CHAPTER – IV

SYNTHESIS OF ZnO NANOSTRUCTURES WITH DIFFERENT CAPPING AGENTS

4.1 INTRODUCTION

Zinc oxide is a versatile material. Nanosized ZnO crystals have attracted a great deal of attention because of their size-dependent opto-electronic properties. During the past decades, reports on the synthesis of various nanostructures of ZnO have increased rapidly, viz., rods, wires, tubes, towers, stars, dendrite, flower like etc. These structures are expected to have more potential applications in building functional electronic devices with special architectures and distinctive opto-electronic properties. Therefore, it is attempted to synthesize ZnO nanostructures in a controllable shape and size to meet the demand and to explore the potentials of ZnO. It is still a challenging task for material scientists, to directly fabricate large-scale ZnO nano crystals with controlled morphology (Xie et al., 2009). In recent years, many researchers are inclined to prepare ZnO nano crystals at a low temperature to reduce energy consumption, improve large-scale production and to obtain special properties. However, synthesis of ZnO nanocrystals generally need a catalyst, such as poly(vinyl)pyrrolidone (PVP), cetyltrimethyl ammonium bromide (CTAB) and hexamethyleneetetramine (HMTA) and long reaction time because of the poor ZnO crystallization at a low temperature. The effect of PVP and CTAB on the ZnO nucleation has been investigated by many researchers (Li et al., 2005; Ni et al., 2005; Baruah and Dutta, 2009). They found that the ZnO nucleation was promoted (or) depressed with a different amount of surfactant at certain temperature.
In the present study, cauliflower-like, granular and hexagonal ZnO nanostructures were synthesized by chemical routes using PVP, CTAB and HMTA as capping agents.

4.2 EXPERIMENTAL

4.2.1 Materials

The source materials, such as zinc nitrate hexahydrate [(Zn(NO$_3$)$_2$.6H$_2$O)], zinc acetate dihydrate [Zn(CH$_3$COO)$_2$.2H$_2$O], potassium hydroxide [KOH], ammonium hydroxide [NH$_4$OH], sodium hydroxide [NaOH], PVP [C$_6$H$_9$NO], CTAB [C$_{19}$H$_{42}$BrN] and HMTA [C$_6$H$_{12}$N$_4$] were of analytical grade and used as purchased. Solutions were prepared by dissolving appropriate amount of the compounds in double distilled water.

4.2.2 Synthesis of PVP Assisted Cauliflower-like ZnO Nanostructures

In this method 0.5 M aqueous solution of zinc nitrate hexahydrate and 1.0 M aqueous solution of potassium hydroxide were prepared in distilled water to form 100 mL solution. Later 0.01 M of PVP was added as capping agent. The reaction solution was heated at 50 °C under continuous stirring for 1 hour. The precipitate formed was collected and washed with ethanol and dried at room temperature. The dried precipitate was calcined at 600 °C in air for 1 hour.

4.2.3 Synthesis of CTAB Assisted Granular ZnO Nanostructures

In this method 6 mL of NH$_4$OH was first dissolved in 94 mL of distilled water in two separate 600 mL conical flasks. Later 0.01 M of CTAB (Sample code: A) and 0.02 M of CTAB (Sample code: B) were added into the previous NH$_4$OH solutions and stirred continuously at room temperature for 30 minutes until homogeneous solutions were obtained. The aqueous solution of Zn(CH$_3$COO)$_2$.2H$_2$O (0.2 M) was added drop
wise into CTAB assisted NH$_4$OH solutions. White precipitates were formed immediately and they were stirred at room temperature for 1 hour. The precipitates were filtered, rinsed with distilled water and absolute ethanol. The precipitates were then dried at room temperature and calcined at 600 °C for 1 hour.

**4.2.4 Synthesis of HMTA Assisted Hexagonal ZnO Nanostructures**

In this method 6.4 g of sodium hydroxide [NaOH] was first dissolved in 100 mL distilled water. Later 0.1409 g of HMTA [C$_6$H$_{12}$N$_4$] was added into NaOH solution and they were stirred continuously for 1 hour until a homogeneous solution was obtained. Simultaneously, 0.2 M aqueous solution of zinc acetate dihydrate [Zn(CH$_3$COO)$_2$.2H$_2$O] was added drop wise into the HMTA assisted NaOH solution. White precipitate was formed and it was heated to 70 °C and maintained at that temperature for 3 hours. The precipitate was cooled to room temperature, filtered, rinsed with distilled water and calcined at 600 °C for 1 hour in air.

