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Raman Scatering And Size Distribution studies Of Sodium Lauryl Sulphate (SLS) – Capped Zinc Oxide Nanoparticles

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Abstract: *Sodium lauryl sulphate was successfully employed as a capping agent in the synthesis of ZnO nanoparticles. Solvothermal technique was used to synthesize the ZnO nanoparticles. The technique involved the thermal decomposition of Zinc acetate dehydrate in diethylene glycol containing sodium lauryl sulphate used for capping. Raman spectroscopy revealed that the ZnO nanoparticles produced has wurtzite hexagonal structure with good crystallinity and stability. The Z-average diameter and polydispersity index (PdI) obtained with cumulants fit error of 0.00281 indicate that the synthesized ZnO nanoparticles were of good size quality and monodisperse. The size distribution by volume specified that ZnO nanoparticles dominant in the sample were 722.3nm in diameter and occupied 68.5% of the entire volume. In size distribution by intensity, the prominent particles were 523.1nm in diameter with 66.3% of the total volume. Based on the results, sodium lauryl sulphate is a good capping material for solvothermal synthesis of ZnO nanoparticles.*

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I. Introduction

Zinc oxide (ZnO) is one of the more attractive semiconducting metal oxides owing to its interesting properties including a wide and direct bandgap (3.37 eV) and large exciton binding energy (60 meV) as well as high transparency (Bekkari *et al*., 2017).In the ambient conditions, ZnO crystallizes in the wurtzite phase is a tetrahedrally coordinated structure with hexagonal lattice (Bekkari *et al*., 2019). ZnO occurs naturally as the mineral zincite (Luptáková *et al*., 2015).Most ZnO used commercially is produced synthetically(Kumar and Sharada, 2015).Solvothermal synthesis is one of the techniques that could be used for the synthesis of ZnO nanomaterials. The process involves the use of a solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction of precursors during synthesis (Gersten, 2018). The technique has proved to facilitate greatly the fabrication of ZnO nanoparticles at ambient temperature with good controllability in the synthesis of ZnO nanocrystals. Zinc oxide nanoparticles can be synthesized using different salt precursors such as Zinc Chloride ($ZnCl_2$), Zinc Acetate ($ZnC_4H_6O_4$), Zinc Nitrate ($ZnNO_3$), Zinc Sulphate Heptahydrate ($ZnSO_4 \cdot 7H_2O$) and Potassium Carbonate (K_2CO_3).

In chemical synthesis, capping agents and stabilizers are extensively used in order to control the size and to avoid agglomeration (Tanner *et al*., 2015). Triethyl amine, Oleic acid, Thioglycerol, EDTA, Tetraethyl Ammonium Bromide, Tetraethyl Orthosilicate, Polyethylene Glycol (PEG), Polyethylene Phthalate (PEP), Ethylene Glycol, Gelatin, Polyvinyl Alcohol (PVA) and Polyvinyl Pyrrolidine (PVP) are the frequently employed capping agents and stabilizers (Haq *et al*.**,** 2017).Sodium lauryl sulfate (SLS), also known as sodium laurylsulfate or sodium dodecyl sulfate is an anionic surfactant commonly used as an emulsifying cleaning agent in household cleaning products such as laundry detergents, spray cleaners and dishwasher detergents (Bondi *et al*., 2015).Sodium lauryl sulphate is used in a variety of products, including: grooming products such as shaving cream, lip balm, hand sanitizer, nail treatments, makeup remover, foundation, facial cleansers, exfoliants and liquid hand soap; hair products such as shampoo, conditioner, hair dye, dandruff treatment and styling gel; dental care products such as toothpaste, teeth whitening products and mouthwash; bath products such as bath

oils or salts, body wash, and bubble bath; and creams and lotions such as hand cream, masks, anti-itch creams, hair-removal products and sunscreen(Schaefer and Whitworth, 2019). It also acts as a food additive like an emulsifier or a thickening agent. Some of the food products that contain sodium lauryl sulphate are marshmallows, dried egg products and dry beverage bases (Goswami, 2019). In this work, sodium lauryl sulphate is used as a capping agent for synthesizing ZnO nanoparticles by solvothermal technique. The crystal structures, particle size distribution by intensity, size distribution by volume and size quality of the synthesized ZnO nanoparticles.

