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Role of alkali metal hydroxide in controlling the size of ZnO nanoparticles in non-aqueous medium

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Abstract

BACKGROUD & OBJECTIVE: The alkali metal hydroxides play an important role in controlling the size of ZnO nanoparticle in alcoholic medium. **METHODOLOGY:** ZnO nanoparticles have been synthesized in alkali metal hydroxides (LiOH, NaOH and KOH). Characterization was carried-out using TEM, XRD, UV-Visible and Fluorescence Spectroscopy. **RESULTS & CONCLUSION:** TEM images showed the mono-disperse and nearly spherical shaped nanoparticles of size from 6.92 to 7.96 to 9.27 nm in LiOH, NaOH & KOH, respectively. XRD results presented that all the three have hexagonal wurtzite structure. UV absorption depicted the Bathochromic shift from 360 nm (LiOH), 362 nm (NaOH) to 375 nm (KOH). Red emission shift occurs in fluorescence spectra from 510 nm to 550 nm in the order of alkali metal hydroxide. The study reveals the mechanisms guiding the tunable crystal size and morphology.

Keywords: Surface Charge Density, Bathochromic shift, Nanoparticle

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1. Introduction

Many scientist in the field of polymer and material science have given significant contribution to the advancement in science and technology¹⁻¹¹. Nanoscience and technology is now the centre of attraction for many young researchers. ZnO has received considerable high attention due to its potential application in nano-scaled electronic, optical, photonic, optoelectronic, electrochemical and electromechanical devices¹². A large direct band gap (3.3 eV), excellent thermochemical stability and a binding energy of the free exciton of 60 meV at room temperature makes it a promising semiconductor material¹³. ZnO nanoparticles have been fabricated by different methods such as thermal evaporation¹³ pulsed laser deposition¹⁴, metal-organic chemical vapor deposition (MOCVD)^{15,16}, hydrothermal synthesis, thermal decomposition method^{17,18} sol–gel synthesis²⁰, flame spray pyrolysis²¹ and precipitation method²². Various methods have been reported^{23,24} for the synthesis of ZnO particles with controlled crystalline morphology, orientation and surface architectures to fine-tune its properties for potential application. It is necessary to achieve control over the ZnO nanoparticle size and size distribution, which is essential for tailoring optical, electrical, chemical, and magnetic properties of nanoparticles for specific applications.

Wet chemical methods allow an easy tailoring of synthesis parameters throughout the whole process that may be exploited to achieve a more precise control of composition, shape and size of the resulting material. Use of different alcohols as dispersing medium, variation in temperature and precursor concentration of Zinc Acetate effects the size and shape of the nanoparticles as reported by Tonto et al,2008²¹. Previously, we had reported the impact of various capping agents on the

*Corresponding author Full Address : Central Scientific Instruments Organisation, Chandigarh, India Phone no. 9041909162 E-mail: jagvira@gmail.com optical behaviour of ZnO nanoparticles¹⁹. In the present study, we explore the effects of various alkali metal hydroxides on the size and optical behaviour of the synthesised nanoparticles keeping other reaction parameters constant.

2. Materials and methods

2.1 Material Preparation

ZnO nanoparticle synthesis method was performed as reported⁵. However, methanol has been used as the solvent in place of ethanol. All chemical reagents are of analytical grade and were used without further purification. Zinc acetate dihydrate and lithium hydroxide monohydrate (LiOH.H₂O) were from Loba Chemie. Methanol was from Spectrochem, Potassium Hydroxide and Sodium Hydroxide were from s.d. fine chemicals.

2.2 Method of Preparation

3.35 mmol of Zn(Ac)₂.2H₂O was dissolved in 31.25 ml of methanol and another solution of lithium hydroxide was prepared by dissolving 6.59 mmol of lithium hydroxide in 50 ml of methanol under vigorous stirring. The lithium hydroxide solution was added slowly to the Zinc acetate solution at 60°C under vigorous stirring. After 1.5 hr, nanoparticles started precipitating and the solution became turbid. The heater and stirrer were removed after 2 h and the solution was allowed to settle for 2 h. The zinc oxide nanoparticles settled at bottom and the excess mother liquor was removed and the precipitates were washed twice with 12.5 ml of methanol. The same procedure was followed for the precipitation of ZnO nanoparticles using NaOH or KOH solution in ethanol under vigorous stirring . nanoparticles was observed on Transmission Electron Microscope (TEM, Hitachi H-7500). Suspension of nanoparticles in ethanol was prepared for TEM analysis.