**4.3 CHARACTERIZATION OF ZNO NANOSTRUCTURES**

The structural and phase formation of the sample was identified by Reich Seifert XRD 3003 diffractometer using Cu-Kα (λ = 1.5406 Å) radiation. The presence of functional groups was analyzed by FTIR spectroscopy (Perkin Elmer Spectrum One FTIR). The morphology and size of the ZnO nanostructures were evaluated by scanning electron microscopy (SEM, JOEL JSM 6335F) and transmission electronic microscopy (TEM, FEI-Technai Sprit). UV-vis measurements were made by Lamda 650 UV-vis diffuse reflectance spectrometer (PerkinElmer) and room temperature PL spectra were taken using a luminescence spectrometer (LS55, Perkin Elmer).
4.4 RESULTS AND DISCUSSION

4.4.1 Structural and Phase Formation

The X-ray diffractograms (XRD) of the synthesized cauliflower-like, granular and hexagonal ZnO nanostructures are shown in Figs. 4.1, 4.2 and 4.3 respectively. The XRD patterns of the samples reveal that all peaks correspond to the characteristic peaks of the hexagonal \textit{wurtzite}-type structure of ZnO with space group P6$_3$mc and lattice parameters, $a = b = 0.3250$ nm and $c = 0.5207$ nm according to the JCPDS number of 36-1451. The indexed ZnO peaks in the spectrum have high intensity and narrow spectral width, which indicates that the products are of excellent crystallinity (Chen B. J. et al., 2004). No peaks of any other phase are detected, indicating that the ZnO samples obtained by the current chemical routes are highly pure. The particle (crystalline) size is calculated by Debye Scherrer equation, $D = \frac{K \lambda}{(\beta \cos \theta)}$, where $D$ – mean crystallite size, $K$ – constant $= 0.89$, $\lambda$ – wavelength of Cu-K\textalpha radiation $= 1.5406$ Å, $\beta$ – full width at half-maximum (FWHM), $\theta$ – diffraction angle. The calculated average particle size for the cauliflower-like ZnO nanostructures is 35 nm, for sample A of granular ZnO nanostructures is 37 nm, for sample B of granular ZnO nanostructures is 25 nm and that for hexagonal ZnO nanostructures is 55 nm.
Fig. 4.1. X-ray diffractogram of cauliflower-like ZnO nanostructures

Fig. 4.2. X-ray diffractograms of granular ZnO nanostructures
Fig. 4.3. X-ray diffractogram of hexagonal ZnO nanostructures

4.4.2 Functional Groups

The FTIR spectrum of the PVP assisted cauliflower-like ZnO nanostructures acquired in the range of 4000-400 cm\(^{-1}\) is shown Fig. 4.4. The peaks located at 480 and 572 cm\(^{-1}\) are correlated to the stretching mode of Zn-O (Ismail, 1991). The broad absorption band centered at 3448 cm\(^{-1}\) is attributed to O-H stretching mode of H\(_2\)O absorbed on the surface of the product. The most striking evidence from FTIR spectrum of the PVP stabilized ZnO is the absorption peaks found at 1285 and 1658 cm\(^{-1}\) which corresponds to C-N stretching motion and C=O stretching motion of monomer for PVP, respectively (Lu et al., 2005 and Feng et al., 2006). The band at 2954 cm\(^{-1}\) is assigned to
the asymmetrical stretching vibration of CH$_2$. The absorption band at 1383 cm$^{-1}$ corresponds to the bending vibration of CH$_2$.

Fig. 4.4. FTIR spectrum of cauliflower-like ZnO nanostructures

The FTIR spectrum of the CTAB assisted granular ZnO nanostructures acquired in the range of 4000-400 cm$^{-1}$ is shown Fig. 4.5. The band located at 460-560 cm$^{-1}$ is correlated to the stretching mode of Zn-O (Ismail, 1991). The band at 3420 cm$^{-1}$ corresponds to O-H mode of vibration. The stretching mode vibration of C=O is observed at 1400-1650 cm$^{-1}$. The absorption peaks at 2342, 2852 and 2923 cm$^{-1}$ correspond to the
stretching modes of methylene groups, which confirm the presence of CTAB capped granular ZnO nanostructures.

