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Back scattering from nano-sized ZnO colloids

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Abstract

We report enhanced back scattering in nanometer-sized ZnO colloids prepared in two different media, by different methods. The FWHM of the back scattered cone and hence the mean free path varied with concentration of ZnO as well as particle size. The Lorentzian profile of backscattered cone indicates the presence of coherence.

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1. Introduction

Light scattering experiments have enjoyed renaissance after the invention of lasers and have gained prominence as potential applications of quantum optics and photon localization are conceived. Coherent backscattering (CBS), the hottest topic in this area, refers to the enhancement in the intensity of light scattered in the exact backward direction. Moving away from this exact backward direction, phase differences will develop and average out the interference effect. The result is a cone on top of diffuse background. The width of this cone will be inversely proportional to the mean free path and hence is a measure of the amount of scattering inside the sample. The backscattering cone contains information about parts deep inside the sample, regions that cannot be accessed with normal optical techniques and hence is a powerful tool in characterizing any random medium-like colloidal suspensions.

Since the first experimental observation CBS from colloidal suspensions [1], extensive work has been done in this area, most of which is in the strong localization region where size of the particle is of the same order as the wavelength used [2,3]. Some recent studies in CBS from liquid crystals have observed systems with larger mean free paths that we usually encounter in the classical localization studies [4]. Study of scattering from Bose Einstein condensates (BEC) of atoms are also reported to show CBS resulting in very narrow cones of a few milliradians [5]. Most of the results have been explained on the basis of Mie theory [6,7]. In the present study, we report the back scattering from dilute colloids of ZnO of the size of a few nanometers. A systematic variation in the width of the backscattered cone with concentration is observed in all the cases.

Colloids of ZnO are prepared in two different media by two different methods. In the first case, colloids are synthesized by a polyol precipitation method. Synthesis in the polyol medium has the advantage that the high melting point of the polyols offers a wider range of operating temperatures, which permit the precipitation to be conducted at atmospheric pressure. Among the different polyols, diethylene glycol (DEG) is chosen because it is reported to give powders with uniform shape and size distribution [8]. The method of preparation involves the hydrolysis of zinc acetate dihydrate (ZnAc;Merck) in DEG medium (DEG;Merck). Different molar concentrations of

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the salt is added to DEG and heated slowly to 160 °C and a milky white precipitate is formed in a few minutes at this temperature. A short aging time is given to obtain a high yield of the precipitate and clusters composed of small crystallites of ZnO are formed. The size of the particles and hence the stability of this colloidal suspension depend on the concentration of zinc acetate as well as on the rate of heating. Up to molar concentrations of 0.05 M, the colloids formed are highly stable for a heating rate of 4 °C/min. Above this concentration, colloids are stable only for 1–2 h, beyond which the particles aggregate and settle. However by ultrasonification, this colloid can be uniformly dispersed for further measurements. When higher heating rates are employed, precipitation occurs even at lower concentrations. In the present study, we have used 0.0025 M precursor solution and a heating rate of 4 °C/min.

In the second method, colloidal ZnO quantum dots are prepared in isopropyl alcohol, by controlling the size using a capping agent, viz., polyvinyl pyrrolidone (PVP) (MW4000). About 0.5 mM zinc acetate solution in Isopropyl alcohol (Merck, HPLC grade) was prepared with stirring at 50 °C. About 0.2 mM PVP (Sisco) was added with stirring. It was then hydrolyzed with 1.25 mM NaOH under ultrasonification for 2 h. This gave different particles sizes according to different PVP:ZnAc ratio. Cooling both ZnAc and NaOH precursor solutions to 4 °C before mixing helps in keeping the particle size minimum [9].

The ZnO colloids synthesized by the two routes are characterized by optical absorption measurements. From the shift of absorption edge, size of the dots is calculated. To get a precise measure of the shift, the first derivative curve of the absorption spectrum is taken and the point of inflection is taken as the absorption edge. Particle size is commonly calculated from the shift of the band edge by theories based on effective mass approximation (EMA) which has the problem of overestimating the size in the small size region [10]. Hence we have used the new empirical formula suggested by Viswanatha et al. [11] as follows:

$$E_g = 100(18.1d^2 + 41.4d - 0.8)^{-1}, \quad (1)$$

where E_g is the shift in the energy band gap and d is the diameter of the particle. When calculated using the above formula, the cluster size is 9 nm in the DEG method and between 4 and 5 nm in PVP capped case. Fig. 2 shows the room temperature absorption spectra of the different samples capped with varying amounts of PVP.

