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Surfactant assisted one-pot hydrothermal synthesis of nano zno and its property observations

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Abstract : Recent developments on materials science acknowledges the objectives of the synthesis of nanoparticle with definite dimensions, size and structure to derive the materials with unique features. Zinc oxide (ZnO) is a familiar semiconductor material exhibit quantum confinement effects within the size range of particle can be accessible experimentally. Particularly, the electronic and optical properties of ZnO is a fascinating one in nano scale regions. In the present work, two nano sized ZnO (n-ZnO) samples were prepared by varying the amounts of surfactant, ethylenediamine ($C_2H_4(NH_2)_2$) using the precursor zinc acetate dihydrate ($Zn(CO_2CH_3)_2.2H_2O$) employing one-pot hydrothermal method. The influence of surfactant in n-ZnO formation is to be explored by changing its content during synthesis while other parameters are remain constant. The structural and crystalline features of the prepared samples were studied employing powder X-ray diffraction (XRD) technique. The results ensured the wurtzite crystalline structure and the crystallite size of the prepared samples were observed to lie within nano scale region. It reveals the weak quantum confinement effect in the prepared samples. The UV-Vis absorption spectroscopy helps to infer the reduction in band gap value than bulk ZnO. The attributes of sample morphology were observed using the scanning electron microscopic (SEM) images. It helps to depict the random distributions in particle size and dimensions of n-ZnO prepared with the content of surfactant 7mL. While increasing the surfactant as 10 mL, the n-ZnO particles could be obtained the particles with almost unvarying dimensions. The transmission electron microscope (TEM) observations supports the freakish emergence of particles as shown in SEM images.

Keywords: Surfactant, one-pot hydrothermal, nano zno, property observations.

Introduction

Nanomaterial gains prodigious attention for the past few decades mainly because of the novel phenomena in nanoscale dimensional dependent properties. Nanotechnology acknowledges the evolution of

novel properties in wide variety of materials leads to have extensive developments in numerous fields. ZnO is one of such a comprehensive material having multifaceted attributes suitable for broad scope of applications. It is known well that ZnO is a type of II-VI compound semiconductor has band gap value of 3.37 eV effectively applied in devices such as chemical sensors, photovoltaics, piezoelectric transducers and single electron transducers[1-7]. Recent developments of nanoscience and technology shed lime light on nano scaled ZnO as result of high surface area and quantum confinement effect.

The unique functionalities of n-ZnO are mainly depends on its structural and dimensional features such as particle size, shape, morphology, orientation, crystallite size and aspect ratio. Hence, the optimisation of synthesis parameters which are all responsible for altering the dimensional aspect of the nano ZnO gains more significance. In the development of nano sized ZnO, distributions of particles within narrow range with controlled and reduced agglomerations is always a challenge. Numerous attempts were made for the past few decades to develop nano ZnO with controlled attributes. Utilisation of different capping agents to control the dimensional characters of ZnO is one of the interesting routes successfully employed in recent efforts[8-10]. It is proven well that nano ZnO can be prepared with desired dimensions while using the precursor zinc acetate with suitable organic additives as a modifying and protecting agent[11,12]. Although many factors involved in nanoparticle synthesis for tuning up its characters, addition of surfactant is a promising way helps to obtain the particle aspects as required[13]. Role of surfactant is more crucial in nanomaterial synthesis. It establishes a controlled synthesis such as prevention of coalescence and recoalescence of particles, reduction in the interfacial tension of nano emulsion, etc. helpful to obtain the nano scale product. It describes the significance of preparation method and its functional parameters rather than the composition of constituent materials.

In the present work, two different nano sized ZnO material is proposed to prepare employing one pot hydrothermal method at the function of amount of surfactant, ethylenediamine ($C_2H_4(NH_2)_2$). By observing the structural, optical and morphological properties of the prepared samples, the influence of surfactant in determining the functional properties of ZnO can be explored. The X-ray diffraction characterisation (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), UV-Vis absorption spectroscopy are the characterisation studies employed to reveal the structural, morphological and optical properties of the prepared samples.