Fig. 4.5. FTIR spectrum of granular ZnO nanostructures

The FTIR spectrum of the HMTA assisted hexagonal ZnO nanostructures acquired in the range of 4000-400 cm\(^{-1}\) is shown Fig. 4.6. The band located at 554 cm\(^{-1}\) is the typical characteristic band of the wurtzite hexagonal phase of pure Zn–O (Wu et al., 2005). The band at 3434 cm\(^{-1}\) is correlated to O–H mode of vibration. The stretching mode vibration of C=O is observed at 1400-1600 cm\(^{-1}\). The absorption peaks at
2854 cm\(^{-1}\) and 2924 cm\(^{-1}\) correspond to the stretching modes of methylene groups, which confirm the presence of HMTA capped hexagonal ZnO nanostructures.

![FTIR spectrum of hexagonal ZnO nanostructures](image)

**Fig. 4.6.** FTIR spectrum of hexagonal ZnO nanostructures

### 4.4.3 Morphology and Size of the ZnO Samples

The SEM image of PVP capped ZnO sample is shown in Fig. 4.7(a). It demonstrates the existence of bulk quantity of flower-like bunches. Each bunch is gathered by closely packed nanometer scale rods and forms a cauliflower-like structure. The TEM image of PVP capped ZnO sample is shown in Fig. 4.7(b). Zinc oxide nanorods holding the cauliflower shaped structure is observable from the TEM image. The diameter of the stalk which holds the cauliflower shaped structure is in the range of 50 nm and that of the individual rods giving the cauliflower shape are 25 nm.
The SEM images of the CTAB capped ZnO samples are shown in Fig. 4.8. The SEM image of sample A apparently exhibits granular ZnO nanostructures. The diameters of the granular ZnO nanostructures are in the range of 30 - 40 nm. The SEM image of sample B also demonstrates granular ZnO nanostructures with diameter in the range of 20 - 30 nm. The TEM images of the CTAB capped ZnO samples are shown in Fig. 4.9. The average size obtained by TEM image of sample A is 33 nm and that of sample B is 24 nm. The TEM images clearly show that the average particle size is reduced with increasing capping agent concentration.
Fig. 4.8. SEM images of CTAB capped ZnO samples

Fig. 4.9. TEM images of CTAB capped ZnO samples

The SEM image of HMTA capped ZnO sample is shown in Fig. 4.10(a). It demonstrates the formation of nanograined ZnO with well faceted hexagonal hollow prism shape, which can be attributed to the high crystallization quality of the sample and contain, therefore, well developed grain boundaries and free surfaces. It has been recently
demonstrated that the physical properties of pure nanograin ZnO strongly depend on the presence of defects free surfaces, interphase boundaries and grain boundaries (Straumal et al., 2013).

![SEM and TEM images of HMTA capped ZnO nanostructures](image)

**Fig. 4.10** (a). SEM image and (b). TEM image of HMTA capped ZnO nanostructures

The TEM image of ZnO nanostructures is shown in Fig. 4.10(b). It depicts the top view of hexagonal hollow prism shaped ZnO nanostructure. The internal diameter of hexagonal ZnO nanostructure is about 32 nm. The growth mechanism of ZnO nanostructure can be discussed as follows. For stoichiometric ZnO, the growth in the [0001] direction usually suppresses other directions because the (0001) atomic planes are close-packed with low surface energy (Hu et al., 2002). The faceted structures observed in Fig. 4.10(a) demonstrate that the growth velocity in lateral directions to that of c-axis exhibit anisotropic nature with higher growth rate along the c-axes. It was proposed that HMTA, being a long chain polymer and a nonpolar chelating agent, will preferentially attach to the non polar facets of the zincite crystal, thereby cutting off the access of Zn$^{2+}$
ions to them leaving only the polar (001) face for epitaxial growth. HMTA therefore acts more like a shape-inducing polymer surfactant rather than as a buffer (Govender et al., 2004; Baruah and Dutta, 2009).

4.4.4 UV-vis Absorption and Diffuse Reflectance Spectra (DRS)

(i) Absorption Spectra

The UV-vis absorption spectra of the cauliflower-like, granular and hexagonal ZnO nanostructures are shown in Figs. 4.11, 4.12 and 4.13 respectively. The fundamental absorption peaks of the cauliflower-like, granular and hexagonal ZnO nanostructures are found at 365 nm, 368 nm (sample A), 361 nm (sample B) and 360 nm respectively. Compared to bulk ZnO, having cut-off wavelength of 373 nm, the ZnO samples synthesized in the present work exhibit a blue-shift in cut off wavelength which may be ascribed to size effect and their unique morphology (Hou et al., 2006).