II. Materials and Methods

The synthesis of sodium lauryl sulphate-capped ZnO nanoparticles was carried out by solvothermal technique at 190^0C. A round bottom flask was washed and dried using mantle heater connected to a temperature control system. A solution of 0.5 mol (8.7g) of sodium lauryl sulphate (SLS) was prepared in 60ml of diethylene glycol at a dissolution temperature of 120^0C on a magnetic stirrer hotplate. The mixture was stirred continuously using magnetic stirring bar until the SLS was completely dissolved in diethylene glycol. 1.0mol (13.2g) of zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$) was added to the solution and stirred continuously until it was completely dissolved in the solution. The mixture was heated on the mantle heater and the temperature was maintained at 190^0C for 1 hour with the temperature control system. The product was centrifuged at 3000RPM to separate the ZnO nanoparticles from the mixture using an electronic centrifuge. Methanol was used to wash excess ZnO nanoparticles that grew on the flask. Propanol was used for precipitation and segmentation of the ZnO nanoparticles. A milky liquid form of the ZnO nanoparticles was produced. The milky liquid of the ZnO nanoparticles wasthen transferred to a crucible boat and was dried in an electric oven at 60^0C for 12 hours. White powder of ZnO nanoparticles was obtained.

Raman Spectroscope (Model No. Pro Raman-L-785-BIS) was used to determine the crystal structures of the synthesized ZnO nanoparticles. Raman spectroscopy examined the ZnO nanoparticles by scattering a high intensity laser light in which few photons interacted with the molecules of the ZnO nanoparticles in their vibrational states emitting light of slightly different wavelengths. The laser light with Raman excitation wavelength of 785nm was used for the inelastic scattering of the molecules of the ZnO nanoparticles samples at room temperature. The scattered light occurred at wavelengths that were shifted (Raman shifts or wavenumbers) from the incident light by the energies of the molecular vibrations.Malvern Instrument (Zetasizer Version 7.01) was used to study the synthesized nanoparticles in terms of size, size distribution by intensity, size distribution by volume and size quality. The sizes of ZnO nanoparticles and their proportions present in the sample were determined. The dispersant used was water. Size distributions of the nanoparticles were determined with a Malvern Zetasizer (Nano Range) by the Dynamic Light Scattering (DLS) technique. Suitable parameters (viscosity, absorption and refractive index) were chosen for the ZnO samples and the dispersant. The synthesized ZnO nanoparticles had absorption of 0.010 and refractive index of 1.59. The water used as dispersant had viscosity 0.8872cP and refractive index of 1.33. The ZnO nanoparticles were dispersed at 25^0C for 60seconds (1 minute).

III. Results and Discussions

The Raman spectrum of the synthesized ZnO nanoparticles is shown in Figure 1. The Raman peaks prominently present in the Raman spectrum were observed at 408cm^{-1}, 426cm^{-1}, 854cm^{-1}, 874cm^{-1} and 2878cm^{-1}. Table 1 compares the observed Raman peaks with the theoretical functional groups/vibrations of crystals and Raman bands/regions.