Experimental

Chemicals with 99.9% purity procured from Sigma Aldrich used without any more purifications for the synthesis of ZnO nanoparticles. The precursor solution was prepared with the desired amount of zinc acetate dihydrate ($Zn(CO_2CH_3)_2.2H_2O$) dissolved in 75 mL of de-ionised water under continuous magnetic stirring at room temperature. In nano ZnO synthesis, the precursor zinc acetate is a best opt due to its low decay temperature and very good solubility[14]. The content of surfactant ethylenediamine ($C_2H_4(NH_2)_2$) was added as 7 mL and 10 mL, respectively in two different synthesis attempts. Based on the surfactant content the samples were named here after as Z7 and Z10. The surfactant was added for 30 min. drop wise in the above solution at constant rate of stirring till obtain white precipitate in the homogeneous mixture of solution. A hydrothermal autoclave treatment was employed with the above prepared homogeneous mixture of solution at 200 °C for 15 hrs by kept in 100 mL Teflon liner vessel. The resultant material was collected from the autoclave after cooling to room temperature and washed with water and dried using hot air oven at 100 °C. The characterisation studies X-ray diffraction (PANalytical system, X'Pert PRO, The Netherlands), High Resolution Transmission Electron Microscopy (JEOL TEM 2010), High Resolution Scanning Electron Microscopy (Hitachi S-3000N, Japan), Photoluminescence (Jobin-Yvon Fluorolog-3 spectrofluorimeter USA) and UV–vis spectroscopy (UV, BECKMAN COLTER DU 800, Conquer Scientific, San Diego, CA, USA) were employed for property observations.

Results and Discussion

The observed X-ray crystallographic results shown in Fig.1 ensured the emergence of crystallinity in both samples Z7 and Z10. It is interesting to note that the emerged characteristic peaks are well defined and quite similar. The results confirm the wurtzite phase of ZnO without any impurities and found agree well with the JCPDS file No.36-1451. The crystalline quality of the n-ZnO samples were evaluated by obtaining the data Full Width at Half Maximum (FWHM) from the characteristic peaks of the XRD traces shown in Fig.1. The crystallite size (D) of the prepared ZnO nanomaterial were estimated using the Scherrer's formula[15] given in

equation (1) applying the details of λ, the wavelength used for X-ray radiation (Kα(Cu) = 0.154056 nm), β, the full width at half maximum (FWHM) of the diffraction peak and θ, the Bragg diffraction angle.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad \text{---------- (1)}$$

The measured crystallite sizes emerged in the samples Z7 and Z10 are tabulated in Table 1. The observed crystallite size values doesn't record large variations rather exhibit almost similar around 30 nm. It is interesting to note that the average crystallite sizes were found to be as 32 and 33 nm respectively for Z7 and Z10 samples. ZnO is well known material for its strong quantum confinement effect. It is meant that the crystallite size observed experimentally to be much lesser than the Bohr radius and hence, the confinement of electron and hole separately occur and their movements are independent of each other. But here, the observed crystallite size is much higher, i.e., ≥ 30 nm than the Bohr radius. It evident the weak quantum confinement effect in the prepared samples[16].

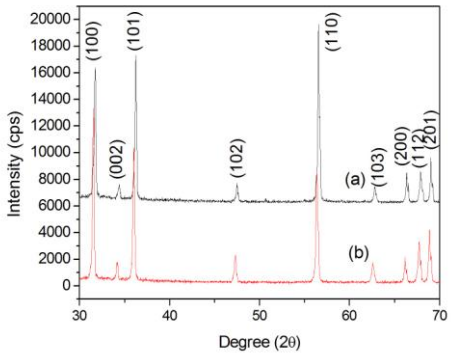

Fig.1. XRD traces of (a) Z7 and (b) Z10 samples ensured resemblance of crystallinity

The obtained SEM images shown in Fig. 2 (a) and (b) respectively, depicts the morphological details of the prepared samples Z7 and Z10. A random distribution of shape and size of ZnO particles found in Z7 while the sample Z10 exhibit almost invariant dimensional features with the average particle size of 81 nm. It reveals the influence of surfactant content in determining the dimensional aspects of particles. The influence of surfactant helps to form the dynamic colloidal templates such as nanoemulsion consists of nano meter sized droplets and thereby produce nanoparticles by reducing the interfacial tension and pressure difference inside and outside the droplet[13].

