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Preparation of metal oxide nanoparticles of different sizes and morphologies, their characterization using small angle X-ray scattering and study of thermal properties

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HIGHLIGHTS

- Fe_3O_4 and CuO nanoparticles of different sizes and morphologies were prepared.
- The morphological evaluation was done using Small Angle X-ray Scattering (SAXS).
- Thermal conductivity (k) of Fe_3O_4 nanofluids follows effective medium theory (EMT).
- CuO nanorod based dispersions show a k enhancement beyond the EMT.
- Abnormal k in CuO is due to the effective conduction of heat through nanorods.

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ABSTRACT

In an effort to shed light into the role of surface morphology of nanoparticles on their thermal properties, we have prepared Fe_3O_4 and CuO nanoparticles of different sizes and morphologies using co-precipitation and precipitation approach, respectively. The prepared particles are characterized using Small Angle X-ray Scattering (SAXS) and the results are compared with X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Dynamic Light Scattering (DLS). The results show that the size distribution and surface morphologies of nanoparticles can be quite accurately measured by using SAXS with the aid of appropriate models. The thermal conductivity of spherical Fe_3O_4 nanofluids follows effective medium theory whereas the CuO nanorod based dispersions show a much larger thermal conductivity beyond the effective medium theory. The abnormal thermal conductivity in CuO is attributed to effective conduction of heat through nanorods of higher aspect ratio. These finding are useful for engineering efficient nanofluids for thermal management.

1. Introduction

One of the most widely used direct techniques for particle size and morphology analysis is Transmission Electron Microscope (TEM). The main advantage of TEM is that it provides direct imaging of particles over a small area. The potential error associated with TEM is large because only a very small area is examined at any time and the analysis is often restricted to a limited number of particles. The main disadvantage is that it requires cumbersome sample preparation methodologies to obtain well dispersed particles on a grid, without overlapping. The determination of primary particle size distributions from aggregated mass-fractal structures is also challenging. Further, it is a subjective approach and requires image/data processing to obtain the distribution statistics. Also, a dedicated high resolution TEM is required to obtain insight into the surface morphologies of extremely fine nanoparticles. On the contrary, Dynamic Light Scattering (DLS) is a relatively inexpensive approach in which the time-dependent fluctuations of the scattered coherent light by diffusive motion of the particles is measured from the decay of autocorrelation function, which is related to the diffusion coefficient of the material. It requires well dispersed and stable nanoparticles in a base fluid for reliable measurements and is temperature and concentration dependent. However, the preparation of stable dispersion of nanoparticles is again a challenging task, especially when particle size is large and is not functionalized.

X-Ray Diffraction (XRD) and Small Angle X-ray Scattering (SAXS) are indirect techniques for the crystallite size measurement. In XRD, the crystallite size of nanoparticles are obtained from the X-

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ray diffraction line broadening using Scherrer equation, where small scale inhomogeneity of the sample does not influence the measurement to the extent as they do in the TEM study. The XRD peak intensity decreases drastically when the grain size is below 4 nm, thereby giving rise to a broad and poorly resolved peak. In such cases, the measurement of full width half maxima (FWHM) becomes difficult and erroneous. In XRD, errors can also originate from the deconvolution of peak broadening due to instrument microstrain and crystalline domain size [1,2].

SAXS is an alternate tool to probe the size distributions by measuring the scattered intensity over a wide range of scattering vector [3–7]. It enables the measurement of size distribution of particles and the morphology of nanoparticles dispersed in a solvent or in a bulk film either using transmission or reflection geometry. SAXS and DLS provide volume averaged particle size but TEM gives the number distribution. Though the onset of aggregation can be detected both by DLS and SAXS, the former is prone to uncertainties due to dust contamination but the latter is not. From SAXS, the structural information on inhomogeneities of the electron density of nanofluids is obtained. SAXS offers advantages over the other techniques because it is a fast non-destructive technique and can cover samples a wide range of particle size 1–100 nm. Though, SAXS does not give the size and morphology information directly, using appropriate model it is possible to determine nanoparticle morphologies quite accurately. As a results of a focused and systematic research on both theoretical and experiment fronts, SAXS has been proved to be an ideal technique for nanoscale structure estimation [6–19]. SAXS has been successfully used to determine the micellar size, morphologies of polymers and many other soft matters [20–23].

