

Study of Structural and Thermo-Acoustic Properties of Cds-Ethylene Glycol Nanocluster

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Abstract – Here, CdS nanoclusters have been synthesized using a chemical route. Structural and morphological analyses have been done using x-ray diffraction (XRD) and transmission electron microscopy (TEM). Synthesized nanoclusters are used to prepare the CdS - ethylene glycol nanofluids, at three different concentrations of CdS (viz 0.2 vol%, 0.6 vol% and 1.0 vol%), using ultrasonication method. Size distribution profile of the suspended particles is analysed by an acoustical particle sizer (APS-100), based on the ultrasonic spectroscopic technique. The crystallite size obtained from XRD is compared with the particle size estimated from the TEM and APS -100 techniques and a proper rationale is provided for the differences in measurements. Frequency-dependent ultrasonic attenuations at different concentrations of dispersed nanoparticles in the nanofluids have been measured by APS-100. The ultrasonic wave exhibits a nonlinear increase in ultrasonic attenuation with frequency in all the samples of nanofluids. The analysis of the observed results enables us to understand the interaction of the ultrasonic wave with the suspended nanoparticle in the nanofluids system.

Keywords – Acoustical Particle Sizer, Nanofluids, Nanoclusters Ultrasonic Attenuation

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1. INTRODUCTION

Nanofluids are nothing but engineered colloidal suspension of the nanosized particles in a base fluid [1]. Nanoparticles have at least one of their characteristic dimensions in the range of 1 to 100 nm. Due to their large surface to volume ratio, they show excellent characteristics compared to their bulk counterpart [2]. Among the various type of nanostructured materials, nanoclusters having dimensions between 1 and 10 nm have attracted research communities due to their exceptional properties resulting from the 'quantum size effect' [3-4]. Nowadays, nanoclusters are extensively used in various advanced industries like microelectronics, electroluminescent displays, optical data storage, sensors, magnetic materials and biological markers for photodynamic therapy [5-7]. When these types of nanostructured materials are dispersed in a base fluid, they also enhance the properties of the fluid significantly [8].

Nanofluids are widely used in the efficient cooling technology as they exhibit an enhanced rate of heat transfer compared to conventional heat transfer fluids such as water, engine oil, ethylene glycol and glycerol [9]. As suspended nanosized particles provide more surface area for the transfer of heat, the thermal conductivity of the nanofluids increases

significantly [8-9]. Other thermophysical properties such as thermal diffusivity and viscosity also get increase due to above mechanism [10]. A comprehensive analysis of the nanofluids for various types of heat transfer systems is a prerequisite for understanding the movement of the suspended particles. Inter-particle interaction within the nanofluid can be better analysed with the help of sound wave propagation in the medium. Ultrasonic offers a non-destructive method to investigate the fluid-particle interaction within the system without modifying the basic characteristics of the medium [11-13]. Ultrasonic study provides important information about the system such as thermal relaxation time, specific heat, energy density, etc. [14]. Ultrasonic attenuation and velocity are the most important thermoacoustic properties for the liquid particle suspension to understand the particle fluid interactions [15-17]. Thus, in the present analysis, we have prepared the CdS nanoparticle/nanocluster via chemical route and three samples of nanofluids with the help of ethylene glycol. The acoustical spectroscopic method has been used to study the size distribution of the suspended particles in the base fluid. Frequency and concentration dependent ultrasonic attenuations in the nanofluids are measured and analyzed.

2. MATERIALS AND METHODS

2.1 Synthesis

A clear uniform aqueous solutions of 0.1 M Cd (CH_3COOH) $_2$. $2\text{H}_2\text{O}$ and 0.1 M sodium sulfide were prepared at room temperature. The prepared Na_2S solution was added drop by drop to cadmium acetate solution at 67°C under continuous stirring. This results in a soft yellow colored solution which is stirred and heated for 6 h at 60°C and then the solution set to rest for the next 24 hours. The precipitate was centrifuged and washed several times with doubly distilled water. The precipitate was incubated for 6 h at 800°C and after grinding it we get a finely powdered sample of CdS nanoclusters. The synthesized CdS nanoclusters were dispersed in ethylene glycol with help of a probe sonicator (Sonic Vibracell) [Model-VC-505] for 30 minutes. We have prepared three samples of CdS-ethylene glycol nanofluids at concentrations of 0.2 vol %, 0.6 vol %, and 1.0 vol % of nanoclusters. Pure ethylene glycol was used as a base fluid for the preparation of nanofluids.