The size of water droplet plays a crucial role in nanoparticle synthesis, it can be stabilised by adding suitable surface active agent. The droplets size can't be exceeded easily since it requires ample amount of energy as it is covered by the surfactant film with finite bending modulus. It is explained elsewhere that the size and shape of nano droplets varied based on the free energy of curvature which depends on the curvature of the added surfactant film and its elastic constants[17]. While increasing the content of surfactant inturn helps to reduce the surface tension and enhance the phase dispersion leads to smaller the droplets and prevents the further droplet coalescence. Thus, the addition of surfactant is the key in nanomaterial synthesis and to restrict the particle size and shape within a desired limit. The growth of homogeneous nanostructures within a restricted particles size can be achieved by increasing the amount and concentration of surfactant. The obtained SEM results of Z10 confirms the yield of regulated particle dimensions nearly spherical at the increased surfactant additions.

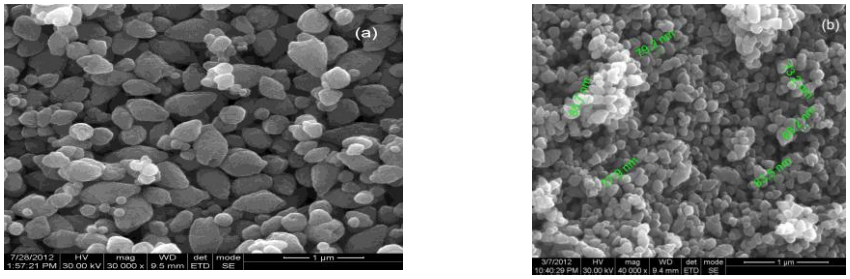

Fig. 2. SEM images of samples (a) Z7 and (b) Z10 exhibit the morphological difference

Table 1. Crystallite size observations using XRD diffraction peaks.

S. No.	2 Theta (deg)		Theta (deg)		FWHM (rad)		Crystallite size (nm)	
	Z7	Z10	Z7	Z10	Z7	Z10	Z7	Z10
1	31.74	31.54	15.87	15.77	0.00481	0.00494	31	30
2	34.42	34.20	17.21	17.1	0.00503	0.00506	30	30
3	36.24	36.02	18.12	18.01	0.00460	0.00456	33	33
4	47.5	47.32	23.75	23.66	0.00545	0.00490	29	32
5	56.56	56.38	28.28	28.19	0.00467	0.00424	35	39
6	62.84	62.60	31.42	31.3	0.00631	0.00555	27	31
7	66.34	66.16	33.17	33.08	0.00505	0.00463	34	37
8	67.88	67.72	33.94	33.86	0.00516	0.00536	34	33
9	69.02	68.86	34.51	34.43	0.00498	0.00492	35	36

The observed TEM image given in Fig. 3 supports of the emergence of multifaceted features in sample Z7. It is clearly exhibit the existence of nanoparticles at random structures including spindle, sphere, rod, pyramid, etc. at various sizes. Yang Yang et al reported the inhomogeneous growth of nanoparticles while using zinc acetate precursor without any surface active agents[18].

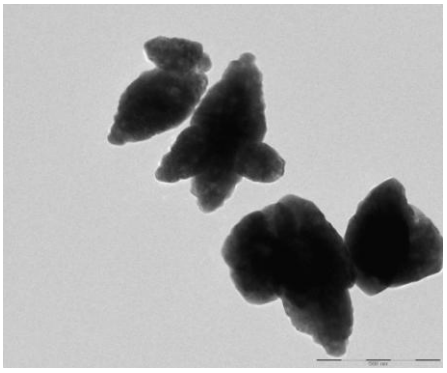

Fig. 3. TEM image of Z7 sample exhibited the random distribution of particles

The present results reveal that though the addition of surfactant ethylenediamine ($C_2H_4(NH_2)_2$) yields the ZnO in nanoscale, its addition up to 7mL doesn't derive the particles with homogeneous structure. The figures 4 (a) and (b) exhibit the UV-Vis absorption spectrum of the prepared nano ZnO samples Z7 and Z10 respectively. In sample Z7, no sharp absorption peak was observed rather a curve at 387 nm is noticed in the obscure trace. The UV spectrum of Z10 shown in Fig. 4 (b) is well defined with sharp absorption peak 372 nm. The estimation of band gap energy (Eg) employing Tauc relation given in equation (2) by characterizing the UV-Vis. absorption spectrum.