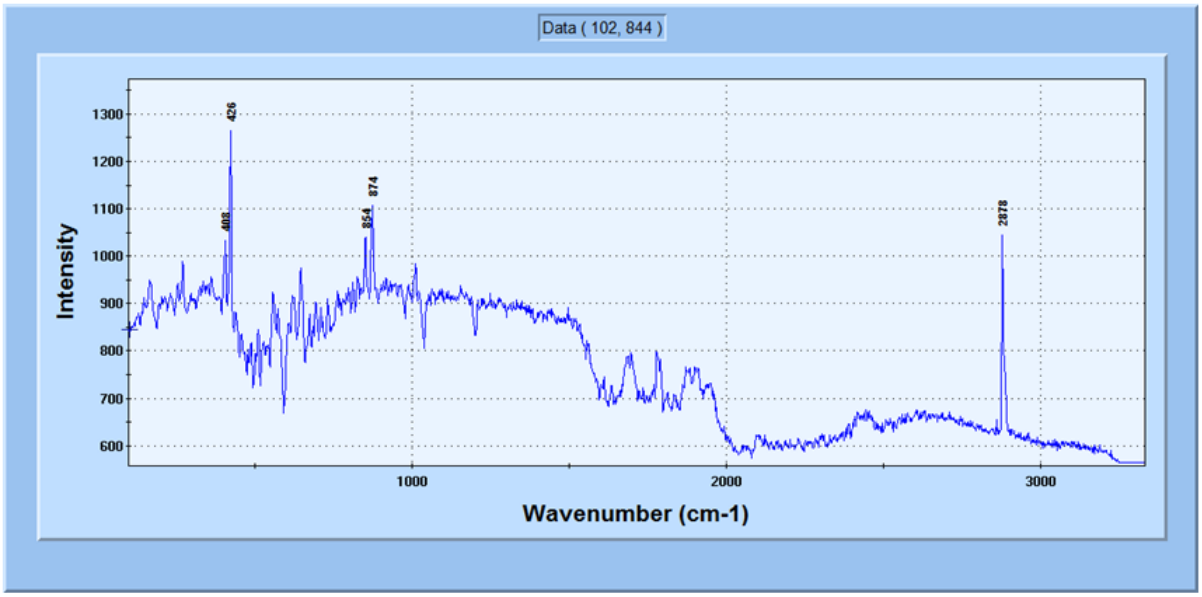

Figure 1 Raman spectrum of the synthesized ZnO nanoparticles

Table 1: The peak positions of Raman Spectra of ZnO nanoparticles produced with SLS compared with the regions of the functional groups/vibrations

Functional groups (Vibrations)	**Wavenumber(cm^{-1}) (Region)**	**Raman Peaks**	**Raman Intensity**
v(metal-O)	150-450	408	Strong
v(metal-O)	150-450	426	Strong
v(O-O)	845 - 900	854	Strong
v (O-O)	845 - 900	874	Strong
v (C−H)	2800 - 3000	2878	Strong

The observed Raman shift or peak of 408cm^{-1} and 426cm^{-1} fall within the region of the functional group of metal oxides. The main peak at 426cm^{-1} has strong and sharp Raman band with the highest intensity which indicates a high concentration of ZnO nanoparticles.The E_2(high) mode obtained is in agreement with E_2(high) zinc phonon mode between 370 cm^{-1} and 440 cm^{-1}(Schumm, 2008). The Raman prominent peak observed at 426cm^{-1} is a characteristic peak of the Raman active dominant E_2(high) mode of Wurtzite ZnO with red shift of 11cm^{-1}. The E_2(high) peak for the synthesized ZnO nanoparticles was within wurtzite hexagonal phase with good crystallinity though the value was shifted from the theoretical Raman vibrational frequency for bulk ZnO nanoparticles wurzite crystal structure for E_2(high) symmetry of 437cm^{-1}(Dakhlaoui *et al.*, 2009 & Khan, 2010). The result differed from the Raman peaks at 434 cm^{-1} and 432$cm^{-1}$for ZnO nanoparticles synthesized at room temperature and 100^0C respectively (Isah *et al*., 2016)and Raman shift at nearly 435 cm^{-1} for wurtzite structure of zinc oxide nanorods (Bhunia *et al.*, 2016). The red shift can be attributed to either phonon confinement within the nanocrystal boundaries or the localization of phonons due to defects in ZnO nanoparticles samples (Taziwa *et al.*, 2017)or high excitation wavelength of the laser light. The observable bands situated at 854cm^{-1} and 874cm^{-1} assigned to O–O stretching vibration mode from intermolecular bonding of oxygen in acetate salt which is associated to O–O stretching vibration mode of oxygen in zinc acetate salt (Tapan *et al*., 2001). It can also be as a result of weaker bands which correspond to C-H vibration of the aromatic ring. The peak at 2878cm^{-1} is a strong and sharp band with high intensity which could be associated with the C-H stretching vibrations. This is consistent with bands 2970 to 2850 cm^{-1}, 2990 cm^{-1} and 2420 cm^{-1} corresponding to C–H stretching vibration mode of methyl groups (Phoohinkong et al 2017). The C-H stretching mode obtained is also in agreement with C-H stretching modes between about 2800 cm^{-1} and 3100 cm^{-1}(Schumm, 2008).

