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Raman Scattering and Particle Distribution Studies of Zinc Oxide Nanoparticles Capped With Linear Alkylbenzene Sulphonate

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Abstract: *Zinc oxide nanoparticles were effectively synthesized through solvothermal method using zinc acetate as a precursor in diethylene glycol (solvent) with linear alkylbenzene sulphonate as the capping agent. The crystalline structure and particle size distribution (PSD) of synthesized ZnO nanoparticles were studied using Raman spectroscopy and Malvern Zetasizer (Nano Range) by the Dynamic Light Scattering (DLS) technique. The Raman E_2(high) obtained was 424cm^{-1} with red shift of 13cm^{-1}indicating a wurtzite hexagonal structure with high crystalinity. The Z-average diameter of the ZnO nanoparticles was 715.2nm and polydispersity index (PdI) was 0.431. The cumulants fit error was 8.27 x 10^{-4}indicating that the ZnO nanoparticles produced were of good size quality and monodisperse in nature. The results obtained from this work are clear indications that linear alkylbenzene sulphonate is a good capping material for solvothermal synthesis of ZnO nanoparticles.*

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I. Introduction

ZnO is a semiconducting material which has a wide band gap of 3.27 eV in bulk. This makes it a very useful material for nano electronics and photonics applications. Its high exciton binding energy of 60 MeV, breakdown strength and its multifunctional (piezoelectric, ferroelectric and ferromagnetic) properties make this material more advantageous over other materials for electronic applications(Look, 2001; Muthukumar *et al.*, 2003 and Gurushankar *et al*., 2018). In the ambient conditions, ZnO crystallizes in the wurtzite phase is a tetrahedrally coordinated structure with hexagonal lattice (Bekkari *et al*., 2019). ZnO has several advantages, which include relatively low-temperature synthesis, controllable morphology, and the particular properties that depend on its size (Septiani*et al*., 2017). Capping agents and stabilizers are extensively used in chemical synthesis 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).

In the present work, linear alkylbenzene sulphonate (LABS or LAS) was used as a capping agent for synthesizing ZnO nanoparticles by solvothermal technique. LABS ($C_{11}.6H_{24}.2)C_6H_4SO_3Na$)) is a mixture of closely related isomers and homologues, each containing an aromatic ring sulphonated at the para position and attached to a linear alkyl chain (HERA, 2013). LABS are among the major anionic surfactants used in detergents, such as laundry powders and dishwashing products (Bradai, 2016). LABS is highly water soluble surface active agents (Akyuz and Roberts 2002) and a biodegradable surfactant. When added to the reaction mixture, the molecules become attached to surface of growing particles, preventing further growth of the particles, either by electrostatic or steric repulsion, thus preventing agglomeration of particlesand controlling the particle size and its morphology.

II. Materials and Methods

The linear alkylbenzene sulphonate capped ZnO nanoparticles were synthesized by solvothermal technique with zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$) precursor, diethylene glycol (DEG) as the solvent and LABS as the capping and stabilizing agent.

A solution of 0.5 mol (8.7g) of linear alkylbenzene sulphonate was prepared in 60ml of diethylene glycol in a round bottom flask at a dissolution temperature of 120^{0}C on a magnetic stirrer hotplate. 1.0mol (13.2g) of zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$) was added to the solution and stirred to dissolve completely in the solution. The mixture was heated on the mantle heater at a steady temperature of 190^{0}C for 1 hour. The solvothermal synthesis was completed at 190^{0}C. Electronic centrifugeset at 3000RPM was used to

separate the ZnO nanoparticles from the mixture. Excess ZnO nanoparticles grown on the flask was washed with methanol. Precipitation and segmentation of the ZnO nanoparticles were carried out using propanol. A milky liquid of the ZnO nanoparticles obtained was transferred to a crucible boat and dried in an electric oven at 60^0C for 12 hours. White powder of ZnO nanoparticles was obtained.

