Synthesis and Characterization of Nano-Crystalline ZnO Quantum Dots via Sol–Gel Route for Dye-Sensitized Solar Cells

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ABSTRACT
In this paper, we have synthesized the Zinc oxide Quantum dots (QDs) via simple sol–gel method using the zinc acetate dehydrate, methanol and sodium hydroxide as starting materials. The synthesized sample was annealed at 500°C for 1 hour. We have found good crystallinity and the average crystallite sizes of the QDs ~14 nm for pH value of 9 from X-ray diffraction and Transmission electron microscopy. We have also found the bandgap as a function of size of the particles was determined using the absorption spectra obtained by UV-Vis-NIR spectrophotometer. The band gap was found to be in agreement with theoretical calculations using effective mass model. The synthesized ZnO QDs were successfully used as the electrode material for dye-sensitized solar cells.

KEYWORDS:- *ZnO, Nanoparticles, Sol–gel method, pH, Optical properties, Structural properties.*

I. INTRODUCTION

Zinc Oxide (ZnO) is an II-VI semiconductor with a wide and direct band-gap of 3.3 eV and a high exaction binding energy of 60 meV at room temperature [1]. ZnO is considered a good candidate for transparent conducting electrodes in solar cells because it is transparent to the visible light. It is also considered as a prime candidate for UV and blue light-emitting devices such as blue LED and Lasers due to its large exciton binding energy of 60 meV [2]. Zinc Oxide is a scientifically important material, specifically for the areas where high transmittance to visible radiation needs to be combined with good electrical conductivity. Due to its excellent properties as a semiconductor material like high electron mobility, high thermal conductivity, good transparency, wide direct band gap (3.37 eV), large exciton binding energy and easiness of growing it in the nanostructure form make ZnO suitable for optoelectronics, transparent electronics, lasing, sensing, and wide range of applications [3-5].
Morphology, crystal type, crystal size, particle shape, particle size distribution, degree of agglomeration, porosity etc. are some of the properties that determines the characteristics of the powder making it suitable for specific applications. These properties are dependent on the conventional and non-conventional methods used for the preparation of zinc oxide powder. Among these are precipitation from solution, solution combustion, hydrothermal synthesis, emulsion evaporation, microwave synthesis, spray pyrolysis, freeze-drying and sol-gel process [6-10].
In the present work, we have synthesized ZnO QDs via sol-gel route and tried to analyse the crystallite size, bandgap and structural properties. X-ray diffraction (XRD) is used to calculate crystallite size. The bandgap as a function of size of the particles is determined using the absorption spectra obtained by UV-Vis-NIR spectrophotometer. Transmission electron micrograph (TEM) is shown to clearly see the particle size and grain size respectively.

II. EXPERIMENTAL DETAILS

Preparation of ZnO nanocrystalline Quantum Dots (QDs)
The ZnO solution was prepared by dissolving a precursor zinc acetate dihydrate [Zn (CH3COOH)2. 2H2O] (purity 99.9%) (Merck Extra pure chemical Ind. Ltd, India) in methanol (solvent) at room temperature. A solution of 0.5M ZnO thus obtained was ultrasonic at 60°C for 120 min to get a clear solution. The prepared sol was transparent and found to be stable with no precipitate or turbidity. To get the desired pH of the sol sodium hydroxide (NaOH) was added drop by drop to it. Once the desired pH is obtained it is stirred ultrasonically for 60 minutes at room temperature. There

transparent sol was kept for one week to complete the gelatin and hydrolysis process. During this period white precipitates of ZnO crystallized and settled down. The white precipitate was filtered by vacuum filtration technique and washed with excess methanol to remove the starting materials and dried at 500°C for 1h. The filtered crystals are then crushed finely to give zinc oxide nanocrystals [11].

Structure and optical was carried out by various characterization techniques. We used PAN Alytical X'pert PRO diffractometer using CuKα incident beam (1.54A˚) to obtain X-Ray Diffraction (XRD) of nanocrystals. The band gap of ZnO nanocrystalline QDs was measured by optical transmittance using a Shimadzu Solid Spec 3700 double beam spectrophotometer. Optical reflection of the Nanocomposites was obtained using a UV-VIS-NIR spectrophotometer (Shimadzu Solid Spec 3700).

III. RESULTS AND DISCUSSION

Structural analysis

The X-ray diffraction pattern of nanocrystalline ZnO QDs is shown in Fig.1. Three reflections (100), (002) and (101) have been observed, which are similar to the observed reflections in ZnO bulk. The diffraction peaks obtained are strong and narrow indicating that the nanocrystalline ZnO QDs has good crystallinity.