![Absorbance vs Wavelength](image_url)

Fig. 4.11. UV-vis absorption spectrum of cauliflower-like ZnO nanostructures
Fig. 4.12. UV-vis absorption spectra of granular ZnO samples

Fig. 4.13. UV-vis absorption spectra of hexagonal ZnO nanostructures
It is also observed that in granular ZnO samples, the absorption peak shifts towards shorter wavelength as the capping agent concentration is increased. No other peak is observed in the UV-vis absorption spectra of the cauliflower-like, granular and hexagonal ZnO nanostructures, which confirms the purity of the ZnO nanostructures (Buong Woei Cheng and Yuet Ying Loo, 2012).

(ii) UV-vis Diffuse Reflectance Spectra

The diffuse reflectance spectra of the cauliflower-like, granular and hexagonal ZnO nanostructures are shown in the inset of Figs. 4.14, 4.15 and 4.16 respectively. The low reflectance values of the samples indicate high absorption in the corresponding wavelength region.

![Graph showing diffuse reflectance spectra](image)

Fig. 4.14. Plot of \((F(R)h\nu)^2\) vs. \(h\nu\), Inset: UV-vis DRS of cauliflower-like nano ZnO
For analysis purposes the diffuse reflectance, R, of the samples can be related to the Kubelka_Munk function F(R) by the relation $F(R) = (1-R)^2/2R$ (Kortum, 1969). The band gap energy ($E_g$) for the cauliflower-like, granular and hexagonal ZnO nanostructures is determined by the plot of the square of the modified Kubelka_Munk function vs. the photon energy ($h\nu$) (Cao et al., 1991), shown in Figs. 4.14, 4.15 and 4.16 respectively. The $E_g$ values of the ZnO samples are determined by the extrapolation of the linear portion of the graph down to $[F(R)h\nu]^2 = 0$.

![Graph showing the plot of $(F(R)h\nu)^2$ vs. $h\nu$ for two samples A and B with band gap energies of 3.40 eV and 3.41 eV respectively.]

Fig. 4.15. Plot of $(F(R)h\nu)^2$ vs. $h\nu$, Inset: UV-vis DRS of granular nano ZnO
The observed band gap for the cauliflower-like ZnO nanostructures is 3.41 eV. For the granular ZnO nanostructures the band gap is increased from 3.40 eV to 3.41 eV when the concentration of CTAB is increased from 0.01 M to 0.02 M. This was explained by the modification of the band structure, i.e., narrowing of the valance band and conduction band (Chakrabarti et al., 2004). The $E_g$ value of the hexagonal ZnO nanostructures is determined to be 3.4 eV. The observed band gap of the ZnO nanostructures are in good agreement with that of the bulk ZnO (3.37 eV) and the band gap enhancement is attributed to the size effect.
4.4.5 Photoluminescence (PL) Studies

Room temperature PL spectra of the cauliflower-like, granular and hexagonal ZnO nanostructures excited by 350 nm UV light are shown in Figs. 4.17, 4.18 and 4.19 respectively. The photoluminescence from cauliflower-like and granular ZnO nanostructures consist of three emission bands at room temperature, a near band-edge (UV) emission and two broad, deep-level (visible) emissions. The visible luminescence is usually considered to be related to various intrinsic defects produced during the preparation of ZnO nanostructures. Normally these defects are located on the surface of the ZnO nanostructures (Wu et al., 2001). For the as-synthesized ZnO samples, a sharp UV emission peak is observed at 397 nm for cauliflower-like ZnO nanostructures, at 398 nm for sample A of granular ZnO nanostructures and at 392 nm for sample B of granular ZnO nanostructures. This emission corresponds to the near band-edge emission resulting from the recombination of free excitons (Jianguo Zhou et al., 2007). A broad green emission is observed around 500 - 570 nm for all the three ZnO nanostructures commonly referred to as deep-level or trap-state emission which is attributed to the singly ionized oxygen vacancy in ZnO and the radiative recombination of electrons at the conduction band with holes trapped in oxygen-related defects (Vanhausden et al., 1996; Dai Y. et al., 2003).