The sodium lauryl sulphate-capped ZnO nanoparticles SLS was also analyzed based on size distribution by volume, intensity and size quality. The solution of the ZnO nanoparticles contained Z-average

particle size of 354nm with Polydispersity Index (PdI) of 0.605 which is less than 0.7polydispersity index. The Polydispersity Index typically has values less than 0.7 for monodisperse test sample of spherical particles (ISO 22412, 2017). Valuesgreater than 0.7 indicate that the sample has a very broad size distribution and is probably not suitable for the dynamic light scattering (DLS) technique. The Z-average diameter is larger than the lower limit of the size distribution histogram in Figure 2 and lower than its upper limit.The solution was therefore suitable for the dynamic light scattering (DLS) technique. It shows that the synthesized zinc oxide nanoparticles were monodispersed in nature. Table 2 gives the results of the PSD analysis by volume of the ZnO nanoparticles. In the table, the dominant ZnO nanoparticles in the sample had the diameter of 722.3nm and occupied 68.5% of the entire volume. This portion of the ZnO nanoparticles is represented in peak 1 of Figure 2 that shows a histogram of the particle size distribution by volume of the ZnO nanoparticles. The results of the analysis indicated the ZnO nanoparticles produced with sodium lauryl sulphate as a capping agent was of good quality. Peak 2 contains ZnO nanoparticles with diameter of 121.5nm which occupies 16.8 % of the entire volume. Peak 3 contains ZnO particles of diameter 4967.0 and occupies 14.7% of the entire volume.

Table 2: Results of PSD analysis by volume

Peak	Size (d.nm)	% volume	Standard Deviation
1	722.3	68.5	348.70
2	121.5	16.8	36.19
3	4967.0	14.7	992.20

