

INVESTIGATIONS ON SYNTHESIS, STRUCTURAL, SURFACE MORPHOLOGICAL, OPTICAL, AND THERMAL PROPERTIES OF COPPER OXIDE NANOFLUIDS

by

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The copper oxide nanofluids were synthesized using a wet chemical technique. The crystal structure and the average grain size of the copper oxide nanofluids were determined by X-ray diffraction pattern. The strong presence of copper oxide was confirmed by the Fourier transform infrared spectroscopy spectrum. The morphology and the particle size were studied using the scanning electron microscope and transmission electron microscopy. Energy dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample. Dynamic light scattering was used to estimate the size of the copper oxide nanofluids. The UV-visible absorption spectrum was used to measure the optical property of the copper oxide nanofluids. The thermal conductivity of the copper oxide nanofluids was analyzed as well.

Key words: *copper oxide nanofluids, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV-visible spectrum, thermal conductivity*

Introduction

Nanotechnology is one of the promising areas to be studied and has much to offer to the world of research and development. It has drawn the attention of researchers and academicians round the globe. Nanofluids are considered to be an alternate and lately invented liquid for transport of heat energy and can be engaged as heat transfer fluids in heat exchangers in place of pure single phase fluids. The applications of nanofluid heat transfer incorporate radiators in automobiles, chemical engineering and process industries, solar water heater, refrigeration, cooling of electronics devices, *etc.* Nanofluids are a latest category of heat transfer fluids containing nanosized particles, fibers, or tubes that are stably suspended in a carrier liquid and find potential applications related with heat transfer, mass transfer, wetting, and spreading [1-6]. In general, the conventional base fluids which are typically used in cooling are not enough to keep pace with the development and to meet the requirements in these fields, particularly in electronic chip and computing technologies. Intensive research on nanofluids was activated using various types of nanoparticles. As the particle size decreases, the surface area increases. This

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property increases the heat transfer ability of the nanoparticles which in turn improves the thermal conductivity of nanofluids. Copper oxide (CuO) nanoparticles have involved increasing interests due to both fundamental and practical reasons. It belongs to monoclinic crystal system where the copper atom is co-ordinated by four oxygen atoms in a near square planar configuration. The CuO is a semiconducting compound with a narrow band gap and is used for photoconductive and photothermal applications [7]. The CuO nanoparticles are industrially important material that was used in applications such as gas sensors, magnetic storage media, solar energy transformation, photovoltaic cells, catalysis, and antimicrobial agent [8-14]. Dispersion method is a two-step method, in which commercial nanoparticles are dispersed into base fluid under ultrasonic agitation or mechanical stirring [15-17]. The improvement of this method is that it could be used to prepare nanofluids in a large scale. However, nanoparticle aggregations are not easy to breakup under ultrasonication or stirring. These physical methods give excellent control on the particle size and can create stable nanofluids. This method is a capable and suitable technique for commercial synthesis of nanofluids. In this study, CuO nanofluid was synthesized with a wet chemical method. The prepared CuO nanofluids were characterized by powder X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), transmission electron microscope (TEM), dynamic light scattering (DLS), and UV-analysis. The thermal conductivity of CuO nanofluids was also studied.

Experimental procedure

All chemicals used in the experiment were of analytic reagent grade. In a usual procedure, 0.2 M copper acetate solution and 2 ml glacial acetic acid were added into a round-bottomed flask and heated to boiling under magnetic stirring. After that, 8 M sodium hydroxide solution was added into the flask. The color of the solution turned from blue to black instantly, and a black suspension formed simultaneously. The reaction was carried out under stirring and boiling for two hours. The mixture was cooled to room temperature and centrifuged. Finally, a wet CuO precipitate was obtained. The wet precipitate was washed twice with distilled water to remove the impurity ions. Normally agglomeration of nanoparticles takes place when nanoparticles are suspended in the base fluid. The CuO nanofluids used subsequently for the estimation of their properties were subjected to magnetic stirring process followed by ultrasonic vibration for about five hours. The CuO nanofluids prepared were kept for observation and no particle settlement was observed at the bottom of the flask containing CuO nanofluids even after four hours.