The crystal structures of the synthesized ZnO nanoparticles were studied using Raman Spectroscope (Model No. Pro Raman-L-785-BIS). Malvern Instrument (Zetasizer Version 7.01) was used to study the size distribution by intensity, size distribution by volume and size quality of the ZnO nanoparticles. Malvern Zetasizer (Nano Range) by the Dynamic Light Scattering (DLS) technique was employed. 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).

The ZnO nanoparticles sample produced with LABS was characterized using Raman spectroscopy. Figure 1 shows the Raman spectrum of ZnO nanoparticles capped with linear alkylbenzene sulphonate. The Raman shift or peak of 408cm^{-1} and 424cm^{-1} observed in the spectrum fall within the region of the functional group (vibration) of 150cm^{-1} to 450cm^{-1} for metal oxides (HORIBA, 2019).The main peak E_2(high) at 424cm^{-1} has strong and sharp Raman band with the highest intensity which indicated a high concentration of ZnO nanoparticles. E_2(low) was 408cm^{-1}. 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). In Raman spectroscopy, the E_2 mode is nonpolar with two modes, namely a high-frequency E_2(high) and low-frequency E_2 (low) modes, which are the characteristics of wurtzite-structured ZnO (Khan, 2014).This shows that the sample contained ZnO nanoparticles with wurtzite (hexagonal) crystal structure, which is the stable structure of ZnO.

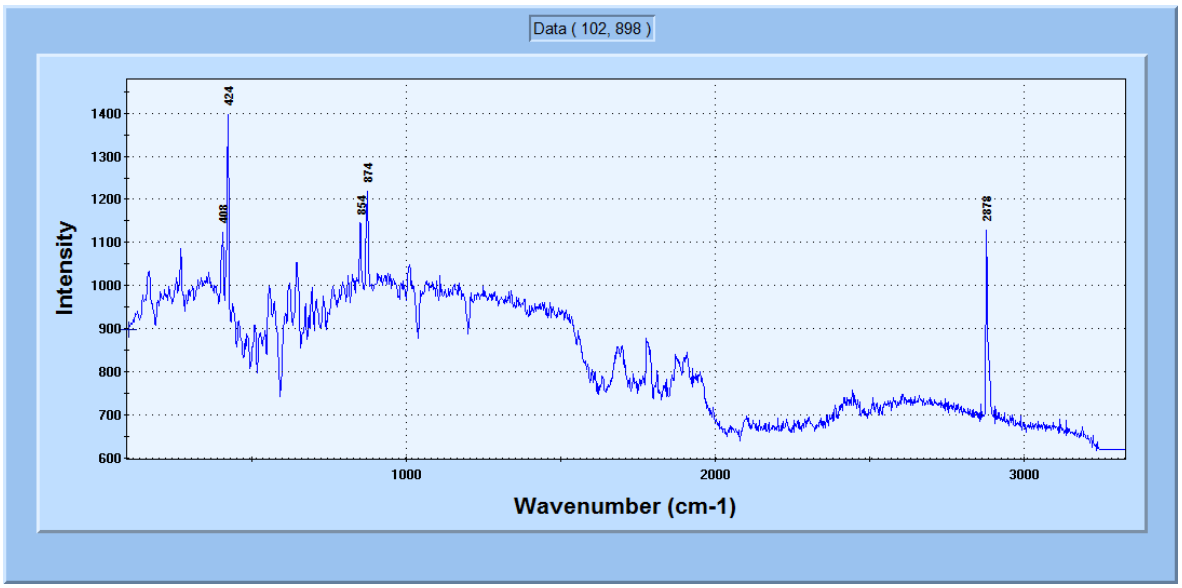

Figure 1 Raman spectrum of ZnO nanoparticles produced with LABS.