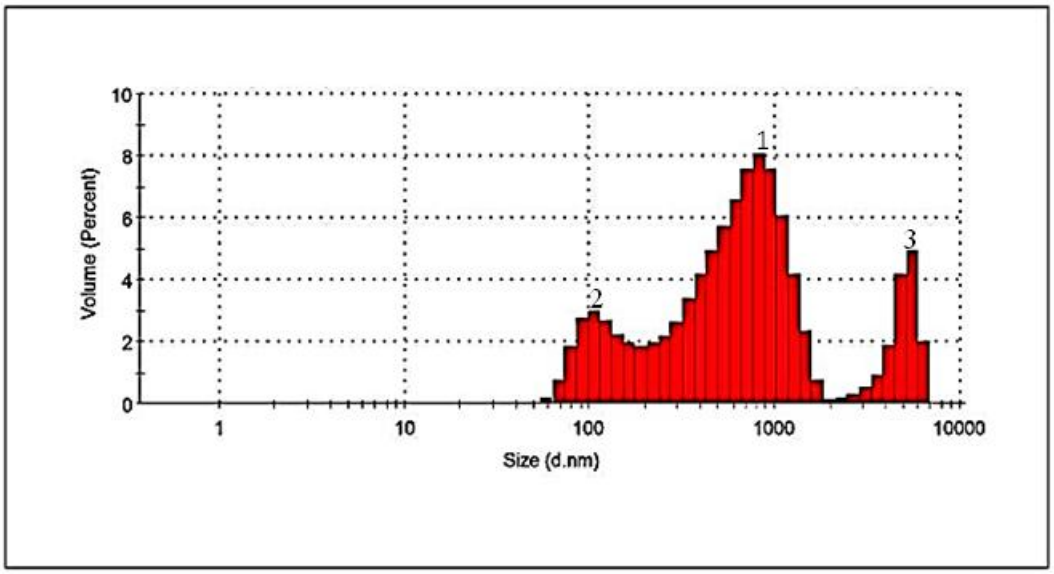

Figure 2 ZnO nanoparticles size distributions by volume

The PSD by intensity was also obtained from the analysis. The results were based on the intensity of each particle size. Table 3 shows the results of the PSD analysis by intensity.

Table 3: Results of PSD analysis by intensity

Peak	Size (d.nm)	% intensity	Standard Deviation
1	523.1	66.3	272.10
2	136.0	23.6	34.11
3	4581.0	10.0	966.80

Figure 3 shows the histogram of the particle size distribution by intensity of the ZnO nanoparticles produced with sodium lauryl sulphate. In table 3, the dominant ZnO nanoparticle in the sample has the diameter of 523.1nm and occupies 66.3% of the entire volume. This portion of the ZnO nanoparticles is represented by peak 1 of Figure 3. Peak 2 represents the ZnO nanoparticles with diameter of 136.0nm which occupies a volume of

23.6%. Peak 3 represents the ZnO particles with diameter of 4581.0nm occupying 10.0% of the entire volume of the sample.

