Synthesis and Characterization of Copper-Copper oxide nanofluids in the confinement regime

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ABSTRACT

Copper-copper nanofluids are synthesized by reduction route from sulphate precursors with surfactant, trioctylphosphine oxide (TOPO).The preparation of nanofluid is carried out by reducing copper sulphate with sodium borohydride as reducing agent in deionised water as base fluid. The structural and morphological characterization of sample are done by X-ray diffraction(XRD),Transmission Electron Microscopy (TEM). The average grain size of the particles lies in the range 7-8nm. Optical characterization has been done by UV- VIS spectrophotometer. Absorption spectra while plotted as Tauc curves show different band edges, keeping band to band transition of the bulk metallic nanoparticles. Bigger particles above 10 nm show bulk like behavior contributing to the band gap of 0.8eV while confined particles contribute to the second and most dominant band edge corresponding to a band gap of 3eV. The particles, because of their smaller size, have much higher band gap than that of bulk material. The elemental analysis of copper nanoparticles is determined by EDX.

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Keywords:Copper,Copperoxide,Nanofluid,Optical, morphological

1 INTRODUCTION

Nanofluids grab the attention of the most of the researchers around the globe. This has become a topic of attraction due to its extraordinary performance in various areas including cooling, power generation, defense, nuclear, space, microelectronics and biomedical appliances[1]. Physical properties arising due to electronic band gap, electrical conductivity and resistivity, color or optical transparency, nonlinear absorption or emission, fluorescence, phosphorescence[2] were reported. Some of the special qualities of nanofluids are rise in thermal conductivity beyond exception and much higher than theoretical predictions, ultrafast heat transfer ability. They sustain better stability than other colloids. They are also benefitted for reduction of erosion and clogging in micro channels as well as in pumping power. They can be used for better lubrication.

2 EXPERIMENTAL DETAILS

Nanofluids are colloidal suspension of ultra-fine metallic or nonmetallic particles in base fluids. Despite all other properties, they exhibit physical and chemical properties due to their limited size and high surface area. They produce quantum confinement effects that arise from the presence of discrete, atom –like structures leading to electronic properties of the material. Nanofluids are of two kinds such as metallic nanofluids and nonmetallic nanofluids. Metallic nanofluids are synthesized by dispersing nanoparticle made from metals such as aluminum, copper, nickel etc. and nonmetallic nanofluids are made by dispersing nanoparticles of nonmetals i.e. metal oxides, various allotropes of carbon (Graphene, CNT) etc[3-5].Synthesis and stability of nanofluids are the two very primary requirements to study nanofluids. The proper utilization of the potential of nanofluids depends on the preparation and stability of nanofluids.

The first foot-step to the experimental studies of nanofluids is preparation of nanofluids. Several single step methods have been arrived for nanofluid preparation. A single-step direct evaporation method developed by Akoh et al. [6]. This process is familiar as VEROS (Vacuum Evaporation onto a Running Oil Substrate).But it was tedious to separate nanoparticles form fluids. Eastman et al. [7] proposed a modified VEROS technique, in which Cu vapor is directly condensed into nanoparticles by contact with flowing low vapor-pressure ethylene glycol. Zhu et al.[8] introduced a single-step chemical process for the preparation of Cu nanofluids by reducing $CuSO_4$.$5H_2O$ with NaH_2PO_2 .H_2O in ethylene glycol under microwave irradiation. This method also proved a good way to produce mineral oil based silver nanofluids. Lo et al. [9] reported vacuum based submerged arc nanoparticle synthesis to prepare CuO, Cu_2O and Cu based nanofluids with different dielectric liquids.

Here we report, synthesis of Cu-CuO nanofluids by chemical reduction method using sodium borohydride as reducing agent and Lewis base, trioctylphophine oxide(TOPO) used as a solvent and passivating ligand. In this, $NaBH_4$(1M) and $CuSO_4.5H_2O$ solution(0.5M) are mixed in a magnetic stirrer for 30 minutes at room temperature. A black precipitate has been formed. The

reaction mixture is then stirred for 30min to ensure complete reaction. The precipitate is then dissolved in the surfactant using TOPO (3mL) inorder to obtain fully dispersed and stabilized nanofluid. The precursors used are of analytical grade with purity greater than 96%. The synthesized particles are then sonicated for homogenization.