The bands at 854cm^{-1} and 874cm^{-1}correspond to the functional group of O-O stretching vibration mode of oxygen present in zinc acetate salt (Tapan *et al*., 2001). The observed peak at 2878cm^{-1} corresponds to C–H stretching vibration mode which can be associated with the presence of propanol in the sample. This is in agreement with bands 2970 to 2850 cm^{-1}, 2990 cm^{-1} and 2420 cm^{-1} of 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 Z-average diameter for the distribution was 715.2nm and Polydispersity index (PdI) was 0.431. Thus, the solution of ZnO nanoparticles from the sample contained average particle size of 715.2nm with polydispersity index of 0.431 which was a clear indication that the synthesized ZnO nanoparticles with LABS were monodispersed in nature. Figure 2 demonstrates the size distribution by volume of the ZnO nanoparticles produced with LABS. Three peaks (1, 2 and 3) were observed from the distribution. Table 2 indicates that the particles within peak 1 occupied 97.3% of the entire volume of the ZnO nanoparticles in the sample. Peaks 2 and 3 occupied 1.8% and 0.9% respectively. The results indicated that ZnO nanoparticles of 981.1nm were predominantly present in the sample.

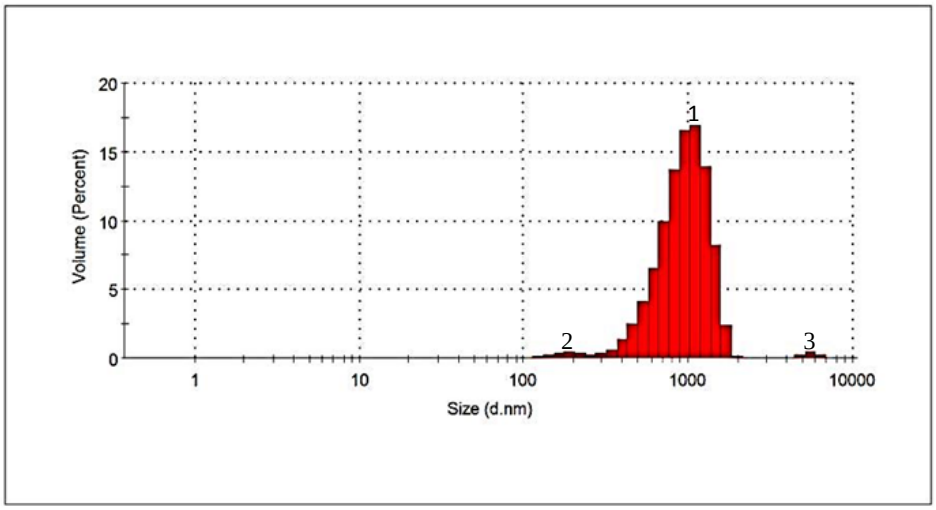

Figure 2 Size distribution by volume of LABS – capped ZnO nanoparticles

Tables 2 Results of size distribution by volume of ZnO nanoparticles produced with LABS

Peak	Size (d.nm)	% volume	Standard Deviation
1	981.1	97.3	311.70
2	188.5	1.8	39.58
3	5534.0	0.9	607.5

The results of the size distribution by volume proved that ZnO nanoparticles synthesized with LABS were of good quality.

Figure 3 shows the size distribution by intensity of ZnO nanoparticles produced with LABS. Three peaks were observed. Table 3 shows the results of size distribution by intensity of ZnO nanoparticles produced with LABS. Peak 1 has 90.9% of the particles with average diameter of 787.1nm. Peaks 2 and 3 have intensities of 8.2% and 0.9% respectively. The results demonstrate that the ZnO nanoparticles produced with LABS as a capping agent were of good quality.