2.2 Characterization

The structural investigation was done using XRD diffractograms which were recorded by RigakuD/max-2200PC diffractometer using $\text{CuK}\alpha_1$ radiation with the wavelength 1.54 \AA in wide-angle range, operated at 40 kV/20 mA. To calculate the crystallite size of the sample, XRD patterns were used. TEM micrograph is used to investigate structural and morphological properties of pure and Nanofluid samples, this characterization is done using Philips CM200 transmission electron microscope at 20–200 kV operating voltage.

2.3 Measurement techniques

After the suspension of CdS NPs in ethylene glycol, the particle size distribution (PSD) is analysed using an acoustical particle sizer (APS-100; Matec Applied Sciences). Frequency-dependent ultrasonic attenuations in the prepared nanofluids at different concentrations are also measured with APS-100. APS-100 is based on the ultrasonic spectroscopic technique. Using this technique, ultrasonic waves of frequencies ranging from 1-100 MHz are allowed to travel through the colloidal suspension and amplitude of attenuation, at each frequency, is measured at various places of the medium. The degree of attenuation is related to particle size distribution. By summation over the ensemble of particle sizes, the ultrasonic attenuation/absorption linked with PSD can be determined, thus by enabling data inversion these attenuation spectra data are converted into PSD successfully using a software based on Carhart and Epstein theory [18]. Here, a specially designed reflector is used to measure the velocity and echo amplitude of the ultrasonic wave and compare the transmitted and reflected waves. To achieve high

accuracy, the APS practices optimal signal averaging via several repetitive measurements [19].

3. RESULTS AND DISCUSSION

Figure 1 shows the X-Ray diffraction pattern of synthesized CdS nanoclusters which have no impurity peaks. The XRD peaks are in perfect agreement with the cubic phase of CdS having JCPDS file No. 100454. Peak positions are found at $2\theta^\circ = 26.56^\circ, 43.56^\circ, 51.80^\circ, 71.41^\circ$ which correspond to the planes with miller indices (111), (220), (311), (331) respectively. The average crystallite size can be calculated using Scherer's equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, D is the crystallite size, λ is the wavelength of the $\text{CuK}\alpha_1$ (1.54 \AA), θ stands for Bragg angle and β is the full-width at half-maximum (FWHM) of peak measured in radian. The average crystallite size of CdS nanoclusters comes out to be 4.2 nm. Thus XRD pattern confirms the formation of CdS nanocluster.

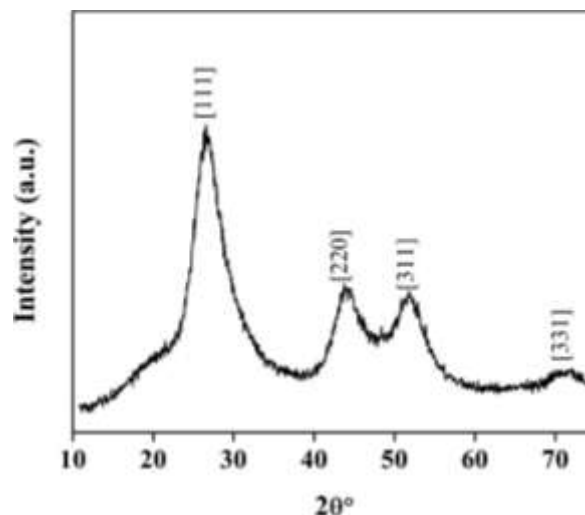


Fig. 1: XRD pattern of CdS nanoclusters.