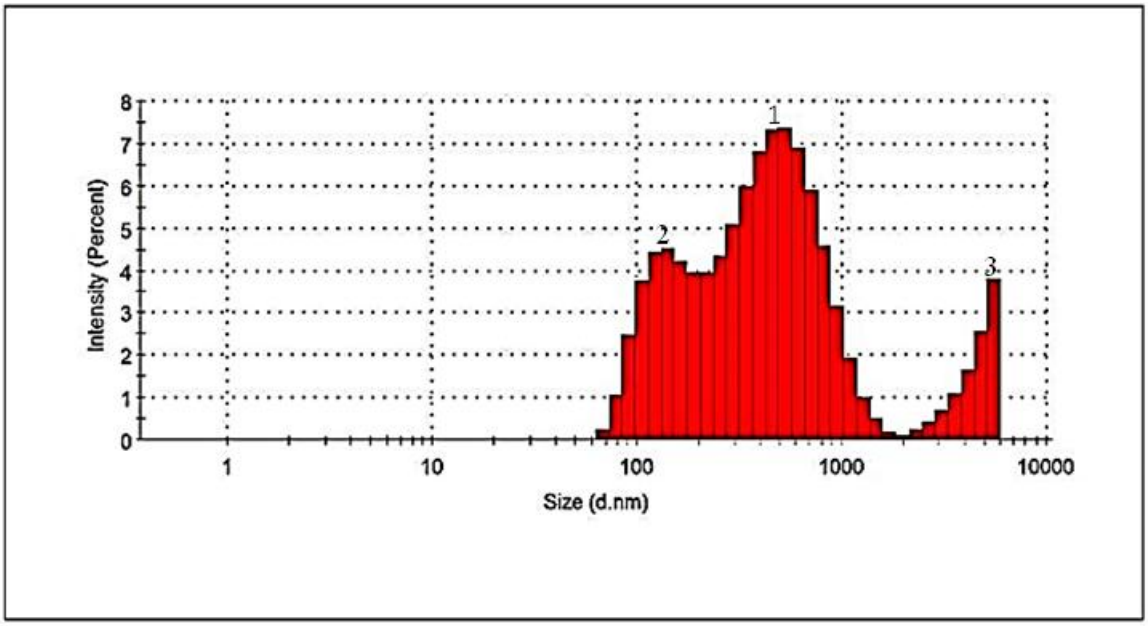

Figure 3 Size distributions of ZnO nanoparticles by intensity

The size quality of the distribution of the ZnO nanoparticles obtained from the analysis was verified. Correlation coefficient was used to evaluate the strength of the relationship between the size (diameter) and the intensity of the ZnO nanoparticles. Figure 4 shows the graph of size distribution by intensity of the ZnO nanoparticles while Figure 5 shows the graph of raw correlation data for the distribution. Figures 4 and 5indicated that there was a relationship between the size distribution of the ZnO nanoparticles and the intensity of the nanoparticles. The correlation coefficients were all positive values which implied that there was a positive linear relationship between the size distribution and intensity of the ZnO nanoparticles present in the sample. The intensity size distribution and the correlation function proved that the ZnO nanoparticles synthesized with sodium lauryl sulphate are capping agent met the quality criteria.

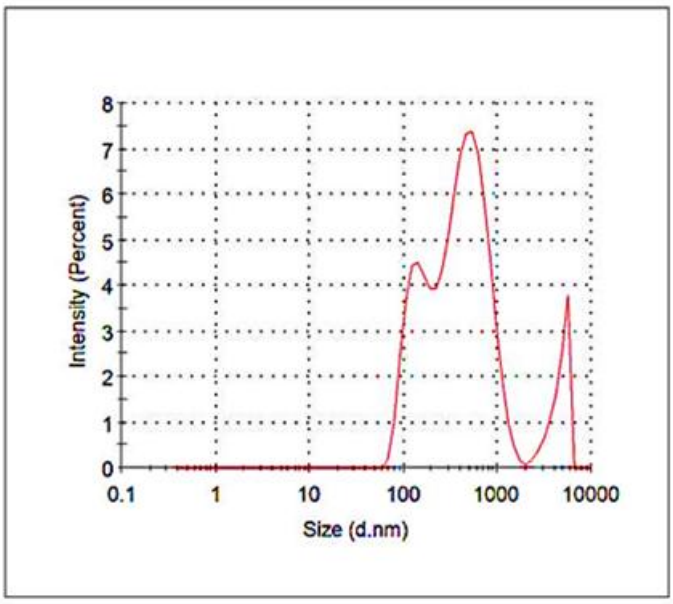

Figure 4 Graph of size distribution by intensity

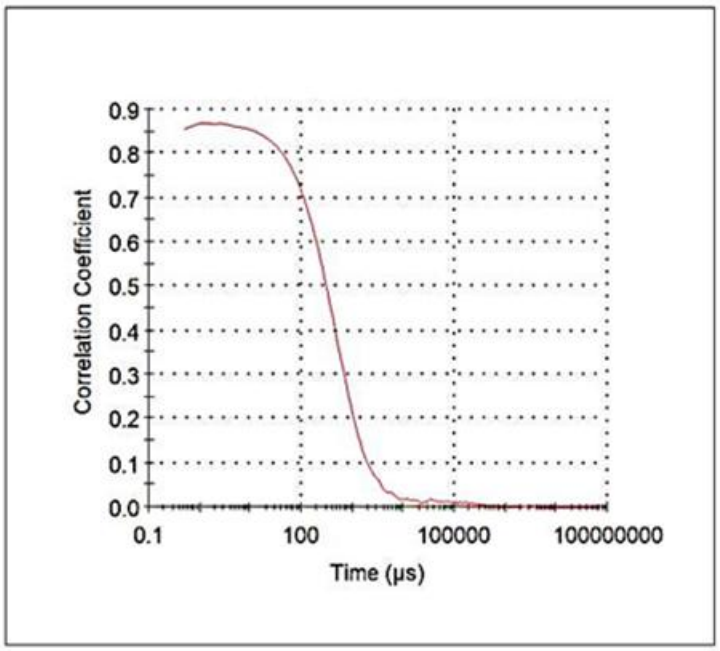

Figure 5 Graph of raw correlation data

The correlation function intercept was used to evaluate the signal-to-noise ratio from the ZnO nanoparticles and to determine its quality. Figure 6 shows the correlation function of the intensity distribution. The intercept value is 0.927 which is in agreement with ISO 22412 (2017) specifications of suitable valuesof intercepts between 10% and 100% or 0.1 to 1.0. It indicates that the synthesized ZnO nanoparticles have suitable concentration, fluorescence and absorption qualities.