With rapid advances in nanotechnology, the demand for nanomaterials with controlled size and morphology is growing every day [24,25]. Nanomaterials exhibit interesting optical, electrical, mechanical, magnetic and thermodynamic properties that are size dependent [26,27]. The quest for efficient cooling materials led to the emergence of a new class of materials called nanofluid [28–33]. Nanofluids have been a topic of interest primarily due to the initial reports of anomalous thermal conductivity enhancement [28,34]. However, several recent studies in stable nanofluids show enhancement within Maxwell's limits [29,35,36]. The reasons for the reported anomalous enhancement in thermal conductivity in nanofluids are still a topic of debate [37,38]. One of the most probable aspects considered in recent years for the enhanced thermal conductivity of nanofluids is the effective conduction of heat through percolating aggregating nanoparticle paths [33,39]. Also, the role of micro-nano convection is still debated, though many studies rule out this possibility [40]. For best results, the nanoparticles employed for various applications should have a minimum polydispersity to effectively reap the benefits of their high surface to volume ratio. Therefore, a knowledge about the size, morphology and distribution of nanoparticles is a prerequisite better understanding and also for practical applications. Lack of understanding of surface morphologies of nanoparticles in base fluids have led to several premature conclusions and controversies.

In an effort to evaluate the accuracy in the size and morphological results using SAXS and to probe the effect of morphology on thermal properties, we have prepared Fe_3O_4 and CuO nanoparticles of different morphologies in the range of 2.5–12 nm using co-precipitation and precipitation approach, respectively and are characterized them using SAXS, XRD, TEM, DLS and compared the results obtained from different methods. These two systems have been chosen because both CuO and Fe_3O_4 have been a topic of intense research due to their interesting physical properties [28,30,31,41–44]. Finally, to understand the role of surface morphologies of nanoparticles on heat transfer efficiency, thermal conductivity of spherical and rod like nanofluids have been carried out and the results are compared.

2. Experimental method

2.1. Synthesis of Fe_3O_4 nanoparticles

Ferric Chloride ($FeCl_3$, $6H_2O$), Ferrous Sulfate ($FeSO_4$, $7H_2O$), Cu-acetate dehydrate, Acetic Acid, 30% NH_4OH used in our experiments were GR grade with 99% purity and were used without any further purification. Elga water of 15 MΩ cm is used in all our experiments. Several approaches are available for the synthesis of uniform size and shape Fe_3O_4 nanoparticles [45]. For the present study, we have synthesized by co-precipitation method [46]. The iron salts used are freshly prepared with 0.8 M $FeCl_3 \cdot 6H_2O$ and 0.4 M $FeSO_4$, $7H_2O$ in an acidic medium of HCl and H_2SO_4, respectively. The iron salt solution was mixed at 1:1 ratio and stirred at 600 rpm. During this stirring, the solution pH was increased rapidly by the addition of ammonium hydroxide and at a constant temperature of 70 °C. At a pH of 10, the solution turned black, indicating the formation of magnetite nanoparticle. The precipitated nanoparticles are washed and dried in a vacuum oven. By changing solvent polarity and temperature, particles of average crystallite sizes were tuned from 2.5 to 12 nm.

2.2. Synthesis of CuO nanoparticles

For synthesis of spherical CuO (hereafter referred as B1) nanoparticle, Cu $(CH_3COO)_2 \cdot 2H_2O$, CH_3COOH, and solid NaOH were used. A simple precipitation approach is used for the synthesis [47,48]. 500 ml of 0.2 M Cu-acetate solution was mixed with 2 ml glacial acetic acid in a round bottom flask. Under vigorous stirring, 0.14 gm of solid NaOH was added in the boiling solution at 100 °C until the pH value of the mixture attain a value of 6–7. After the addition of NaOH, the color of the solution changed from blue to black. The black precipitates were sediment. After cooling the sample to the room temperature, the precipitate was centrifuged and washed with distilled water, ethanol, and finally dried in a vacuum oven at room temperature.

The rod shaped nanoparticles (hereafter referred as B2 and B3) were synthesized from Cu $(NO_3)_2$, $3H_2O$ with slow addition of 40 ml of NaOH (0.5 M in pure ethanol) under stirring at 80 °C with a rate of 0.1 ml min^{-1} [48]. After this step, 40 ml of water was added at a rate of 0.2 ml min^{-1}. The product solution was aged together with the mother solution at the same temperature for 6–10 h to obtain particles of different sizes.

2.3. Characterization of nanoparticles

The hydrodynamic size distribution of nanoparticles was determined by dynamic light scattering using a Zetasizer-Nano (Malvern Instrument) for both nanoparticles. A Tecnai F30 instrument with an acceleration voltage of 200 kV was used to record TEM images. The samples were prepared by slowly evaporating a drop of nanoparticle suspension in acetone on amorphous carbon-coated copper grids at room temperature. The samples were characterized by X-ray diffraction using Rigaku Ultima IV X-ray diffractometer. The Small Angle X-ray Scattering (SAXS) studies were carried out using Rigaku Ultima IV instrument. It uses Cu K_α ($\lambda = 1.5418$ Å) as X-ray source. The scattering intensity $I(q)$ was measured as a function of the scattering vector ($q = 4\pi \sin\theta/\lambda$). The samples are scanned in the q range of 0.007–0.156 Å. The background subtracted data was fitted with an appropriate model to determine the particle size and polydispersity [49].