The visible blue emission observed at 469 nm for cauliflower-like ZnO nanostructures, at 461 nm for sample A of granular ZnO nanostructures and at 455 nm for sample B of granular ZnO nanostructures is likely attributed to electron transition, mediated by defect levels in the band gap. The PL spectra of granular ZnO nanostructures
also reveal that the emission becomes more intensive and shifts towards smaller wavelength or higher energy when the concentration of CTAB is increased in the preparation of ZnO nanostructures, which may be due to the decrease in their particle size and the reduced defects in their structure.

![Graph showing PL spectrum of cauliflower-like ZnO nanostructures](image)

Fig. 4.17. PL spectrum of cauliflower-like ZnO nanostructures

The PL spectrum of as-synthesized hexagonal ZnO nanostructures reveals a strong dependance on surface morphology and grain structures. The PL spectrum of hexagonal ZnO nanostructures is composed of two emission bands: an intense, sharp and dominated ultraviolet (UV) band at 395 nm and a suppressed and broad green emission band centered at around 513 nm. As we know, the UV emission is originated from the free-exciton recombination, indicating the growth of good quality ZnO nanostructures (Li et al., 2006). Especially for smooth surface covered by well-ordered grains, the UV emission is dominant with a narrow peak, indicative of good optical property. It is
understandable that the intrinsic defects are reduced within the well-ordered grains, enhancing luminous efficiency of the UV band.

Fig. 4.18. PL spectrum of granular ZnO nanostructures

Fig. 4.19. PL spectrum of hexagonal ZnO nanostructures
Generally, high crystalline quality ZnO shows a dominated UV emission with weak visible emissions (Fan et al., 2005). In our investigations the near band-edge is dominated over the deep-level emissions, which indicates that the synthesized ZnO nanostructures are good in crystal quality and are exhibiting good optical properties. Therefore, the ZnO nanostructures synthesized in the present work would be a promising material for applications in optoelectronic nanodevices in future.

Zinc oxide nanostructures are being extensively used in the fabrication of a new class of solar cells namely quantum dot sensitized solar cells (QDSSCs) (Singh et al., 2011). It is expected to be an alternating material for nano titanium dioxide (TiO$_2$), because of its properties, such as being environment friendly, stability and that it can be synthesized into different shapes and sizes very easily.

Fig. 4.20. Schematic diagram of QDSSC using ZnO as front electrode
The schematic diagram of a sandwich type QDSSC using ZnO nanoparticles (ZnO NPs) as front electrode, a thin platinum (Pt) sheet as counter electrode, quantum dots (QDs) as sensitizer and an electrolyte (I⁻/I₃⁻) is shown in Fig. 4.20. The front ZnO electrode passes the photons in the visible range to the underlying QD layer. Quantum dots are excited by uptake of energy contained in photons. The excitation process creates excitons in the QDs. The electrons are then quickly injected into the conduction band of ZnO. The injected electron in the conduction band of ZnO percolates through the porous ZnO nanostructure and is fed into the indium tin oxide (ITO) layer. Through ITO, the electron moves to the external circuit. At the Pt counter electrode, triiodide (I₃⁻) is reduced to iodide (I⁻) by taking the electrons from Pt electrode. Iodide is transported through the electrolyte towards the ITO photo electrode, where it reduces the oxidized QD. The QD is then ready for the next excitation/oxidation/reduction cycle. So, here we can see that ZnO layer plays a major role in functioning of QDSSC.

The as-synthesized cauliflower-like, granular and hexagonal ZnO nanostructures via chemical routes using PVP, CTAB and HMTA as capping agents can be used for QDSSC application.

4.5 CONCLUSION

In summary, cauliflower-like, granular and hexagonal ZnO nanostructures were prepared by a simple and low cost chemical routes assisted with PVP, CTAB and HMTA capping molecules. The XRD and FTIR results confirm hexagonal wurtzite-type ZnO of excellent crystallinity with the functional groups of the capping agents. The as-synthesized ZnO nanostructures exhibit uniform morphology, facilitated by PVP, CTAB
and HMTA which act as shape-inducing polymers. The effective reduction of grain size in nanorange confirms the quantum confinement effect to the as-synthesized ZnO samples, which confers as a blue shift due to band gap enhancement. In these investigations, a strong near band-edge emission and relatively weak deep-level emission band are observed, suggesting that nanograined ZnO has a small number of defects or impurities and, thus, of high crystalline quality which will have a significant advantage for applications in optoelectronic nanodevices.