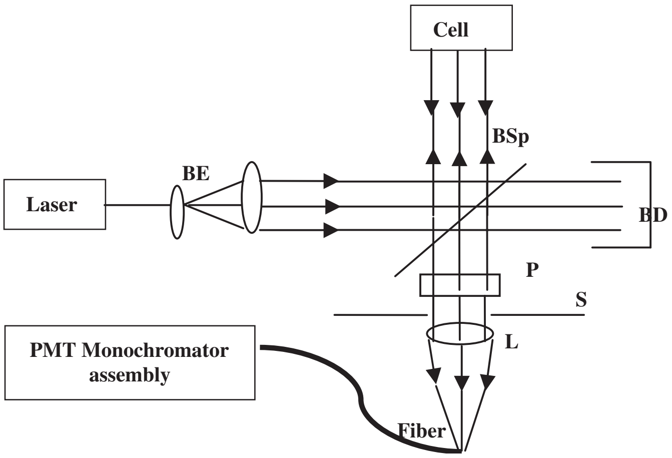

Fig. 1. Schematic representation of experimental setup. BE: beam expander, BSp: beam splitter, BD: beam dump, S: screen, P: polarizer, L: lens, and PMT: photomultiplier tube.

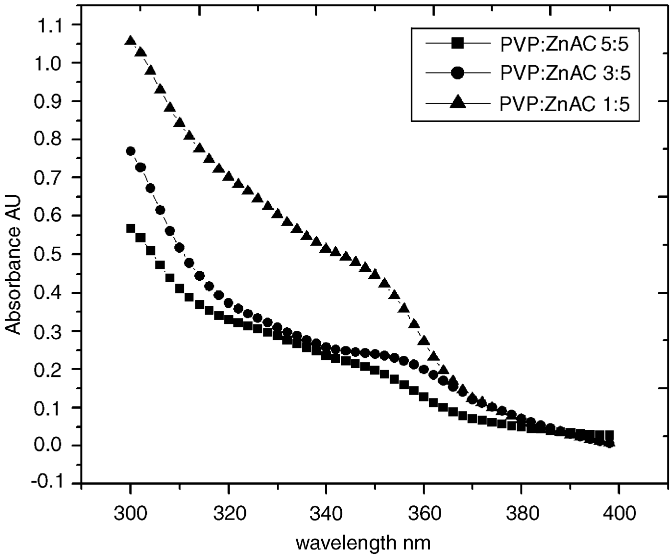

Fig. 2. Absorption spectra of samples of ZnO samples capped with varying concentrations of PVP.

In our back scattering experiment shown in Fig. 1, the source of light is a diode pumped solid state laser (DPSS BWT 50, 40 mW, 532 nm). The beam expander (BE) assembly provides a collimated parallel beam with less divergence. The half-silvered mirror allows observations in the exact backward direction. The sample cell is turned slightly so that specular reflection from the glass cell is kept away from the detector. After passage through lens, L, the beam is focused onto a fiber tip of diameter connected to a monochromator-PMT setup. The output of the DPSS was plane polarized. This together with polarizer P ensured detection in polarization preservation channel.

The back scattering cone for DEG sample is shown in Fig. 3. The concentration of sample is varied by adding known volumes of pure DEG to the ZnO colloid. The Lorentzian profile of backscattered cone indicates the presence of coherent structure. Relationship between backscattered cone width (θ) and mean free path (l) is

$$\theta = 0.7\lambda/2\pi l, \quad (2)$$

where λ is the wavelength of light used. Since mean free path decreases with increase in concentration, we expect enhancement in BS cone width as is clearly seen in Fig. 4. In the present case, magnitude of mean free path varies from 36.13 to 43.61 as the concentration of ZnO in DEG

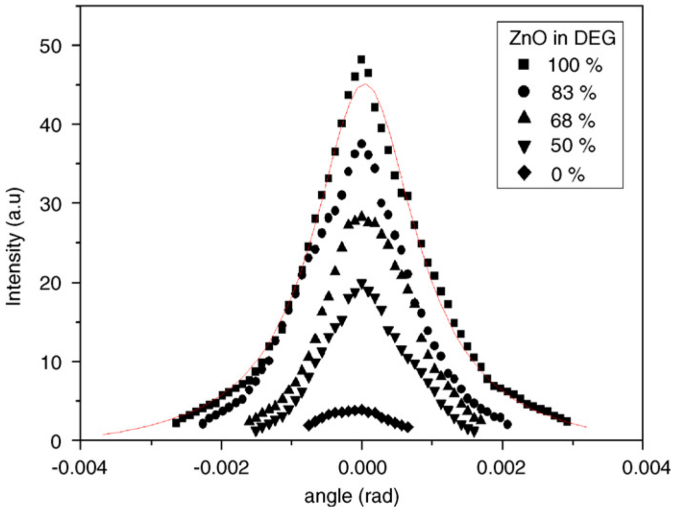

Fig. 3. Back scattering profile for various volume percentage of ZnO in DEG.

