Structural characterization of starch capped ZnO nanoparticles

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Abstract. Zinc oxide nanoparticles have been synthesized by a simple green synthesis route using soluble starch as a capping agent in an aqueous medium. The results of structural investigation of ZnO nanoparticles using various techniques such as X-ray diffraction, scanning electron microscope and Fourier transforms spectroscopy have been presented. XRD confirms the formation of c-axis orientated hexagonal wurtzite crystalline structure of ZnO with an average particle size in the range of 21 nm to 25 nm. The morphology of the ZnO samples were determined by SEM images, indicating nanorod like structure with hexagonal phase for starch capped ZnO nanoparticles. Further, the presence of starch and different functional group in synthesized ZnO nanoparticles have been studied by Fourier transform spectroscopy approve the different bonding between starch with Zn.

1. Introduction
The Metal oxide nanostructured materials have been identified for their notable optical, electronic properties and versatile applications. Zinc oxide has been emerged as favorable metal oxide for optoelectronic and biological applications. It is a wide bandgap compound semiconductor material having the bandgap 3.37eV, and large exciton binding energy 60meV.[1] High thermal and chemical stability and excellent optoelectronic properties, making it useful in large-scale studies and in many optoelectronic and biological applications. Also, high electrical conductivity and optical transparency in the visible region makes it beneficial as a transparent electrode for flat panel display, short-wavelength LED, and Solar cell [2-4]. It has been used as a buffer electrode for LED applications. Many research papers have reported ZnO as a good conducting electrode with better transparency [4,5]. Moreover, antibacterial and antifungal properties of ZnO have been utilized for cosmetic and biological applications, it can be used as a photocatalyst, biosensor, biomarkers, since its fluorescence in the visible region [6,7]. Furthermore, the preparation of zinc oxide nanoparticles by various chemical methods have been reported [2-8]. Organic capping agent or polymeric encapsulations has been used to prevent aggregation of nanoparticles. The environmentally benign synthetic way
has become popular and necessary, to sidestep environmental and health hazards [7,8]. A procedure with nontoxic chemicals, an environmentally benign solvent, and a renewable stabilizing agent are called green synthesis. The soluble starch \((C_6H_{10}O_5)_n\) is a polymeric carbohydrate consisting of a large number of glucose units joined by glycosidic bonds[8,9]. It is a combination of amylopectin and amylose [9]. Amylose is known as soluble starch [9]. In this report, zinc oxide has been synthesized by a one-pot synthesis route using soluble starch as a capping agent at low 75℃. We presented the effect of soluble starch on structural and spectroscopic properties of zinc oxide nanoparticles.

2. Materials and Method
In the present study, analytical grade (AR) chemicals were used without any further purification. One-pot green synthesis method was used to synthesize ZnO Nanoparticles. Soluble starch is used as a stabilizing agent to prevent agglomeration of particles. In this process, 4 mM zinc acetate dihydrate and 20 mM of NaOH were taken. Initially, both the aqueous solutions were cooled in an ice bath, and then NaOH solution was added dropwise to zinc acetate dihydrate solution with constant stirring. Further, the white color colloidal solution was heated at a constant temperature at 75℃ for 30 min. The pH of the resultant solution was 9.5. The final solution was washed many times with acetone and distilled water alternatively, thereafter, centrifuged and dried at 40℃ to get ZnO in powder form. In the case of starch capped ZnO sample, 0.5 wt. percent of soluble starch was taken. The starch solution was added to the precursor, before adding to NaOH solution. The same procedure was followed in the starch capped ZnO sample.

Chemical Reaction
\[
\text{Zn } (\text{CH}_3\text{COO})_2.2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{ZnO} + 2\text{Na CH}_3\text{COO} + \text{H}_2\text{O}
\]

Characterization
The samples were characterized by X-ray diffractometer (Rigaku ultima diffractometer at 40kV) with Cu Ka radiation (\(k = 1.5404 \text{ Å}\)) from 10° to 80° step size 0.20°. The surface morphology and particle size were determined by using FE-SEM (Zeiss EVO40). FTIR – Bruker (ALPHA-T) spectrometer was used for the FTIR study.