2.1 Experimental techniques

The prepared copper copper oxide nanofluid was characterized by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDXA), transmission electron microscopy (TEM), UV-VIS spectroscopy.

The nanofluid was diluted by centrifuging for one hour. The separated Cu-Cu_2O nanoparticles were then given repeated washes with water and the particles were dried at 80 °C. XRD patterns of the nanoparticles were taken on a X-RayDiffraction, Rigaku Miniflex diffractometer, using Cu Kα (λ=1.5404 A^0) radiation.

The TEM images of the nanofluids were recorded on a LIBRA 200 TEM (M/s Carl Zeiss, Germany) operating with an accelerating voltage of 200 kV with a resolution of 2.4 Å. The samples for TEM were prepared by sonicating the nanofluid and later placing it on carbon-coated copper grid for analysis. The EDXA was carried out on Hitachi SU6600 Variable Pressure Field Emission Scanning Electron Microscope (FESEM). The obtained micrograph is then examined for the particle size and shape.

Absorption spectra are determined using UV-VIS spectroscopy (PG-T80+UV VIS spectrophotometer). It shows the quantum confinement effects at nanoregime.

3 RESULTS AND DISCUSSIONS

The peaks apparent in the Fig. 1 indicate good crystallinity of the copper copper oxide nanoparticles, characteristics peaks of phase of Cu-Cu_2O were observed. X-ray diffraction studies confirmed that the synthesized materials agreed according to the literature JCPDS data[10]. The average crystal size is 7-8 nm which is calculated using Debye–Scherrer formula. As shown in Figure 3 the ratio of Cu and Cu_2O-NPs in the sample is 85% and 15%, respectively.

The XRD pattern of Cu-Cu_2ONPs is in the angle range of 2θ (30–100) indicated the formation of the intercalated Cu@Cu_2O nanostructure The peak values are located at 50.32° and 74.07°(Figure1), which correspond to the miller indices (200) and (220), respectively and represent face centered cubic (fcc) crystal structure of Cu-NPs [11]. The diffraction angles observed at 36.23°, 61.24° and 74.07° (Figure 1) are relevant to Cu_2O.

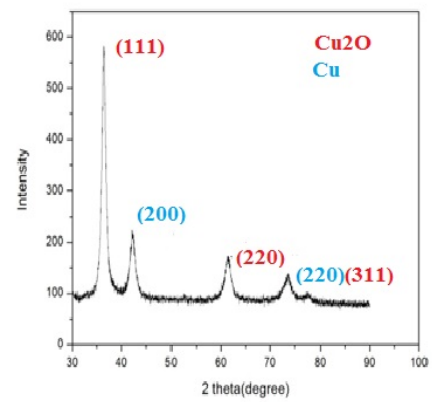

Figure1.The powder X-Ray Diffraction of Copper copper oxide Nanoparticle

Chemical reduction of aqueous solution of copper sulphate for the formation of Cu-Cu_2O nanofluids was investigated. In order to examine size and shape controlled nanoparticles in aqueous suspensions, the reaction mixtures were characterized by UV-visible spectroscopy (Figure2). The increase in intensity of light over the time indicates the completion of the reaction in the sample. Absorption spectra of nanofluids formed in the reaction media have absorbance peaks at about 300 ,370 and 510nm might be assigned to the step like characteristics of copper nanoparticles above 650nm due to quantum confinement at nanoregime [12,13,14].

The spectra were plotted as Tauc curves in which different band edges were depicted shown in figure 3.The absorption edges corresponds to1.14eV and 2.44 eV. These are due to the narrow size distribution of the particles in which confined particles below 10nm contribute to band edge corresponding to a band gap of 3eV. NP's with narrow size distribution show narrow absorbance and that of broad size distribution shows broad absorbance [15,16,17]. As the particle size decreases, the band gap of the material decreases leading to blue shift region.

