ISSN: 2517-9934 Vol:5, No:7, 2011

Thermal Diffusivity Measurement of Cadmium Sulphide Nanoparticles Prepared by γ-Radiation Technique

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Abstract—In this study we applied thermal lens (TL) technique to study the effect of size on thermal diffusivity of cadmium sulphide (CdS) nanofluid prepared by using γ -radiation method containing particles with different sizes. In TL experimental set up a diode laser of wavelength 514 nm and intensity stabilized He-Ne laser were used as the excitation source and the probe beam respectively, respectively. The experimental results showed that the thermal diffusivity value of CdS nanofluid increases when the of particle size increased.

Keywords—Thermal diffusivity, nanofluids, thermal lens

I. INTRODUCTION

POLYMER-nanocomposites have recently been the subject of extreme interest because of their electrical, optical and mechanical properties [1-3] and their potential specific applications in nonlinear optics, photoelectrochemical cells, heterogenerous photocatalysis, optical switching, and single electron transistors [4-7]. Due to the great properties of chalcogenide nanomaterials, many works chalcogenide/polymer nanocomposites have been reported [8-10]. Among them all, cadmium sulphide (CdS) is one of the most assuring compound materials because of its wide range of applications in optoelectronic [11], piezoelectronic [12] and semiconducting devices [13]. In the present study CdS nanoparticles hosted by polyvinyl alcohol has been successfully prepared. In such method, the ionizing γ radiation is being used as a reducing agent to reduce cadmium ions from Cd (NO₃)₂ into CdS nanoparticle. Thermal lens spectrometry (TLS) is one of sensitive photothermal techniques upon temperature gradient which is due to absorption of electromagnetic radiation and nonradiative relaxation of the excited molecules. In the TLS experiment the excitation laser must have Gaussian profile, so when sample absorb the beam with Gaussian distributed intensity the temperature distribution has a radial dependence. The temperature gradient causes refractive index gradient which behaves like a converging or diverging lens depending on whether the change rate of refractive index with respect to temperature, is positive or negative [15,16]. High sensitivity character of this technique makes it very appropriate for

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measuring the thermal diffusivity of samples relies on physical changes that happen in the sample. In the present paper, we report measurements of the thermal diffusivity of nanofluids containing various sizes of CdS nanoparticles in order to determine the effect of particle size on thermal diffusivity by using TLS.

II. EXPERIMENTAL METHOD

Cadmium nitrate tetrahydrate (Cd (NO₃)₂.4H₂O 98%), sodium thiosulfate (Na₂S₂O₃ 99%) and Polyvinyl alcohol (PVA 99%, MW 31,000, Aldrich) were used as received without further purification. Double distilled and deionized water (Purelab Prima Elga) was used throughout the sample preparations. To synthesize CdS/PVA nanocomposites, the PVA solution was prepared by adding 4 g PVA in 200 ml deionized water and stirring until a viscous transparent solution was obtained. Then the appropriate amount of Cd (NO₃)₂ and Na₂S₂O₃ were added to above PVA solution and the mixture was stirred for 2 hours at room temperature in order to achieve good dispersion of Cd2+ in PVA matrices followed by appending 4 ml Isopropyl alcohol to scavenge oxidative radicals such as OH. Afterwards, the transparent prepared solution was divided into 4 containers and each one was isolated from air and bubbled with nitrogen gas (99.5%) in order to remove oxygen. A gamma ray facility (60Co) was then used to irradiate the solutions at 30-60-90 and 120 kGy radiation doses. A yellowish precipitate was obtained after the radiation. These precipitated fine powders were collected through centrifuge and washed several times with double distilled water and absolute ethanol to remove any unreacted chemicals and the impurities. The final products were dried and used for further analysis. Optical absorption spectra were obtained using a UV visible spectrophotometer (Shimadzu-UV 1650PC) in the wavelength range 250-900 nm using distilled water as a reference. Optical measurements were taken before and after radiation. Transmission electron microscopy (TEM) observation was performed on a Hitachi (H-7100) electron microscope at accelerating voltage of 120 kV. A drop of the acetone solution of the products was placed on a copper grid that was left to dry before transferring into the TEM sample chamber for viewing.