The drop of the suspension was placed on the carbon-coated Cu TEM grid. Optical characterisation was performed at room temperature on UV-Vis Spectrophotometer (Perkin Elmer Lambda 35) and Fluorescence Spectrophotometer (VARIAN, Carrier Eclipse).

3. Results and discussion

XRD patterns of powders synthesized by the solvo thermal reaction in presence of various metal hydroxides are shown in Figure I. All peaks of the obtained product were corresponding to the hexagonal wurtzite structure of ZnO with lattice parameters a and c of 3.253 and 5.215, respectively. Three diffraction peaks corresponding to (100), (002) and (101) are observed. All the XRD peaks are indexed to the hexagonal wurtzite phase of ZnO (JCPDS Card No. 80-0074) as shown in Figure I. No peak from either ZnO in other phases or impurities was observed which implies that pure hexagonal phase ZnO was successfully synthesized by the solvothermal reaction in the presence of all hydroxides investigated. UV-Vis spectra of the synthesised nanoparticles dispersed in methanol is shown in Figure II. Intensity difference of the spectra is due to dissimilar concentrations. λ_{OS} (onset of absorption-determined by the linear extrapolation of the steep part of the UV absorption toward the base line) was observed which showed a bathochromatic shift from LiOH (λ_{OS} = 360 nm), NaOH $(\lambda_{OS}=362 \text{ nm})$ to KOH $(\lambda_{OS}=375 \text{ nm})$.

Two maxima are observed in the Fluorescence spectrum (Figure III), one coinciding with λ_{OS} of respective absorption spectra, and a green emission in the range of 510-550 nm, again indicating the red shift from LiOH to KOH. Morphology of the as synthesized ZnO particles was examined from TEM images, as shown in Figure IV which shows highly uniform evenly distributed size of spherical shaped nanoparticles.

The particle size of ZnO can be determined from the absorption onset Figure II using the effective mass model derived by before Brus, 1992^{23} , where the band gap can be approximated by the equation Eq. I:

$$E^{*} = E_{g}^{bulk} + \frac{\hbar^{2}\pi^{2}}{2er^{2}} \left(\frac{1}{m_{e}m_{0}} + \frac{1}{m_{h}m_{0}} \right) - \frac{1.8e}{4\pi\varepsilon\varepsilon_{0}r} - \frac{0.124e^{3}}{\hbar^{2} \left(4\pi\varepsilon\varepsilon_{0} \right)^{2}} \left(\frac{1}{m_{e}m_{0}} + \frac{1}{m_{h}m_{0}} \right)^{-1}$$

Where E_g^{bulk} is the bulk band gap (eV), \hbar is Plank's



Figure II: (a) UV-Vis Spectra of ZnO synthesised in LiOH (b) UV-Vis Spectra of ZnO synthesised in NaOH (c) UV-Vis Spectra of ZnO synthesised in KOH



constant (\hbar =6.626x10⁻³⁴ J·s), r is the particle radius, e is the charge on electron (1.602x10⁻¹⁹ C), m_e is electron effective mass, e is the relative permittivity, m_h is hole effective mass, e₀ is the permittivity of free space (8.854 x10⁻¹⁴ F cm⁻¹) and m₀ is free electron mass (9.110x10⁻³¹ kg). Size was obtained from λ_{OS} , related to the band gap through the relation $Eg = (hc/\lambda)$ and solving Eq. (I) by considering $m_e = 0.24$, $m_h = 0.45$, and $\varepsilon = 3.7$ the cut-off wavelength was determined from the intersection of the tangent of the excitonic peak threshold with the wavelength axis after removal of the absorbance tail due to scattering by



Figure III: (a) Florescence Spectra of ZnO synthesised in LiOH (b) Florescence Spectra of ZnO synthesised in NaOH (c) Florescence Spectra of ZnO synthesised in KOH

particles at wavelength larger than λc . The scattered intensity, *I*scat, was calculated from the fit at large wavelength of the absorption curve ($\lambda > 400$ nm) using as function: *I*scat = 1/ $(a+\lambda_b)$, *a*, *b* being the adjustable parameters. The particle derived from Brus Formula comes out to be 6.8 nm, 7.9 and 9.0 nm in LiOH, NaOH and KOH respectively²³. From the absorption maxima, it is clear that nanoparticles having lower size showed blue shift in the spectra. Though, the nanoparticles synthesized in all the three cases are of quantum well size.