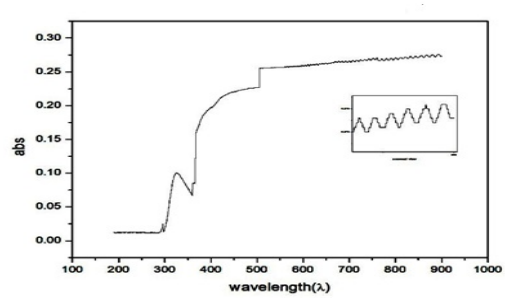

Figure 2: Absorption Spectra of nanofluids

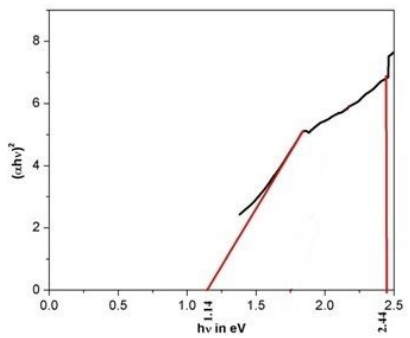

Figure3: Band gap analysis of Nanofluids

Figure 4a,4b,4c demonstrates the TEM images and size distribution Cu@Cu2O-NPs dipersed in base fluid. The TEM images and their size distributions showed that the mean diameters of Cu@Cu2O-NPs were about 7-8 nm. The number of Cu@Cu2O-NPs counted in the TEM images was around 8 nm. In addition, the TEM image clearly shows the core-shell structure of produced nanoparticles.

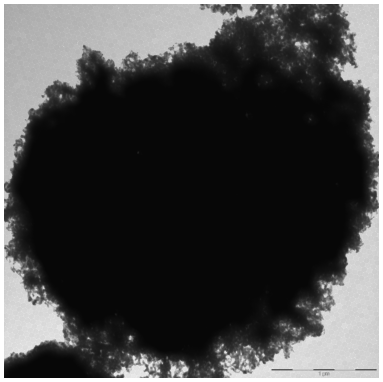

Figure 4a) TEM image of nanofluid showing scale of 1µm

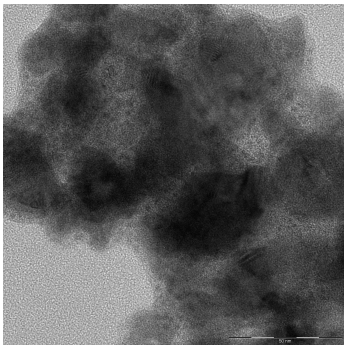

Figure 4b) TEM image of nanofluid showing scale of 50nm.

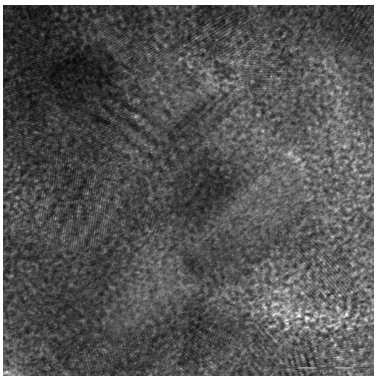

Figure 4c) TEM image of nanofluid showing scale of 10nm.

The chemical composition and purity of the products were also examined using EDXA. The EDX spectrum revealed copper as the only detectable element, indicating that the sample is without any contamination.(figure 5)

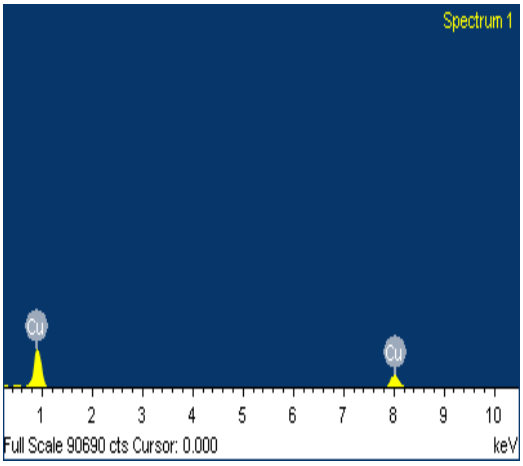

Figure 5) EDX of copper nanoparticle

CONCLUSION

Copper –copper oxide nanofluids are synthesized by reduction route method using trioctylphophine oxide(TOPO) as surfactant. The formation of nanoparticles are analyzed using XRD,TEM,UV-VIS spectroscopy and EDX.The chemical route addressed here for the present work of nanofluids are cost –effective and eco-friendly. The particles are stable and reproducible for biomedical applications.

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