Characterization techniques

The crystallite size and the structure of the powder were analyzed by XRD using a powder X-ray diffractometer (Schimadzu model: XRD 6000 and $\text{CuK}\alpha$ ($\lambda = 0.154$ nm)) with a diffraction angle between 20 and 80°. The FTIR spectrum was taken using an FTIR model Bruker IFS 66W spectrometer with KBr pellets. The surface morphology of the powder was observed by a SEM using JEOL; JSM- 67001. The TEM image was taken using an H-800 TEM (Hitachi, Japan) with an accelerating voltage of 100 kV. The particle size of the CuO nanofluids was analyzed using the DLS experiment. The UV-Visible absorption spectrum for the CuO nanofluids was recorded using a Varian Cary 5E spectrophotometer in the range of 300-800 nm. For the measurement of thermal conductivity, KD2 Pro was used.

Results and discussion

The XRD is used as a primary tool to characterize the crystal structure and crystallite size of the nanoparticles. Structural identification of CuO nanofluids was done using XRD in the range of an-

gle 2θ between 20° and 80° as shown in fig. 1. All the peaks were clearly indexed to a monoclinic structure of CuO. The broadened peak showed the nanometer-sized crystallites. All peaks obtained by XRD analysis were assigned by comparison with data from the Joint Committee on powder Diffraction Standards. The average grain size was obtained from the most intense peak, corresponding to (111) reflection using the Scherrer formula. The average grain size was calculated from X-ray line broadening using Scherrer equation and it was found to be about 11 nm.

The FTIR spectroscopy finds extensive use in the study of the nature of surface adsorbents in nanoparticles. Because of their large surface area, the modification of the surface of the nanoparticles by a suitable adsorbate can generate different properties. The high surface to volume ratio influences the activity at the surface of the nanoparticles, which differentiates it from that of the bulk. The study of the oxidation levels of nanoparticles prepared at different partial oxygen pressures could be made from the FTIR data. In order to determine the chemical structure of the CuO nanofluids, the FTIR spectrum was observed over the frequency range of $4000\text{--}500\text{ cm}^{-1}$, as shown in fig. 2. The spectrum has absorption bands at about 3400 cm^{-1} and 1622 cm^{-1} were due to the stretching and bending vibrations of --OH group. In the region 552 cm^{-1} the signature band of CuO vibration was observed.

The SEM provided further approaching into the morphology and size details of the nanoparticles. The surface morphology of the prepared CuO nanofluids was revealed through the SEM image as shown in fig. 3. It provides the clear evidence of spherical shaped particles and their uniform dispersion. The average crystallite size was found to be in the range of $\sim 9\text{--}11\text{ nm}$, which is in good agreement with the XRD analysis.

The EDX spectroscopy showed the presence of copper and oxygen in the synthesized CuO nanofluids by the distinct peaks as observed in the EDX spectrum shown in fig. 4.

The TEM micrographs also demonstrated that the formed nanoparticles were homogeneous, with no significant phase separations or coatings on the surface. The TEM images of the CuO nanofluids are shown in fig. 5. The particle