The Tauc relation[19] is given by,

$$\alpha h\nu = A(h\nu - Eg)^n \text{ ----------} \quad (2)$$

Where E_g the band gap, A is the proportionality constant different for different transitions, (hν) is energy of photon and n is an index of values ½, 3/2, 2 and 3 depends on the nature of electronic transition responsible for the absorption.

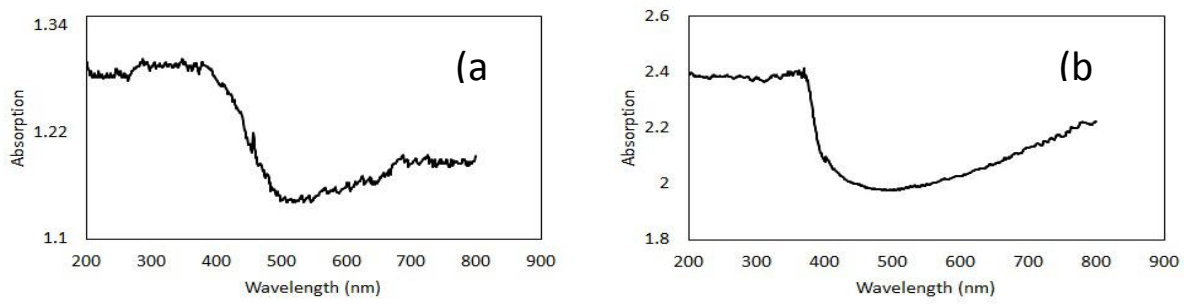

Fig. 4 U V-Vis absorption spectrum of samples (a) Z7 and (b) Z10

The drawn Tauc plot of samples Z7 and Z10 exhibit in figure 5 (a) and (b) taken the photon energy (hν) on the X axis and $(\alpha h\nu)^2$ on the Y axis. The band gap energy (Eg) value obtained by extrapolating the linear portion of the curve to the X axis yields the energy gap values 2.95 and 2.85 eV. Both of these values are lower than that of bulk ZnO (3.37 eV).

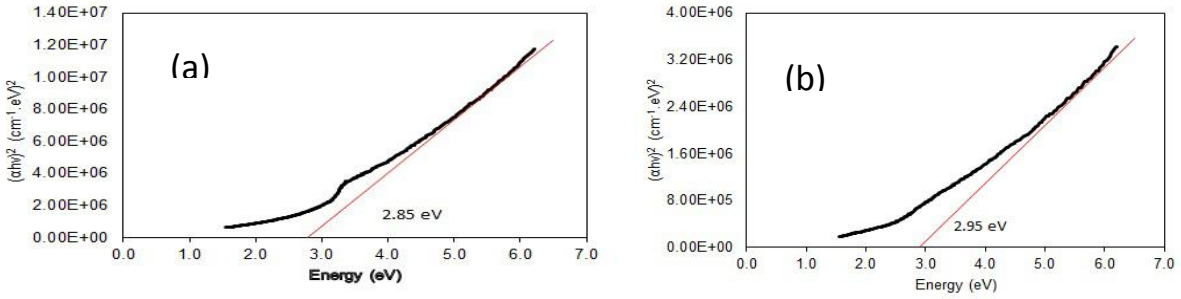

Fig. 5. Tauc's plot for deriving band gap energy values of (a) Z7 and (b) Z10 samples

Conclusion

The surfactant ethylenediamine assisted ZnO nanomaterial have been synthesised successfully employing one pot hydrothermal method. Structural, optical and morphological properties of the prepared samples were observed and used to explore the role of surfactant and its content in obtaining the nano ZnO with regular attributes. The synthesised ZnO using 10 mL of surfactant is more homogeneous than the sample prepared with 7 mL surfactant. The measured crystallite size values are much higher and confirms the weak quantum confinement effect. Both samples exhibiting the lower band gap energy values than the bulk ZnO.

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