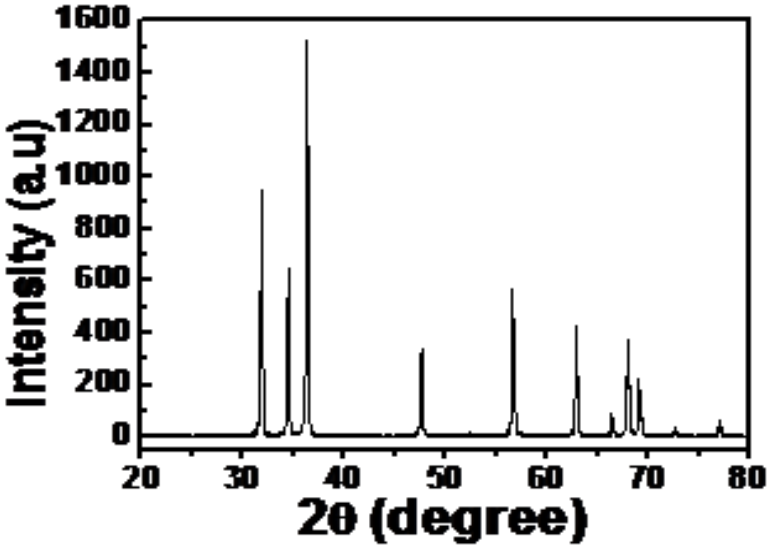

Fig.1 XRD pattern of Nanocrystalline ZnO QDs.

The XRD spectra has been used to calculate the crystallite size of ZnO by scherrer's formula [12]

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where, k is polarization factor, λ is wavelength of CuKα line (1.5406°A) and β is the full width half maximum (FWHM) of (002) reflection peak and is the Bragg's angle about (002) peak. The value of crystallite size thus calculated is coming out to be ~14nm.

The strain induced in powders due to crystal imperfection and distortion was calculated using the formula

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (2)$$

From Equations 1 and 2, it was confirmed that the peak width from crystallite size varies as 1/cosθ strain varies as tanθ.

Assuming that the crystallite size and strain contributions to line broadening are independent to each other and both have a Cauchy-like profile, the observed line breadth is simply the sum of Equations 1 and 2.

$$\beta = \frac{K\lambda}{D\cos\theta} + 4\varepsilon\tan\theta \quad (3)$$

By rearranging the above equation, we get

$$\beta\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\tan\theta \quad (4)$$

The above equations are W-H equations. We have found the strain ~ 0 .00142×10^{-4}.

Transmittance electron microscopy:-

TEM photograph of nanocrystalline ZnO powder at different resolution and diffraction mode are shown in Fig.2. A hexagonal shape of ZnO particles having diameter ~12 nm is observed [Fig. 2(c)]. The selected area electron diffraction (SAED) pattern of ZnO powder is also shown as inset in Fig.2 (d). From the SAED pattern, the diffraction rings show the polycrystalline nature of nanocrystalline ZnO powder. The results of TEM are consistent with the observation from XRD.

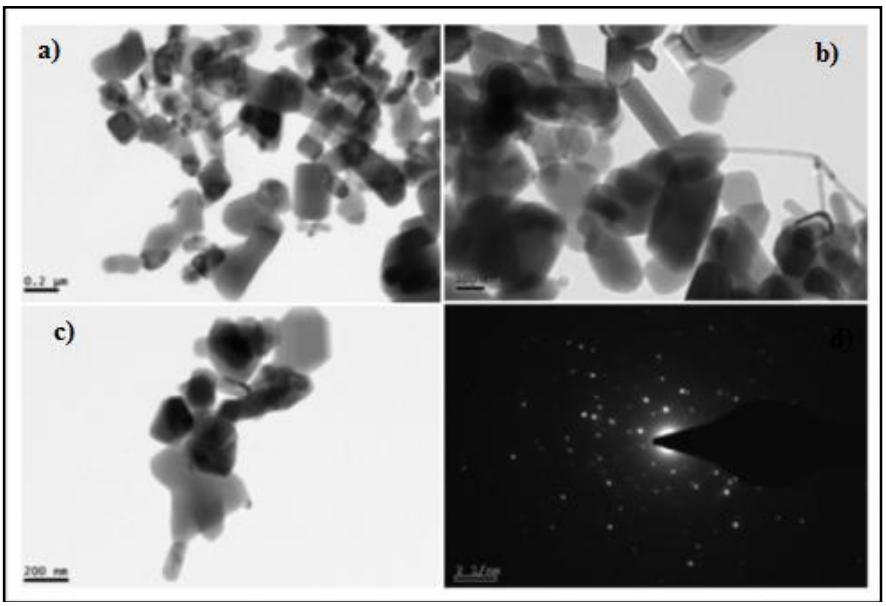

Fig.2 Transfer Electron Microscopy of Nanocrystalline ZnO QDs.