The Morphology and particle size of the prepared sample is analysed using transmission electron microscopy (TEM) shown in Fig. 2. From the figure, it is clear that most of the particles are distinguishable and have an irregular spherical shape. The size distribution lies in the range of 4 – 12 nm confirming the formation of nanoclusters. The size distribution of the suspended particles in the matrix of base fluid can be effectively analysed using an acoustical particle sizer. The PSD profile of CdS nanocluster in ethylene glycol is shown in Fig. 3. As APS can produce PSD profile in the range of 10 nm to 1 mm, we get a sharp line at the value of 10 nm indicating only half portion of PSD curve. Assuming a symmetric curve, we can say that most of the particles are in the range 7 -13 nm. In

general, crystalline size determined by XRD technique comes out to be slightly lesser than that obtained by TEM [20] and APS. This is due to the underestimation of grain boundary while considering the lengths of coherence. Other possibilities like twinning defects and lattice dislocation that result in microstraining of the lattice points cannot be excluded. These defects arise due to the spontaneous arrangement of lattice atoms through the nucleation process [20].

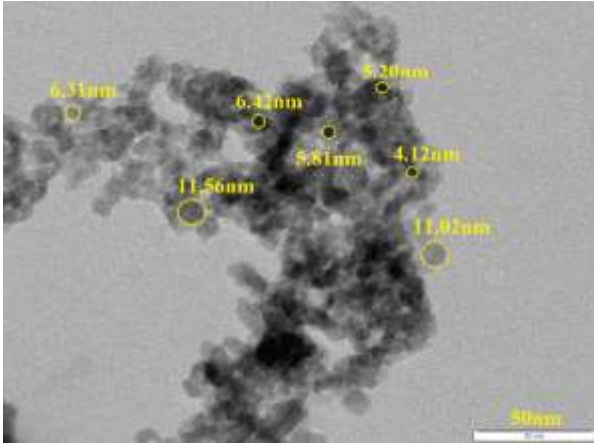


Fig. 2 TEM image of CdS Nanoclusters.

In the PSD curve, the size of particles is not greater than 13 nm which confirms the inhibition of the agglomeration of the CdS nanocluster in the base matrix of ethylene glycol because the upper limit of the particle size obtained from TEM analysis is also come out to be alike.

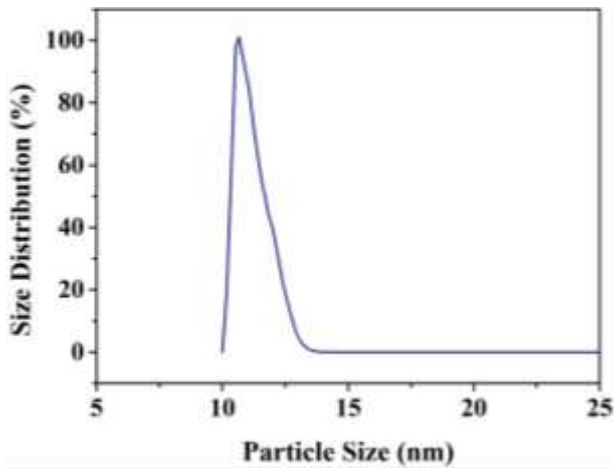


Fig. 3 Normalized particle size distribution of CdS nanoclusters in ethylene glycol

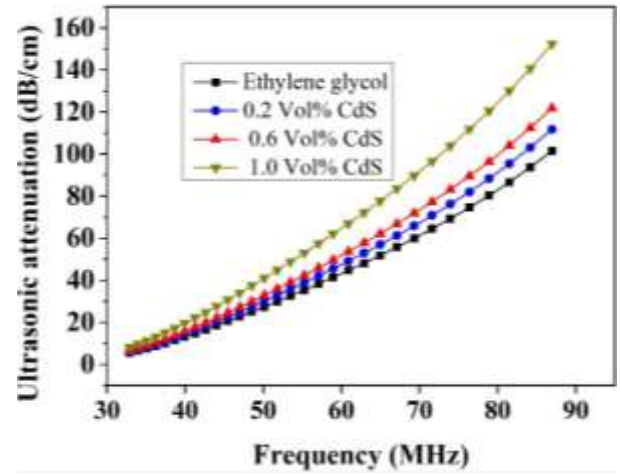


Fig.4 Variation of ultrasonic attenuation with frequency in CdS-ethylene glycol nanofluids