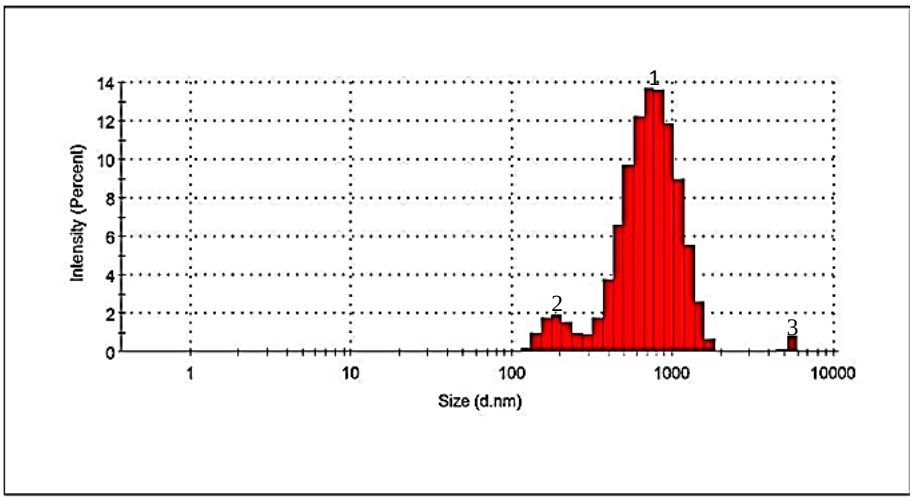

Figure 3 Size distributions by intensity of ZnO nanoparticles with LABS

Tables 3 Results of size distribution by intensity of ZnO nanoparticles produced with LABS

Peak	Size (d.nm)	% intensity	Standard Deviation
1	787.1	90.9	283.50
2	202.3	8.2	47.59
3	5478.0	0.9	235.60

The value of Z-average of the sample with LABS was very close to Z-average 735nm of ZnO nanoparticles dispersed in water (Marsalek, 2014). However, the result differs greatly from Z-average of 145.1 nm with PdI of 0.189 for ZnO particles synthesized using ixora coccinea leaf extract (Yedurkar *et al.*, 2016), Z-Average size of 46.61 nm and Polydispersity index of 0.552 from extracellular synthesis of zinc oxide nanoparticle using seaweeds o*f* gulf of Mannar, *India* (Nagarajan *et al.*, 2013) and Z-average of 64.4nm and PdI of 0.418 from ZnONPs from Vitis vinifera Peel Extract (Divya *et al*., (2018). The disparities in Z-average diameters and Polydispersity Indices could be because the results depended on the dispersant used, its refractive index and viscosity, the measurement technique, synthesis techniques and the purpose for which the ZnO nanoparticles was be used.

Figure 4 is a graph of size distribution by intensity of ZnO nanoparticles produced while Figure 5 is a graph of raw correlation data of the intensity distribution. It was evident that there was a relationship between the size distribution and the intensity of the ZnO nanoparticles. The positive correlation coefficients indicate a positive linear relationship between the size distribution and intensity of the ZnO nanoparticles present in the sample. Hence, the result met the quality criteria.

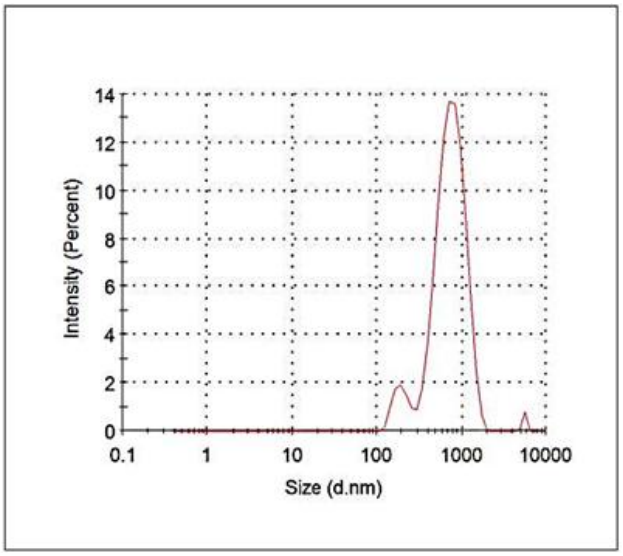

Figure 4 Graph of particles size distribution by intensity of ZnO nanoparticles produced with LABS