Fourier transform infrared spectroscopy (FTIR):-

FTIR measurement was performed in order to verify the bond structure of ZnO nanoparticles prepared using optimized parameters. Fig.3 shows the infrared absorption spectra of ZnO nanoparticles in the 4000-400 cm-1 wave-number range.

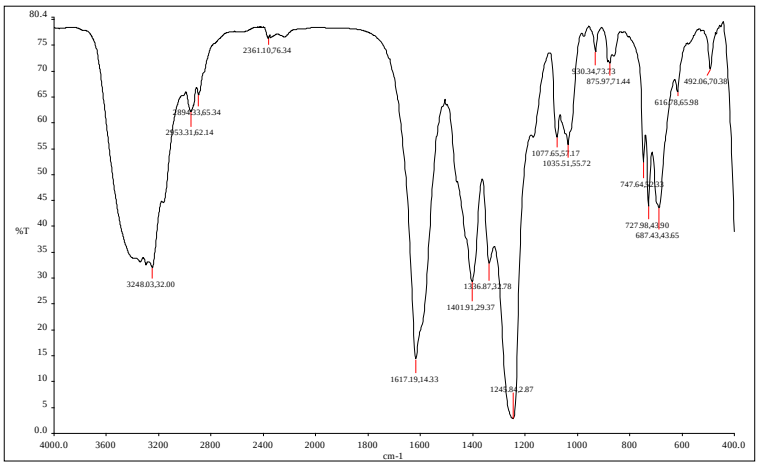

Fig.3. Fourier Transform Infrared Radiation Measurement Nanocrystalline ZnO QDs.

The bands at 3543-3393 cm^{-1} to the O-H mode of vibration. The strong asymmetric mode of vibration of C=O was observed between 1612 and 1560 cm^{-1}. The symmetric stretching occurs between 1453 and 1333 cm^{-1} because of presence of C-O. C-O-C peak is also present there. The IR-spectrum corresponds to nano ZnO QDs with average size about ~14 nm.

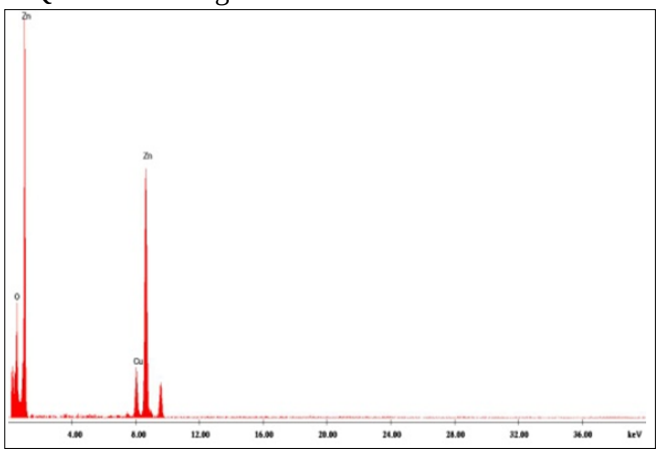

Fig. 4 Energy dispersive X-ray spectroscopy spectrum of ZnO Quantum Dots.

EDX

Energy dispersive X ray spectroscopy (EDX) is chemical Microanalysis technique is a co-junction with TEM, EDX analysis. It was characterized the element composition of the typical EDX pattern of ZnO (Fig. 4). ZnO was Cu = 11.8, O = 17.7, Zn = 70.4 % found. It is also confirmed that all other elements can be removed after degradation of metal from waste water.

Optical properties

The graph between absorbance and wavelength from in the range from 300 to 800 nm is shown in Fig.5. A clear shift towards blue light wavelength has been absorbed in the absorbance graph.

The absorption coefficient α is given by the following equation

$$\alpha = \frac{1}{d}\ln(A) \tag{6}$$

The optical band gap of ZnO Nanocomposites was calculated by Tauc's plot method [13]

$$\alpha h\nu = B\left(h\nu - E_g\right)^{1/2} \tag{7}$$

Where, h is the plank's constant and ν is frequency of incident photon E_g is the optical band gap and B is a constant. Figure 6 shows the Tauc plot [$(\alpha h\nu)^2$ versus $h\nu$] of the ZnO nanocomposites, where α is the absorption coefficient and $h\nu$ is the photon energy. The band gap energy as determined from the Tauc plot is found to be 3.27 eV for ZnO QDs which is corresponding to the bulk ZnO

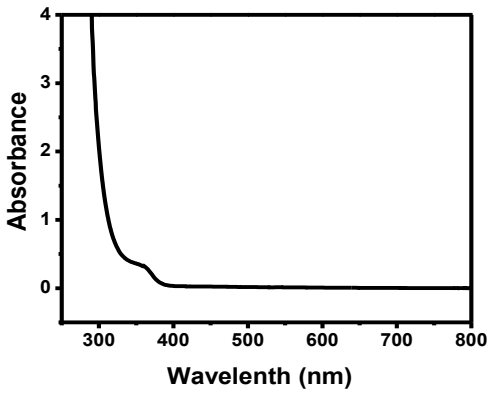

Fig.5 Absorbance Graph for Nanocrystalline ZnO QDs.

