods. To deal with such high heat load, scientists are looking for heat transfer fluids with tunable thermo-physical properties.

Thermophysical properties of a fluid can be manipulated by dispersing solid particles into it. Although not beyond debate, significant enhancement in thermal conductivity of a fluid (base fluid) is possible by dispersing highly conducting solids [2–5]. Usually, colloidal particles are used to obtain a stable dispersion. Such dispersions are called nanofluids. Unlike macroscopic slurry, nanofluids do not clog narrow flow channels or do not impart an excessive load on pumping devices. The enhancement in thermal conductivity of nanofluids is strongly influenced by factors such as size [6], shape [7], volume fraction [8] and thermal conductivity [9] of the dispersed particles.

The thermal conductivity of coinage metals, i.e. silver (Ag), gold (Au) and copper (Cu) is significantly superior to other metals and metal oxides. Thus, higher enhancement can be expected in coinage metal nanofluids with lesser loading of solid. As colloids are less stable at higher particle loading, a lower concentration of dispersed phase is always favourable.

The degree of enhancement that can be achieved with coinage metal

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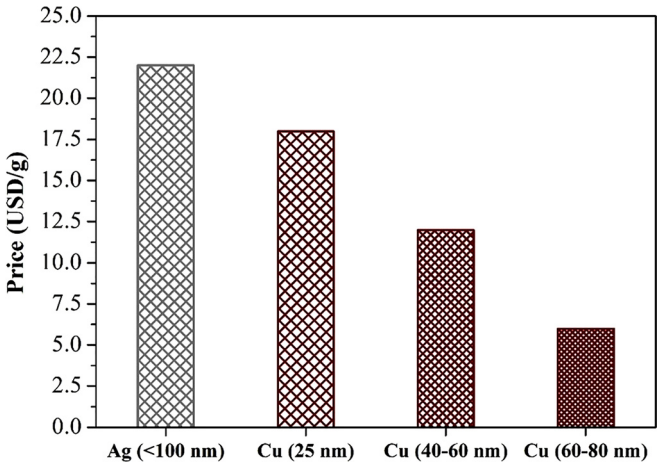

Fig. 1. Price of commercial Cu and Ag nanopowder obtained from an internationally reputed vendor website.

dispersion is not very clear. 3% enhancement in thermal conductivity was reported with 0.001 vol% of silver nanoparticles in water [9]. Similarly, 5% enhancement was reported for 0.00026 vol% gold nanoparticles in water [9]. However, such data has not been substantiated by other workers in this area [10].

Notwithstanding the disparity, reasonable improvement in thermal conductivity can be expected with the low loading of coinage metal nanoparticles. However, silver or gold is too expensive for commercial applications, and the only feasible option is copper. Copper is a cheap engineering material with very high thermal conductivity (k = 400 W/m.K). Almost 40% enhancement in thermal conductivity have been reported with 0.3 vol% of copper in ethylene glycol (EG) [11] and 78% enhancement for 7.5 vol% copper in water [12]. Hence, cheap and highly conductive nanofluids can be prepared by dispersing copper nanoparticles in suitable base fluids.

Although copper is much cheaper than silver and gold, the price of copper nanoparticles is similar to that of silver (Fig. 1). This is possibly due to complicated synthesis method used [13]. To produce small monodispersed copper nanoparticles at a cheap rate, wet chemical methods are needed. Although a number of wet chemical synthesis methods are available (Table 1), the concentration of copper in such method is very less. It can be seen from Table 1, that the Cu concentration is usually below 0.2 M. It is challenging to obtain good amount of powder from such dispersions. Although a few studies have obtained copper colloid with higher concentration (~0.6 M) but production of dry copper nanopowder has not been reported [14,15]. A few recent reports [16,17] concentrate on production of copper nanopowder at gram-scale, but much higher production rate is needed for nanofluid applications. In this study, copper nanoparticles (CuNPs) have been synthesized with highest reported metal concentration (1.2 M) via aqueous chemical reduction route. A high throughput (120 g CuNPs/h) continuous synthesis using a CSTR has also been demonstrated.