The thermal lens (TL) experimental setup is shown in Fig. 1. Measurement was carried out using a diode laser (532 nm at 80 mW) as an excitation beam modulated at 10 HZ frequency and focused by a 21 cm focal length onto the sample which is positioned at its focal plane. The probe beam is focused by 5cm focal length lens and is aligned at an angle

ISSN: 2517-9934 Vol:5, No:7, 2011

smaller than 1.5° with respect to the excitation beam. The sample was laced at $\sqrt{3}$ $Z_{\rm C}$ from the probe beam waist. Two adjustable mirrors (M1, M2) were used to increase optical length from the sample to a pinhole. An optical band pass filter putted in front of the pinhole to prevent stray light entering the photodiode (PD). The output signal of the PD was sent to the digital oscilloscope (Tektronix TDS 210) to record the time history of signal change. The Lab VIEW software was used to capture the time history data from oscilloscope and to normalized it with respect to signal at time t=0.

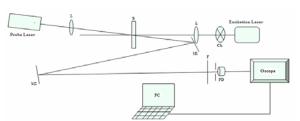


Fig. 1 Schematic diagram of experimental apparatus

The intensity of probe beam at the detector can be given by [16]:

$$I(t) = I(0) \left[1 - \frac{\theta}{2} \tan^{-1} \left(\frac{2mV}{\left[(1 + 2m)^2 + V^2 \right] \frac{t_c}{2t} + 1 + 2m + V^2} \right) \right]^2$$
 (1)

$$V = \frac{z_1}{z_c} \quad \theta = -\frac{p_e A_e L}{\kappa \lambda} \left(\frac{dn}{dt}\right) \quad m = \left(\frac{w_p}{w_e}\right)^2 D = \frac{w_e^2}{4t_c}$$
 (2)

Here, I(0) is the initial intensity when t is zero, p_e is the excitation beam power (80 mW), A_e is the absorption coefficient (cm⁻¹), L is the sample thickness, λ is the laser wavelength (632.8 mm). The dn/dT is the change refractive index of the sample, $z_c = w_0^2/\lambda$ is the confocal distance (cm), Z_I is the distance of the probe laser beam waist to sample, D is the thermal diffusivity of the sample (cm²/s), t_c is the characteristic thermal time constant. The parameter, θ and t_c can be determined by fitting the experimental data to Eq. (1). Thus thermal diffusivity was calculated using Eq. (2).

III. RESULTS AND DISCUSSION:

Fig. 2 shows typical TEM images of CdS nanoparticles prepared at 30, 60, 90 and 120 kGy radiation dose. It can be seen that nearly monodisperse particles are observed with spherical morphology and average diameter of the particle slightly increasing from 52 nm at 30 kGy to 67 nm at 120 kGy. This result is tabulated in Table 1.

The further evidence of the formation of nanocomposites comes from UV-Vis spectrum and the influence of the absorbed dose on the CdS nanoparticle was studied by recording the absorption spectra of solutions irradiated with different doses, using distilled water as reference. Fig. 3 shows the absorption spectra before radiation and after radiation at different doses. It is clear that for the non-radiated

sample, 0 kGy, there is a noticeable peak at 290 nm which is related to PVA in the medium, but there is no peak for CdS which prove the fact that the CdS nanoparticles are produced after γ radiation. The inception of the successive absorption depends on the size of particles owing to the quantum confinements of the photogenerated electron-hole carriers

