CHAPTER VII

EFFECT OF ANNEALING

7.1 Introduction

The results and discussions of previous chapter concluded that slow additions of sodium chloride solution into chitin-zinc chloride solution (section 4.4) effect the formations of chitosan-ZnO nanostructures with increased optical band gap. From the literature, it was found that there were no reports on the effect of annealing temperature on the properties of chitosan-ZnO nanostructures.

In this chapter, the effect of annealing temperature on the as-prepared chitosan-ZnO nanostructure samples such as Z15N45, Z30N45 and Z30N30 were discussed. The preparation procedure for the above samples was given in the section 4.4.1, 4.4.2 and 4.4.3 respectively. The results and discussion were made in the subsequent sections.

7.2 Annealing

The as-prepared chitosan-ZnO nanostructure samples were heated in furnace at the rate of 10°C/ min and held for 2 h at 200-600°C. The prepared Z15N45 sample is annealed at 200°C, revealed that the particles have a definite boundary, which indicates that there is no inflection at this temperature and then the temperature was raised at 300 and 600°C. When Z30N30 sample was
induced to grow more number of the rods with hexagonal structure at 300°C and at 600°C, the rod-like structure is collapsed. The annealed chitosan-ZnO nanostructure samples such as Z15N45, Z30N45 and Z30N30 were used for further characterizations.

7.3 Characterization of annealed chitosan-ZnO nanostructures

7.3.1 X-ray diffractrometry

The X-ray diffraction (XRD) pattern of chitosan–ZnO nanostructures are shown in Figure 7.1. All the diffraction peaks could be indexed as hexagonal phase of ZnO, and the lattice parameter values are consistent with the reported values (JCPDS 36-1451). The crystallite size of the zinc oxide was calculated by the Scherrer's formula [216]:

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]

Where D is the average crystallite size, \( \lambda \) is the X-ray wavelength of CuK\( \alpha \), \( \beta \) is the full width at half maximum, and \( \theta \) is the diffraction angle.

The calculated average crystallite size was found to be ~34.83, 25.14, and 24.51 nm corresponding to the samples Z15N45, Z30N45, and Z30N30, respectively. The lower value of crystallite size for Z30N30 sample is mainly due to the formation of hexagonal structure of ZnO nanorods as was evidenced from the SEM micrographs (Figure 7.2c).
Figure 7.1: XRD pattern of chitosan–ZnO nanostructures annealed at 300°C

(a) Z15N45, (b) Z30N45 and (c) Z30N30.
7.3.2 SEM analysis

SEM was used to study the morphological features of annealed chitosan–ZnO nanocomposites shown in Figure 7.2 (a–c). Figure 7.2a shows that the chitosan–ZnO particles of Z15N45 sample are in agglomerated state with the average particle size in micro-crystalline. SEM image of this same sample, after heating at a temperature of 200 °C, revealed that the particles have a definite boundary (inset Figure 7.2a), which indicates that there is no inflection at this temperature. Nuernberg et al. [217] reported that the inflection point occurred at 250°C for Mg–Al–chitosan and at 350°C for pure chitosan.

In our study, the collapsed state of particles was noticed at the temperature of 300°C for Z15N45 sample (Figure 7.2a) which indicates that presence of Zn ions in the Z15N45 sample reduced the inflection point temperature than that of pure chitosan at 350°C [217]. This is also in close agreement with the finding of Almerindo et al. [218] in which they reported that presence of magnesium leads to the removal of carbonaceous materials at lower temperatures.

As the concentration of ZnCl₂ increases from 15 to 30 % for other two sample preparations (Z30N45 and Z30N30), more number of sheets and needle-like structures were noticed without apparent agglomeration (Figure 7.2b) and more number of rods with hexagonal structure are noticed (Figure 7.2c). The average diameter of the chitosan–ZnO nanorods was found to be ~50–100 nm.
Figure 7.2: SEM image of chitosan–ZnO nanostructures (a) Z15N45, (b) Z30N45, and (c) Z30N30 annealed at 300°C and (d) Z30N30 annealed at 600°C. Inset Z15N45 annealed at 200°C (a) and lower magnification of Z30N30 annealed at 600°C (d).
When the sample Z30N30 was annealed at 600°C, the rod-like structure is collapsed (Figure 7.2d). This may be due to the elimination of volatile materials, and a solid rearrangement may take place in forming the crystalline matrix (inset of Figure 7.2d). The foregoing discussion revealed that the Z30N30 sample was induced to grow more number of the rods with hexagonal structure at 300°C than that of the other two samples.