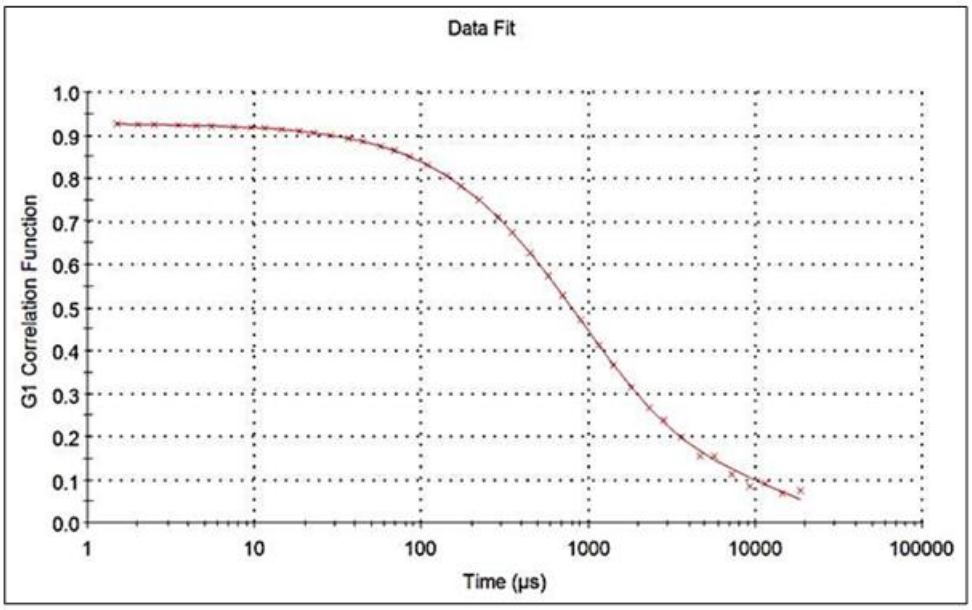

Figure 6 ZnO nanoparticles intensity distribution fit

The cumulants fit error was used to determine the quality of the cumulants adjusted to the measured data, that is whether the polydispersity (PdI) and z-average diameter obtained from the analysis are reliable values.Figure 7 shows the correlogram for the cumulants while figure 8 shows the cumulants fit error obtained from the analysis of the data with cumulants. The cumulants fit recorded a cumulants fit

error of 0.00281. The error is less than 0.005 and in agreement with ISO 22412 (2017). The PdI and Z-average diameter obtained from the synthesized ZnO nanoparticles are reliable values. Hence, the ZnO nanoparticles are monodisperse and of good size quality.