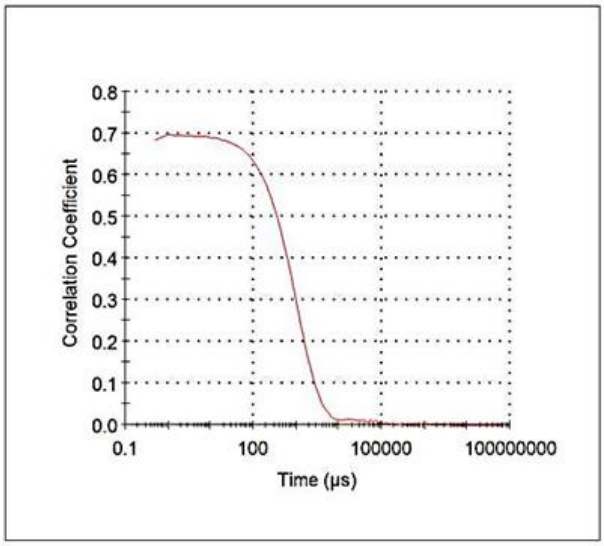

Figure 5 Graph of raw correlation data

The intercept was used to evaluate the signal-to-noise ratio and the quality of the ZnO nanoparticles. Figure 6 shows the correlation function of the intensity distribution.The correlation function intercept was 0.831 which is in agreement with ISO 22412 (2017) specifications of suitable values of 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.

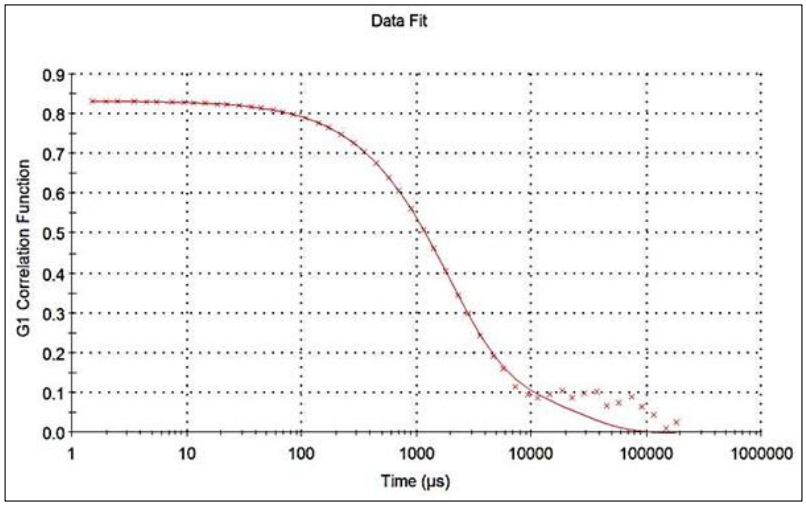

Figure 6 ZnO nanoparticles intensity distribution fit

Figures 7and 8 respectively show the correlogram for the cumulants and the cumulants fit error obtained from the analysis of the data with cumulants. The cumulants fit error determines whether the polydispersity (PdI) and Z-average diameter obtained from the analysis are reliable values. The cumulants fit error was 8.27 x 10^{-4}. The cumulants fit error is much less than 0.005 which is ISO 22412 limit for reliability of the cumulants. Thus, PdI and Z-average diameter obtained from the synthesized ZnO nanoparticles were reliable values. Hence, the ZnO nanoparticles are monodisperse and of good size quality.