For the production of large quantity of nanopowder, separation of particles from the reaction mixture is very important. In this study, copper nanopowder has been successfully extracted from the colloid using controlled flocculation. Finally, the nanopowder has been redispersed in water and ethylene glycol to prepare stable Cu-water and Cu-EG nanofluids respectively. Cu-EG nanofluid has shown significant enhancement in thermal conductivity which is much higher than that predicted by effective medium theory (EMT). For Cu-water nanofluid, enhancement comparable with EMT has been observed.

2. Experimental section

2.1. Materials used

Copper acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 80% solution), trisodium citrate dihydrate ($Na_3C_6H_5O_7{\cdot}2H_2O$), L-ascorbic acid (Vitamin C), polyethylene glycol (PEG 200, MW-200) and ammonia (25% aqueous solution) were purchased from Merck Chemicals, India. Polyvinylpyrrolidone (PVP K30, MW-40000) was bought from SRL Chemicals, India. All chemicals were used as received without further purification. Double distilled water and ethylene glycol (purchased from Merck Chemicals, India) were used as solvent and base fluid.

2.2. Synthesis of copper nanoparticles in batch mode

25 mL of 25% ammonia solution was taken in a 500 mL round bottom flask and 8 mL of double distilled water was added to it. Then 14.37 g of copper acetate monohydrate was dissolved in the aqueous ammonia solution. The solution became royal blue due to the formation of cuprammonium complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Fig. 2a). pH of this solution was 11.5 (PCTestr 35, Eutech Instruments, Singapore). Then 6.18 g of trisodium citrate dihydrate was added to the solution and stirred till complete dissolution (Fig. 2b). pH of the solution reduced slightly after this step (pH = 11). This precursor solution was heated to 60 °C. Then, 17.5 mL of preheated (at 60 °C) hydrazine hydrate solution was added to it (at once) under vigorous stirring, and the stirring continued for additional 20 min (Fig. 2c). At the end of this step, the solution turned dark brown as shown in Fig. 2d.

The synthesis was also conducted at room temperature without preheating the precursors. The synthesis can also be conducted without any stabiliser. In that case, all other steps remain identical, and the citrate addition step was omitted. For producing polymer stabilised particles, PVP K30 and PEG 200 were added in place of trisodium citrate.

2.3. Synthesis of copper nanoparticles in continuous mode

First, the copper precursor solution was prepared in the same way as the batch method and stored in a 2 L round bottom flask. The reducing agent (hydrazine hydrate, 80%) was also stored in a 1 L round bottom

Table 1
Summary of reported methods for synthesis of CuNPs in large scale and high concentration.

Synthesis Method	Product description	Yield	Cu concentration	Batch volume/ throughput	Ref.
Batch mode, wet chemical reduction	Nearly spherical, size = sub 10 nm	~90%	0.6 M	50 mL	[15]
Batch mode, wet chemical reduction	Spherical CuNPs, size ~40 nm	~70%	0.2 M	5 L	[18]
Batch mode, polyol chemical reduction	Uniform spherical CuNPs, size ~135 nm	98%	0.2 M	0.5 L	[19]
Batch mode, wet chemical reduction	Spherical CuNPs, size ~20–80 nm	Not mentioned	0.1 M	100 mL	[20]
Continuous mode, wet chemical reduction	Spherical CuNPs, size = sub 10 nm	Not mentioned	0.01 M	20 mL/min	[16]
Continuous mode, wet chemical reduction	Nearly spherical CuNPs, size = sub 10 nm	~80%	0.04 M	100 mL/min	[17]
Batch and continuous mode, wet chemical reduction	Nearly spherical, size = sub 50 nm (FESEM)	~94%	1.2 M	28 mL/min	Present work