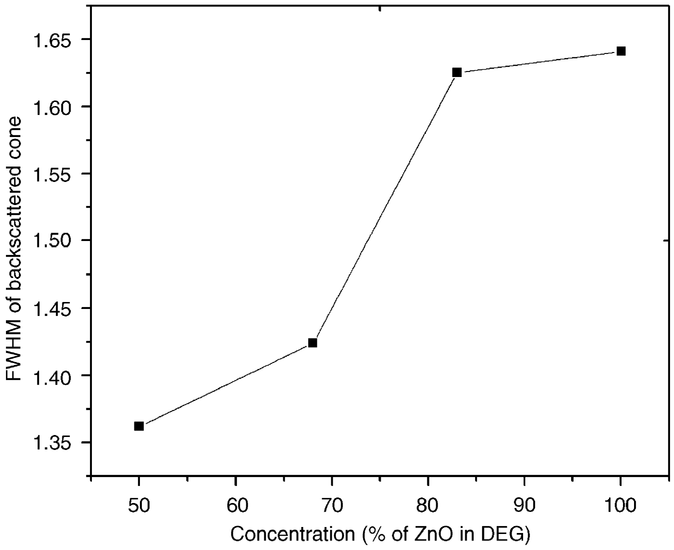

Fig. 4. FWHM of back scattering cone versus concentration of ZnO in DEG.

decreases from 100% to 50%. Fig. 4 gives the plot of FWHM of back scattering cone versus concentration. Here amount of pure DEG added (in ml) to ZnO colloid so as to keep the total volume as 3 ml is plotted.

For the ZnO samples capped with PVP, size varies with PVP ratio. Table 1 shows that as we change PVP:ZnAc ratio, the particle size shows a small but definite change. This is accordingly reflected in the backscattering profile as well. Fig. 5 shows the back scattering profile for samples with gradually increasing PVP concentration.

From the back scattering data, we can see that the back scattered cone width and hence the mean free path shows inverse dependence with dilution. The fact that the mean free path of half-dilution is almost 1/1.414 of that of undiluted sample, matches with the diffusion approximation. In the case of capped samples, increasing the ratio of the capping agent slightly but gradually decrease the size of the quantum dots in the range between 3–5 nm. This trend is observed in the back scattered cone width too.

Table 1
Particle size variation with PVP concentration

PVP:ZnAc ratio	E_g (eV)	Size ± 0.5 nm
5:5	3.3668	2.6
3:5	3.647	3.4
1:5	3.594	4.6

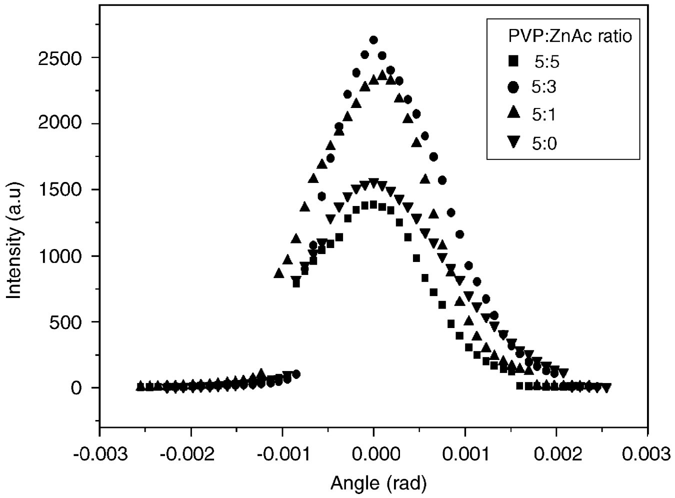

Fig. 5. Back scattering profile for ZnO capped with varying amounts of PVP.

2. Summary

Backscattering of light from colloidal suspension ZnO particles of nanometer size has been investigated and is found to be a good method to characterize and study the colloidal medium. The width of the scattering cone decreases with the concentration of ZnO in DEG as well as ZnO size in the case of PVP capping. The profile exhibits Lorentzian one, which characterizes the coherent nature of BS light. We are modifying the experimental setup to get better resolution in the scattering cone with respect to coherent and incoherent scattering.

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