When an ultrasonic wave travels in a medium it gets attenuated. The attenuation of the ultrasonic wave with frequency in the ethylene glycol and nanofluids is displayed in Fig. 4. The graph shows a nonlinear increase in ultrasonic attenuation with frequency in the ethylene glycol. After the loading of nanocluster in the base fluid, the wave exhibits more attenuation and it increases further with an increase in the concentration of nanoparticles. The propagation of the wave is greatly influenced by the local environment of the medium. Here, the total attenuation in the nanofluid is the cumulative sum of three components. First, attenuation due to the CdS nanoparticles, second, due to molecules of basefluid, and third, due to the interaction between nanoclusters of CdS and molecules of ethylene glycol affecting the thermo-physical properties of the liquid-particle suspension.

The foremost causes of ultrasonic attenuation in the particles- fluid suspension are scattering, thermoacoustic loss and viscous loss. If the size of suspended particles is of the order of millimetre then scattering plays important role in the attenuation of the wave but for nanosized particles, it is insignificant as the wavelength of the ultrasonic wave is not comparable to the size of the dispersed CdS nanoclusters in the ethylene glycol [21]. The trends of attenuations in the obtained graph (Fig. 4) suggest that at a lower frequency, from 30 MHz to 42 MHz, the level of ultrasonic attenuations are almost similar to that of basefluid and all the three nanofluids. As frequency increases beyond this point, the absorption of the wave increases sharply with the concentration of the loading nanoparticles. The expressions for viscous wavelength and thermal wavelength [18] are given as follows

$$\lambda_v = \sqrt{2\eta / (\sigma\omega)} \quad (2)$$

$$\lambda_T = \sqrt{2K / (\rho C\omega)} \quad (3)$$

Here, ω is the frequency of the propagating ultrasonic wave. η , K , ρ or σ , and C represent the viscosity of the base matrix, thermal conductivity, density, and specific heat of the suspended particles. For frequency up to 42 MHz, the viscous wavelength is comparable to the average size of the nanoparticle making it dominating factor for ultrasonic attenuation in this frequency regime. For the frequency greater than 42 MHz, the thermal wavelength becomes comparable to the size of suspended particles and play dominating role to ultrasonic attenuation. A typical polynomial fit study to ultrasonic attenuation shows that the absorption in the nanofluids can be expressed as $\alpha = \sum \alpha_i f^i$. For $i = 0$, the coefficient of frequency is equal to attenuation in the matrix of ethylene glycol. While for $i \neq 0$, the coefficient of frequency is dependent on the size of dispersed particles.

4. CONCLUSIONS

We have successfully synthesized CdS nanocluster and CdS-ethylene glycol nanofluids via chemical route and ultrasonication method, respectively. XRD analysis confirms the formation of cubic phase CdS nanocluster. The crystalline size determined by the XRD technique comes out to be slightly less than the particle size obtained by TEM and APS due to the underestimation of grain boundary while considering the lengths of coherence. Nonlinear enhancement in the ultrasonic attenuation with frequency and concentration of nanocluster was observed in the CdS-ethylene glycol nanofluids. At smaller frequencies, viscous loss plays a crucial role in the absorption of the wave while at higher frequencies thermal loss becomes responsible for ultrasonic attenuation. The study will provide further insight into the efficient heat transfer management system with the understanding of inter-particle interaction in the nanofluids colloidal system.