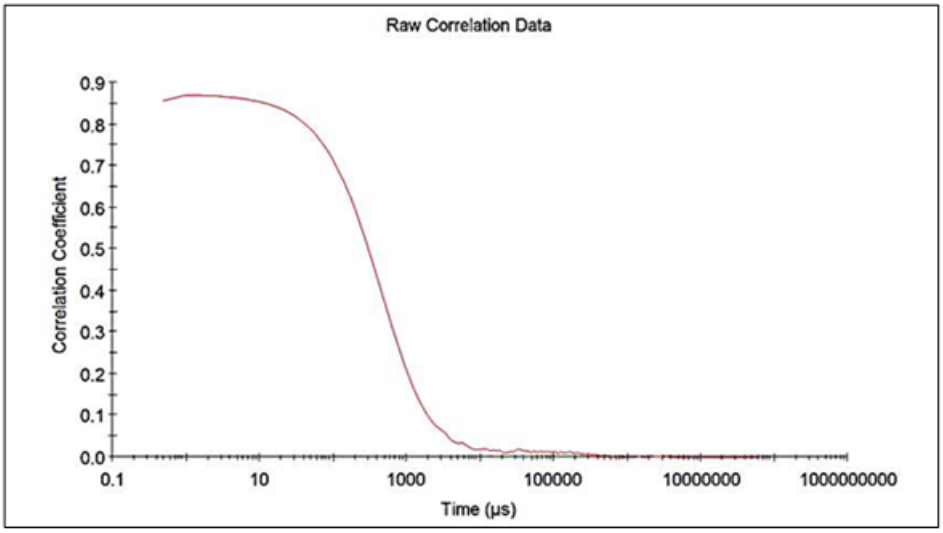

Figure 7 Correlogram for the cumulants for the ZnO nanoparticles

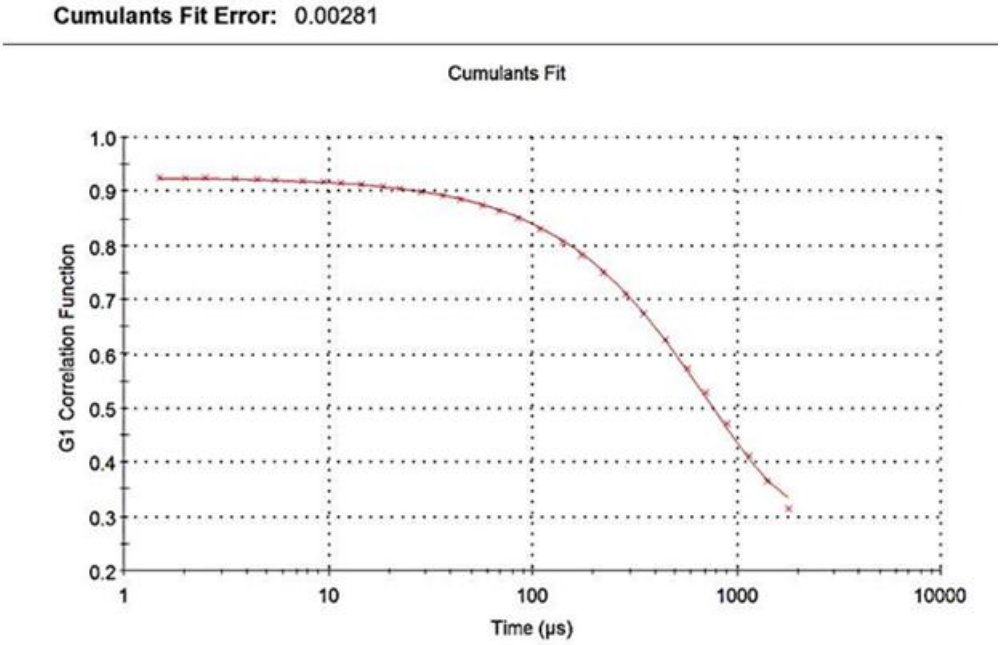

Figure 8: Cumulants fit for the ZnO nanoparticles

IV. Conclusion

ZnO nanoparticles were successfully obtained by solvothermal technique. Zinc acetate dehydrate (precursor)and diethylene glycol (solvent)were used for the synthesis.The capping agent used for the synthesis was sodium lauryl sulphate. The solvothermal synthesis was completed at 190^0C. The E_2(high) obtained was $426cm^{-1}$ which was within wurtzite hexagonal phase. The synthesized ZnO nanoparticleshave good crystallinity and stable structure. The Z-average diameter was 354nm and Polydispersity Index (PdI) was 0.605. The cumulants fit error was 0.00281 showing that the synthesized ZnO nanoparticles were of good size quality and monodisperse. The dominant ZnO nanoparticle in size

distribution by volume had diameter of 722.3nm and occupied 68.5% of the entire volume. The dominant ZnO nanoparticle in size distribution by intensity haddiameter of 523.1nm and occupied 66.3% of the entire volume. The results are indications that the sodium lauryl sulphate is a good capping material for solvothermal synthesis of ZnO nanoparticles.

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