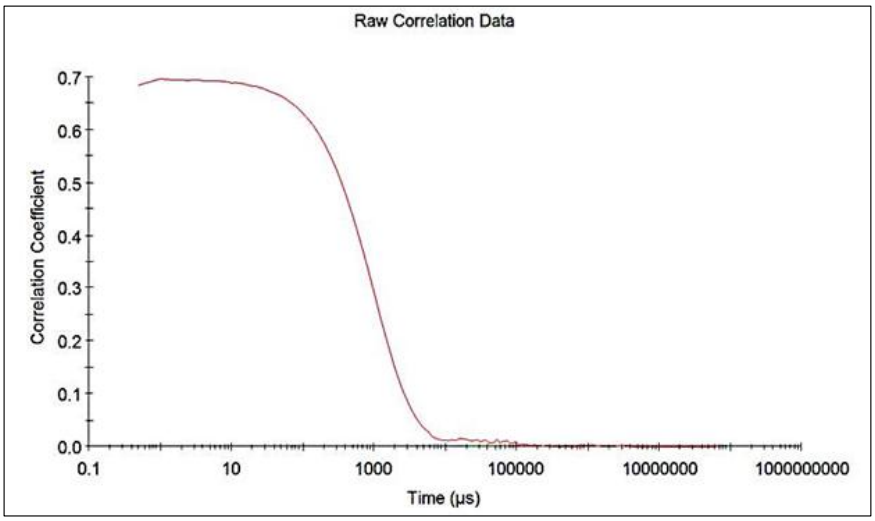

Figure 7 Correlogram for the cumulants for the ZnO nanoparticles

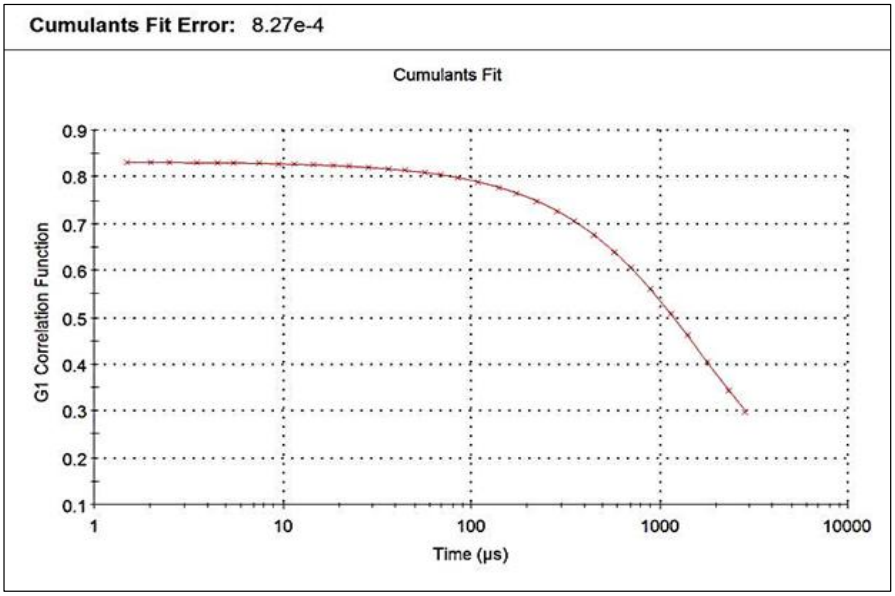

Figure 8 Cumulants fit for the ZnO nanoparticles

III. Conclusion

Zinc acetate dehydrate (precursor) was solvothermally synthesized to ZnO nanoparticles in diethylene glycol (solvent) with linear alkylbenzene sulphonate as the capping agent. The solvothermal synthesis was successfully completed at 190^0C. The Raman E_2(high) of 424cm^{-1}indicating a wurtzite hexagonal structure was obtained. The synthesized ZnO nanoparticles have good crystallinity and stable structure. The Z-average diameter was 715.2nm and polydispersity index (PdI) was 0.431. The cumulants fit error was 8.27 x 10^{-4} which indicates good size quality and monodispersity of the ZnO nanoparticles. ZnO nanoparticleswith diameter of 981.1nm occupying 97.3% of the entire volume were dominant in size distribution by volume.In size distribution by intensity ZnO nanoparticles with diameter of 787.1nm occupying 90.9% of the entire volume dominated. The results obviously indicate that linear alkylbenzene sulphonate is a good capping material for solvothermal synthesis of ZnO nanoparticles.

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