To investigate the synthetic fundamentals for bottom up approach, we study the reaction in the presence of different alkali metal hydroxides that can influence the morphology and size of ZnO nanostructures. The two factors that are responsible for the particle growth are:-

Ostwald ripening where the particle grows at the expense of the smaller particles, reducing the surface energy at the constant volume

Role of the available precursors in the solution which is mainly dependent upon the number of particles available, atoms on the surface of the seed particles and the composition of the solution.

The possible reaction process can be illustrated as follows:

$$Zn(CH_3COO)_2 \rightarrow Zn^{+2} + 2CH_3COO^{-}$$
(1)

$$Zn^{+2} + 2OH^{-} \rightarrow Zn(OH)_{2}$$
⁽²⁾

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$
 (3)

Reaction (3) above occurs in the basic medium $Zn(OH)_2$ that gets adsorbed onto the surface of the ZnO by decomposition process by replacing the cations of alkali metal hydroxide. It has been reported that the particle size and shape depend upon the alkali metal hydroxide that is used to obtain $Zn(OH)_4^{2-1}$ ions. The rate constant for the growth²⁴ is given by Eq. II :

$$k = \frac{8\gamma V_m^2 c_{r=\infty}}{54\Pi\eta a N_A}$$

where γ is the surface energy, V_m is molar volume, $c_{r=\infty}$ is bulk solubility, N_A is Avogadro's number, η is solvent viscosity, and a is the solvated ion radius. Now, the ionic radius of the octahedral co-ordinated cations follows the order as:-

Li⁺ (76 pm) < Na⁺ (102 pm) < K⁺ (138 pm)

The surface charge density increases with decreasing ionic radius, thereby, increasing rate constant for particle growth,

92

Figure IV: (a) TEM image of ZnO synthesised in LiOH (b) TEM image of the ZnO synthesised in NaOH (c) TEM image of the ZnO synthesised in KOH



that is, increasing the rate of the ZnO precipitation. So, the rate of ZnO precipitation from the $Zn(OH)_4^{2-}$ ions in aqueous solution depend upon base as :-

LiOH < NaOH < KOH

In case of Na⁺ and K⁺ ions, the Zn(OH)₄²⁻ ions can be adsorbed onto the ZnO surface by replacing these cations easily. That's why here the rate determining step was the decomposition process of the Zn(OH)₄²⁻ ions. And they follow the first order rate kinetics. The experimental calculated rate constants K for NaOH and KOH is = $1.167 \times 10^{-2} \text{ s}^{-1}$ and $1.983 \times 10^{-2} \text{ s}^{-1}$, respectively, which means that precipitation of ZnO is faster in case of KOH as compared to NaOH which explains the larger size in case of KOH in comparison to NaOH.

In case of LiOH, it does not follow the first order kinetics; Since Li^+ ion has the very strong charge density, so it is adsorbed on the precipitated ZnO surface strongly as compared to other cations. The strong adsorption of Li^+ ions inhibit the adsorption of the $\text{Zn}(\text{OH})_4^{2-}$ ions on the ZnO surface, and hence, rate determining step was not the decomposition process. The rate of ZnO formation is slow and the size is less as compared to NaOH and KOH.

Conclusion

The work presented clearly shows that the size of ZnO nanostructures can be effectively controlled by the alkali metal hydroxide used to obtain $Zn(OH)_4^{2-}$ ions. The employed synthesis method is simple and reproducible on a potentially large synthetic scale. Since the surface area and morphology have a crucial role in many applications such as photo-emitters, transducers, actuators, varistors, sensors and catalysts, so by optimising the dimensions of ZnO nanoparticles we can achieve better and improved photovoltaic performance.

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