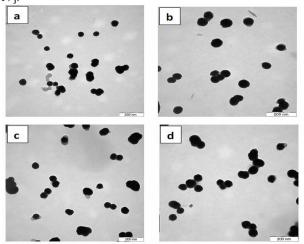


Fig. 2 TEM micrographs of CdS nanoparticles prepared at a) 30, b) 60, c) 90 and d) 120 kGy radiation dose

It is recognized that the wavelength at the maximum exciton absorption (λ_{max}) increases as the size of the nanoparticles increases. Therefore, the red absorption shift observed on increasing the radiation dose results from the size increase of CdS particles [18]. As the radiation dose goes higher the optical absorption gradually increases, which means that with higher dose more Cd²⁺ has reacted with S²⁻ in the environment and more CdS particles are produced.

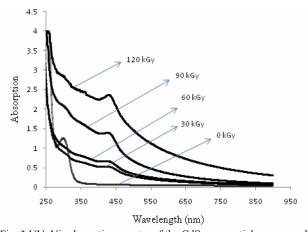


Fig. 3 UV–Vis absorption spectra of the CdS nanoparticles, prepared at different doses of γ -radiation

Fig. 4 shows the TL signal for CdS nanoparticles prepared at 30 kGy dose and from fitting the values of $\theta = (2.013\pm0.076)$ and $t_c = (0.0144\pm0.0009)$ s, the obtained thermal diffusivity is $(14.95\pm0.93) \times 10^4$ cm²/s. Similar TL signals evolution were obtained for other CdS nanoparticles

ISSN: 2517-9934 Vol:5, No:7, 2011

sizes and their corresponding θ 's, t_c 's and D's were also obtained and are tabulated in Table 1.

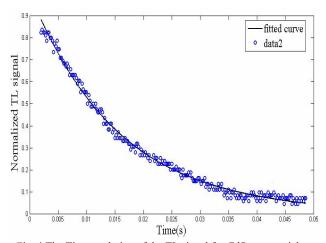


Fig. 4 The Time evolution of the TL signal for CdS nanoparticles prepared at 30 kGy dose. Solid line corresponds to the best fit of Eq. (1) to the TL experimental data

Fig. 5 shows the thermal diffusivity in term of particles size. The symbols represent the obtained thermal diffusivity and the solid line corresponds to the best linear fitting of this thermal parameter.

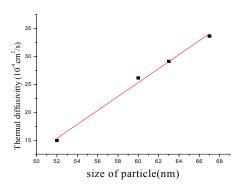


Fig. 5 Thermal diffusivity in term of particles size

From the obtained results it can be seen that there is an increase in the fluid thermal diffusivity when the particle sizes increase. This increase of thermal diffusivity with increasing particle size is due to increase of volume fraction of nanoparticles [18] dispersed in solution as is clear from the UV-Vis spectrum. The other reason is related to phonon scattering at interface or to transfer of energy from nanoparticle to liquid, and when the particle size become small this scattering affects the particle and therefore less energy transferred to liquid.

TABLE I EXPERIMENTAL θ and τ C and calculated D for solvents with CDS Nanoparticles with different sizes

NANOFACTICLES WITH DIFFERENT SIZES				
Dose (kGy)	Average particle size (nm)	$t_c(\mathbf{s})$	θ	$D(10^4 \text{cm}^2/\text{s})$
30	52	0.0144 ± 0.0009	2.013 ± 0.076	14.95 ± 0.93
60	60	0.0082 ± 0.0006	0.166 ± 0.091	26.14± 1.91
90	63	0.0073 ± 0.0005	0.083 ± 0.001	29.10 ± 1.79
120	67	0.0064 ± 0.0005	0.041 ± 0.001	33.64 ± 2.62

IV. CONCLUSION

We measured thermal diffusivity of CdS nanofluid at different particle prepared by γ -radiation. Our result shows that thermal diffusivity increase when size of particles increase. Increasing in volume fraction of particles with increasing particle size and phonon scattering at interface of liquid and nanoparticles can be reasons for this increment.

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