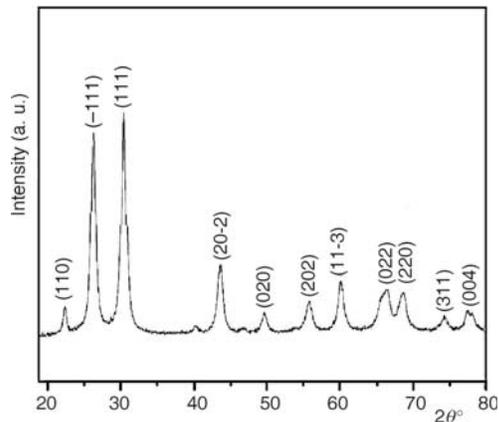


Figure 1. The XRD pattern of CuO nanofluids

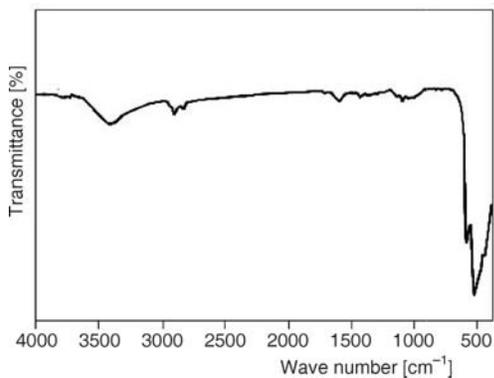


Figure 2. The FTIR spectrum of CuO nanofluid

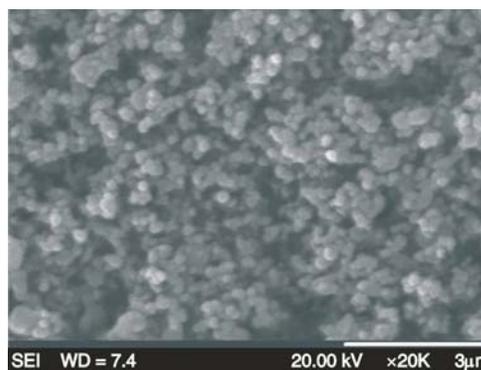


Figure 3. The SEM image of CuO nanofluids

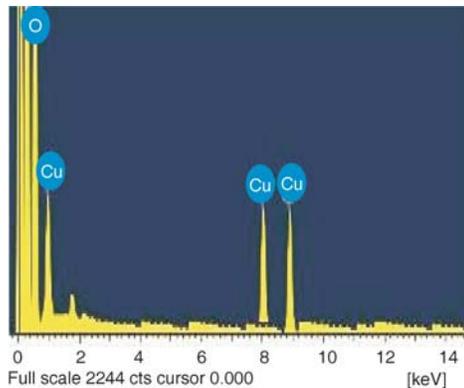


Figure 4. The EDX spectrum of CuO nanofluids

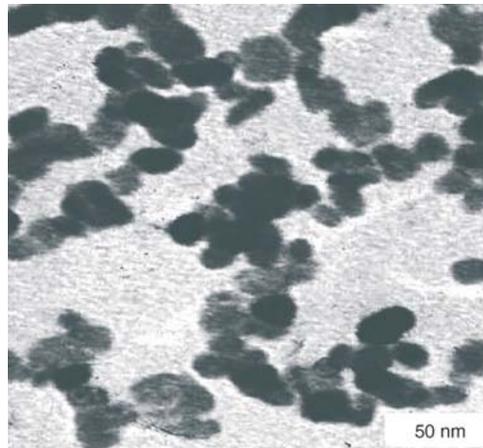


Figure 5. The TEM image of CuO nanofluids

size-distributions for CuO nanofluids were estimated from TEM image. It is clear from the flexural chains that the grains are segregated together to form large sized agglomerates. It can be seen that the particle size distribution is in the range 30-50 nm. The average particle size was found to be 50 nm.

The DLS is a valuable tool for determining and measuring the agglomeration state of the nanoparticles as a function of time or suspending solution. Figure 6 shows the graphical representation of average particle size distribution of CuO nanofluids. They were in a range of 20-140 nm. However, beyond 100 nm range the percentage of CuO nanofluids present was very less. The highest fraction of CuO nanofluids present in the solution was found to be 53 nm. From the plot it was evident that the CuO nanofluids had various sizes which were indeed in quite agreement with the result obtained by TEM analysis.