### 7.3.3 UV-Vis spectroscopy

The UV–Visible absorption spectra of chitosan–ZnO nanostructures annealed at 300°C are shown in Figure 7.3. In our previous study [32], as prepared, these three samples (Z15N45, Z30N45, and Z30N30) show absorption peaks at 323, 351, and 359 nm, respectively [32].

In the present study, after annealing at 300°C, all the three chitosan–ZnO nanostructure samples show the same absorption at 363 nm (Figure 7.3 (a–c)) but slightly higher than that of samples with no annealing. Still, this value is lower than that of the macro crystalline ZnO (about 372 nm). The blue shift of absorbance indicates that ZnO has nanostructures, as was evidenced from the SEM and XRD pattern [219].

The red shift of absorption peak over with annealing was due to the influence of size effect on the energy level of confined exciton, because the average size of nanoparticles obviously became bigger after annealing the same chitosan–ZnO nanostructure [220].
Figure 7.3: UV-vis spectra of chitosan-ZnO nanostructures annealed at 300°C (a) Z15N45, (b) Z30N45, and (c) Z30N30.
7.3.4 Energy band gap

The energy band gaps of chitosan–ZnO nanostructures annealed at 300°C are shown in Figure 7.4 (a–c). It is obvious that the powder used in a highly transparent mode is quite visible. Based on the absorption spectra, the band gaps of all the samples were observed as estimated from the following equation [221];

\[(\alpha h\nu)^2 = E_D (h\nu - E_g)\]

Where \(\alpha\) is the optical absorption coefficient, \(h\nu\) is the photon energy, \(E_g\) is the direct band gap, and \(E_D\) is constant in a direct band gap (\(E_g\)).

Figure 7.4: Energy band gap of chitosan-ZnO nanostructures annealed at 300°C (a) Z15N45, (b) Z30N45, and (c) Z30N30.
When extrapolating the linear portion of the graph plotted \((\alpha h)^2\) Vs \(h\), it tends to become zero. Figure 7.4 (a–c) shows the energy band gap level at 3.20, 3.35, and 3.49 eV for Z15N45, Z30N45, and Z30N30, respectively, for chitosan–ZnO nanostructure annealed at 300°C.

The value of band gap obtained at 3.49 eV for Z30N30 sample may be due to the formation of nanorods (Figure 7.1c) and shift of absorbance at wavelength towards the blue region (Figure 7.3c), compared to the other two samples after annealing temperature at 300°C.

7.3.5 Photoluminescence spectroscopy

Figure 7.5 shows the photoluminescence (PL) spectra of chitosan–ZnO nanostructures annealed at 300°C with excitation at 325 nm. UV emission peak noticed at 368 nm for all the three samples (Figure 7.5) were related to a near band-edge transition of ZnO, namely, the recombination of free excitons through an exciton–exciton collision process [222]. The centre of deep-level emission (visible emission) band with a broad feature in the range of 380–580 nm was noticed at 432 nm (Figure 7.5 a), 431 nm (Figure 7.5 b), and 412 nm (Figure 7.5 c), respectively, for Z15N45, Z30N45, and Z30N30 samples.

Generally, the intensity ratio between the UV emission band and the deep-level emission band is regarded as an indicator of the crystallinity of ZnO materials. The materials would have much better crystallization according to the larger intensity ratio [223]. The relative PL intensity ratio of UV emission to deep-level emission of our samples was estimated to be about 0.55, 0.69, and 0.72.
corresponding to Z15N45, Z30N45, and Z30N30, respectively. The deep-level emission band blue shift and higher emission ratio confirmed the presence of more ZnO crystalline structure [224] after annealing at 300°C. The intensity of the PL spectrum decreases with an increase in ZnCl₂ concentration (Z30N45 and Z30N30), which may be due to the formation of more ZnO. This is evidenced by Sinha et al. [225] who reported a decrease in PL intensity with increasing ZnO concentration.

Figure 7.5: PL spectra of chitosan–ZnO nanostructures annealed at 300°C

(a) Z15N45, (b) Z30N45, and (c) Z30N30.
7.3.6 Cyclic voltammetry

In order to explore the electrochemical activity of annealed chitosan–ZnO nanostructures, cyclic voltammetry technique was used to analyze the electron transfer process, which results in the formation of ZnO. A chitosan–ZnO nanostructure with glassy carbon electrode was used as a working electrode, platinum was used as a counter-electrode, and Ag/AgCl was used as a reference electrode in the electrolytic solutions.

Figure 7.6 shows the cyclic voltammograms of chitosan–ZnO nanostructures annealed at 300°C sample was taken in a working electrode with a potential range -0.8 -1.2 V using scan rate at 50 -100 mV. The noted oxidation peak potential is ~0.41 V vs. Ag/AgCl and the reduction potential value is ~0.18 V for Z15N45 sample. Also, the 70 and 80 mV/s scan rate emit the same ionic separation, whereas 90 and 100 mV/s scan rate shows anomalous shift due to the increase of electrolyte concentration.