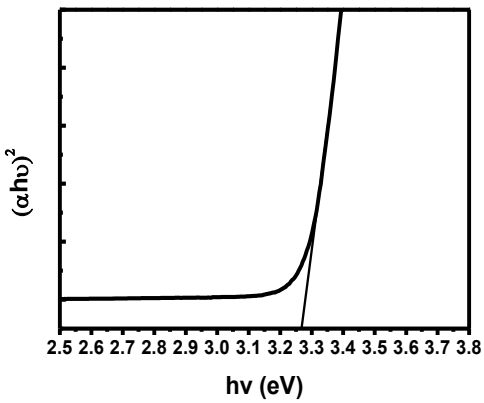

Fig.6 Taucs' Plot for Nanocrystalline ZnO QDs.

The variation in the band gap of Nanocomposites can also be evaluated from the effective mass model expression [14] as

$$E = E_g + \frac{h^2}{8m^* R^2} - \frac{e^2}{4\pi\varepsilon_o \varepsilon R}$$

(8)

Where, E_g = band gap of the bulk semiconductor, h = Planck's constant, R = crystallite size
ε = dielectric constant of the semiconductor. m* (effective mass) = $(m_e \times m_h)/(m_e+m_h)$. m_e = effective mass of electron m_h = effective mass of hole. It is noticed that the band gap measured from absorption spectra closely coincides with the theoretical results.

IV. CONCLUSION

We have successfully synthesized Nanocrystalline ZnO QDs by sol-gel method. The crystalline nature and uniformity of ZnO QDs have been shown using XRD analysis as well as TEM images. The band gap of ZnO nanoparticles obtained is found to be 3.27eV using Tauc plot, corresponding to the bulk ZnO. FTIR measurement shows the presence of O-H mode of vibration along with C=O, C-O and C-O-C peaks in various regions. These ZnO QDs could be applicable for Solar cell application.

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REFERENCES

[1] A. Ohtomo, M.Kawasaki, I. Ohkubo, H. Koinuma, T. Yasuda, Y. Segawa, Appl.Phy. Lett. **1999** 75, 980.
[2] J. A. Ronovich, D. Golmoy, A. L. Fahernbruch and R. H. Bube, J. Appl. Phys., **1980** 51, 4260.
[3] V. Spirant and D. R. Clarke, J. Appl. Phys., **1997** 81, 6357.
[4] H. W. Ryu, B.S. Park, S.A. Akbar, W.S. Lee, K. J. Hong, Y.J. Seo, D.C. Shin, J. S. Park, G. P. Choi, Sens. Actuators, B, Chem. **2005** 96, 717.
[5] T. Minami, H. Nat and S. Taka., Thin Solid Films, **1985** 124, 43.
[6] J. Lu, Q. Zhang, J.Wang, F. Saito, M. Uchida, Powder Technol. **2006** 162**,** 33.
[7] Z.Wang, X.F. Qian, J. Yin, Z.-K. Zhu, Langmuir. **2004** 20**,** 3441.
[8] T.Q. Liu, O. Sakurai, N. Mizutani, M. Kato, J. Mater. Sci., **1986** 21 3698.
[9] A.M. Peiro, J.A. Ayllón, J. Peral, X. Doménech, C. Domingo, J. Cryst. Growth, **2005** 6, 16.
[10] Sanjeev Kumar, Fouran Singh and A. Kapoor J.n.phys. Science 24 **2013** 1.
[11] Fouran Singh, Sanjeev Kumar and A Kapoor et.al. J. Appl. Phys. **2012** 112, 073101.
[12] V. L. Azaroff, Elements of X-ray Crystallography, McGraw Hill, New York, **1968**.
[13] H. S. Kang, J. S Kang, J.W Kim and S.Y. Lee, J. Appl. Phys. **2004** 95, 1246.
[14] K. F. Lin, H. M. Cheng, H. C. Hsu, L. J. Lin, W. F. Hsieh, Chem. Phys. Let **2005** 409, 208.