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REFERENCES

1. H. Chiam, W. H. Azmi, N.A. Usri, R. Mamat and N. M. Adam (2017). Thermal conductivity and viscosity of Al_2O_3 nanofluids for different based ratio of water and ethylene glycol mixture. *Exp. Therm. Fluid Sci.* 81, pp. 420–429.
2. J. Jeevanandam, A. Barhoum, Y. S. Chan, A. Dufresne and M. K. Danquah (2018). Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations, *Beilstein J. Nanotechnol.*, 9, pp. 1050.
3. G. Peng, Z. Huma, M. Umair, I. Hussain and I. Javed (2020). Nanosilver at the interface of biomedical applications, toxicology, and synthetic strategies, in M. R. Shah, M. Imran, S. Ullah (Ed), *Metal Nanoparticles for Drug Delivery and Diagnostic Applications*, Elsevier, pp. 119-139.
4. W. Tang, L. Zhang and G. Henkelman (2011). Catalytic Activity of Pd/Cu Random Alloy Nanoparticles for Oxygen Reduction, *J. Phys. Chem. Lett.*, 2, (11), pp. 1328-1331.
5. H. C. Yeh, J. Sharma, J. J. Han, J. S. Martinez and J. H. Werner (2010) A DNA-Silver Nanocluster Probe That Fluoresces upon Hybridization, *Nano Lett.* 10 (8), pp. 3106–3110.
6. K. Zheng, M. I. Setyawati, T. P. Lim, D. T. Leong, and J. Xie (2010) Antimicrobial Cluster Bombs: Silver Nanoclusters Packed with Daptomycin, *ACS Nano* 10(8), pp. 7934–7942.
7. Y. F. Liu, L. Wang, C. P. Bu, G. Q. Wang, Y. H. Zhang, S. M. Fang, W. Z. Shi (2015). Synthesis of luminescent ag nanoclusters with antibacterial activity, *Journal of Nanomaterials*, 2015(7), pp. 7.
8. F. Mashali, E.M. Languri, J. Davidson, D. Kern, W. Johnson, K. Nawaj. and G. Cunningham (2019). Thermo-physical properties of diamond nanofluids: A review, *Int. J. Heat Mass Transf.* 129, pp. 1123-1135.
9. J. A. Eastman, S. U. S. Choi, S. Li, W. Yu, L. J. Thompson (2001). Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles, *Appl. Phys. Lett.* 78(6), 2001, pp. 718-720.
10. K. V. Wong, O. D. Leon (2010). Applications of Nanofluids: Current and Future, *Advances in Mechanical Engineering*, 2, pp. 1-11.
11. N. Ye. Nikitina, L. A. Ostrovsky (1998). An ultrasonic method for measuring stresses in engineering materials, *Ultrasonics*, 35(8), pp. 605-610.
12. C. Ruirun, Z. Deshuang, M. Tengfei, D. Hongsheng, S. Yanqing, G. Jingjie, F. Hengzhi (2017). Effects of ultrasonic vibration on the microstructure and mechanical properties of high alloying TiAl, *Sci Rep.* 41463 (7), pp. 1-15.

13. D.H. Yoo, K.S. Hong, H.S. Yang (2007). Study of thermal conductivity of nanofluids for the application of heat transfer fluids, *Thermochim. Acta.* 455, pp. 66–69.
13. X. H. Li, C. H. Xing, H. L. Cui, R. Z. Zhang (2019). Elastic and acoustical properties of Cr₃AlB₄ under pressure, *J. Phys. Chem. Solids* 126, pp. 65–71.
14. K. F. Herzfeld and T. A. Litovitz (1959). *Absorption and dispersion of ultrasonic waves* (New York, Academic Press INC).
15. L.W. Schmerr Jr. (2016). *Fundamentals of ultrasonic non-destructive evaluation* (Switzerland, Springer International Publishing).
16. J. Dong, B. Kim, A. Locquet, P. McKeon, N. Declercq, D.S. Citrin (2015). Nondestructive evaluation of forced delamination in glass fiber-reinforced composites by terahertz and ultrasonic waves, *Composites Part B: Engineering* 79, pp. 667- 675.
17. P.S. Epstein and R.R. Carhart (1953). The absorption of sound in suspensions and emulsions. I. waterfog in air, *The Journal of the Acoustical Society of America* 25, pp. 553–565.
18. Y. Wang. and E. Forssberg E. (2006). Production of carbonate and silica nanoparticles in stirred bead milling, *Int. J. Miner. Process.* 81, pp. 1–14.
19. Deepika and H. Singh (2018). Study of size distribution in nanostructured Se₅₈Ge₃₉Pb₃ glass using various characterization methods, *Mapan J. Metro. I Soc. I.* 33(2), pp. 165–168.
20. S. Biwa, Y. Watanabe, S. Motogi and N. Ohno (2004). Analysis of ultrasonic attenuation in particle-reinforced plastics by a differential scheme, *Ultrasonics* 43(1), pp. 5.

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