Figure.7.7 and 7.8 shows the oxidation of the chitosan–ZnO composite was at 0.58, and 0.6 V, whereas the reduction peaks were observed at 0.2, and 0.3 V vs. Ag/AgCl for Z30N45, and Z30N30 samples respectively. Increase in oxidation and reduction potential of Z30N30 sample compared with other two samples clearly indicate the formation of ZnO nanocrystals / nanorods which was evidenced from the SEM image (Figure 7.2d) and XRD pattern (Figure 7.1). The electrochemical performance of 300°C annealed chitosan–ZnO nanostructures of all the samples shows oxidation peak shift towards positive potential with an increase of scan rate.
Figure 7.6: Cyclic voltammograms of annealed at 300°C Z15N45, chitosan–ZnO nanostructure with different scan rates at 50–100 mV/s.

But this shift has uniformity and reproducibility for the annealed Z30N30 sample at 300°C. Also, the 70 and 80 mV/s scan rate emit the same ionic separation, whereas 90 and 100 mV/s scan rate shows anomalous shift due to the increase of electrolyte concentration.
The voltammetric traces confirm the formation of ZnO in the chitosan–ZnO nanostructure. Both anodic and cathodic currents of the first redox couple increase linearly with scan rates up to 100 mV/s. This is an indication that the electron transfer process involves a surface-confined species.
Figure 7.8: Cyclic voltammograms of annealed at 300°C Z30N30 chitosan–ZnO nanostructure with different scan rates at 50–100 mV/s.

However, the ratio of anodic to cathodic peak currents has exactly no unity, and the peak-to-peak separation is not zero. For an ideal surface-confined redox species, the peak separation should be zero, and the current ratio is expected to be of unity [226].
7.3.7 Impedance spectroscopy

Figure 7.7 (a-c) shows Nyquist plots of chitosan–ZnO nanostructures annealed at 300°C. The straight line peak appears at the high-frequency region of chitosan–ZnO nanostructures annealed at 300°C, making it clear the presence of ZnO nanoparticles (Figure 7.7 a).

Figure 7.9: Representative Nyquist plot of electrochemical impedance data of samples annealed at 300°C (a) Z15N45, (b) Z30N45, and (c) Z30N30 chitosan–ZnO nanostructures with frequency of 0.05–10⁵ HZ and an amplitude of 50 mV.
The grain boundary effect dominates the grain effect and hence plays a major role in enhancing the physical properties of the material. This result is much expected in nanostructured material due to their high surface to volume ratio. Moreover, in this regime, the long-range conduction mechanism contributes more to the conductivity. Surface state density is slightly decreased due to the improved crystallinity and the recombination process mainly controlled by the conduction band electrons (Figure 7.9 b & c).

Although its decreased surface areas partly reduce the surface state density, the collapse of porous structure will contribute some new surface states. The straight line indicates that electron transport in the nanorods features a transmission line behaviour, which has been observed for nanoparticle and nanotube [227]. The contribution from the electrolyte is neglected since the current flowing through the cell was low.

### 7.3.8 Electrical Conductivity

The electrical conductivity value was calculated from the equation $\sigma = R_{ct}$, where $\sigma$ = conductivity and $R_{ct}$ = charge transfer resistance. The calculated conductivity value $\sigma$ of Z15N45, Z30N45, and Z30N30 samples are 2.27, 2.38, and $2.85 \times 10^{-5}$ S/m, respectively (Figure 7.10).
Figure 7.10: The conductivity bar graph of chitosan–ZnO nanostructures.
7.4 Conclusion

Chitosan–ZnO nanostructures were prepared by chemical precipitation method and annealed at 200-600°C. The crystallite size of annealed chitosan–ZnO nanostructures were calculated by XRD analysis. The annealed chitosan–ZnO nanostructures sample of Z30N30 show better surface morphology at 300°C and collapsed state at 600°C. Impedance spectroscopy and cyclic voltamagrams revealed that the composites have better electrical conductivity. The optical property of synthesized Z30N30 composites shows higher intensive peaks. The effects of annealing temperature on the chitosan–ZnO nanostructures have the high conductivity of $\sigma = 2.85 \times 10^{-5}$ S/m by IS. The sample prepared by slow addition of 30% sodium hydroxide into 30% zinc chloride and chitin solution shows better surface morphology and optical and electrochemical conductivity when annealed at 300°C than that with 600°C annealing temperature.