To investigate the optical properties of CuO nanofluids the UV-visible absorption spectrum was analyzed. Figure 7 shows the UV-visible absorption spectrum of the prepared

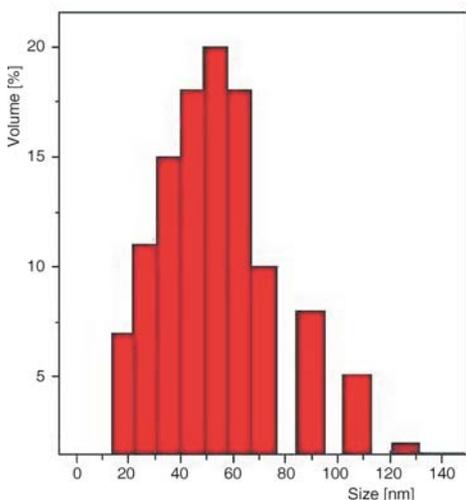


Figure 6. Particle size distribution of CuO nanofluids

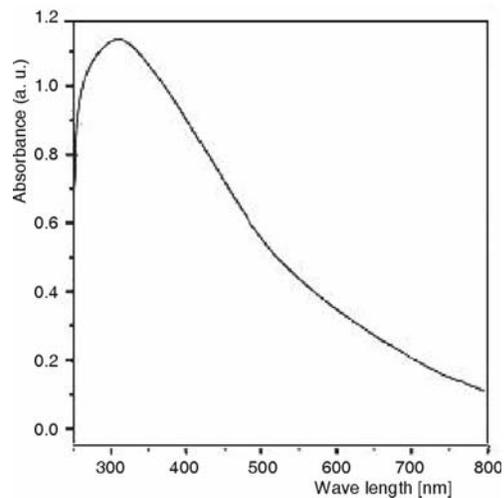


Figure 7. The UV-visible absorption spectrum of CuO nanofluids

CuO nanofluids. The prepared nanofluid begins to agglutinate and sediment for being saturated, thus leading to the low suspension dispersion. The absorption spectrum showed a strong absorption peak located at ~ 350 nm (3.2 eV). It is well known that if the size of CuO particle decreases, the width of the band gap increases and the optical absorption shows a blue shift. From that, the indication of blue shift in the absorption spectrum corresponds to a quantum confinement effect arising with the decreasing particle size [18]. As a result, the absorbance value is reduced.

Nanofluids are expected to demonstrate superior heat transfer properties compared with the conventional heat transfer fluids. One of the expectations is that the suspended particles extremely increase the thermal conductivity of nanofluids. It is known that the thermal conductivity of nanofluid is strongly dependent on the volume fraction dimensions and properties of nanoparticles. Figure 8 shows the thermal conductivity ratio of the CuO nanofluids. It can be observed that the thermal conductivity ratio increases as the particle volume fraction increases, this agrees well with the reported results [19, 20]. The present results definitely confirm the important role of agglomeration on thermal properties of nanofluids and the importance of surface functionalization of nanoparticles for improved stability.

Conclusion

A wet chemical method was used to prepare stable CuO nanofluids. The formation of CuO nanofluids was confirmed by XRD. The average crystallite size CuO nanofluids was found to be 11 nm. From the FTIR analysis of the synthesized nanofluids the structure of the CuO nanofluids was ascertained. The SEM revealed the morphology in the synthesized samples showing that CuO nanofluids were spherical in shape. The chemical composition was studied by EDX and this showed the presence of copper and oxygen. The particle size of the CuO nanofluids was estimated using TEM and it was found to be 53 nm from the results of the DLS experiment and it was in good agreement with the TEM analysis. Optical properties of the CuO nanofluids were investigated by means of UV-visible absorption spectrum. The thermal conductivity of the CuO nanofluids increased with the increase of particle loading.

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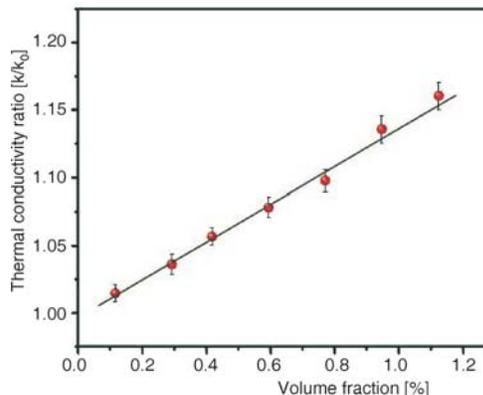


Figure 8. Thermal conductivity ratio as a function of CuO volume fraction

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