3. Results and Discussions
A typical XRD pattern of the ZnO without starch and with starch samples are shown in figure1. The pattern obtained has been indexed as a hexagonal unit cell with a wurtzite structure (JCPDS Card No. 36-1451) with space group P63 mc. Sharp peaks signifying the high crystalline nature of samples. Although, the decrease in intensity of peaks was observed for starch capped ZnO, it indicates a change in the crystallinity of the sample. The most intense peak at 2θ= 36.1° was attributed to (101) hexagonal phase. Average grain size (D) was calculated by Debye-Scherrer formula with full width of half maxima of prominent (101) peak [10].

\[
D = \frac{k\lambda}{\beta\cos\theta} \tag{1}
\]
where $\lambda$ is the wavelength of incident X-rays (1.5402 Å), $\theta$ is angle of diffraction and $\beta$ is FWHM of (101) peak. The lattice constant $c$ and $a$ are calculated from the interplanar spacing $d$ of different $hkl$ planes using the following equation [10].

$$\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2}$$

(2)

The particle size and unit cell parameters are tabulated in Table 1. The broadening of the peak shows the nanocrystalline nature of the sample. Usually, the peak broadening may be ascribed to residual stress, instrumentation error, and grain size. Therefore, the actual size may differ from the calculated size from Scherrer’s equation [10]. To achieve precise determination of size, the Williamson–Hall method has been used [11]. In which the crystallite size and strain of the sample are related to the measure $\beta_{\text{total}}$. Generally, the size broadening $\beta_S$, and strain broadening $\beta_D$, fluctuate quite differently for Bragg angle $\theta$ [11].

$$\beta_s = 4\varepsilon \tan \theta$$

$$\beta_D = 4\varepsilon \tan \theta$$

$$\beta_{\text{total}} = \beta_D + \beta_S$$

$$\beta_{\text{total}} = 4\varepsilon \tan \theta + k\lambda/D \cos \theta$$

$$\beta_{\text{total}} \cos \theta = 4\varepsilon \sin \theta + k\lambda/D$$

Figure 2 depicts the W-H plot for ZnO nanoparticles using equation 3, which is a straight line. The slope of the linear plot gives the value of residual strain, while the average particle size is determined by the reciprocal of intercept on the y-axis. The calculated size of starch capped ZnO was smaller than un-capped ZnO nanoparticles. The steric hindrance effect of soluble starch prevents the agglomeration between the particles by adsorption of large molecules on the surface of particles. With the heating of the solution, starch granules swell and release an amylose molecule. The hydroxyl group of starch polymer work as stabilization agent, it interacts with Zn$^{2+}$ ions and form complexes [8]. Moreover, the high solubility of Zinc acetate and NaOH helps to decrease the particle size. In alkaline medium, during the reaction swelling of starch granules coordinate with Zn$^{2+}$ ions and gelatinization process control the size, shape and morphology of the ZnO nanoparticles [9].

![Figure 1 XRD pattern of ZnO nanocrystals](image-url)
Table 1 Calculated Structural Parameters of ZnO Nanoparticles.

| Sample Name | Crystallite size (nm) | Strain $\times 10^{-3}$ | Dislocation density $\times 10^{-4}$/nm$^2$ | $d$ (Å) | Lattice Parameters Å |
|-------------|-----------------------|------------------------|-------------------------------------------|--------|---------------------|
| ZnO         | 23.5                  | 61                     | 0.255                                     | 2.63   | 3.266               | 5.32               |
| ZnO (Starch)| 21 nm                 | 53                     | 0.233                                     | 3.44   | 3.255               | 5.31               |

The morphology of the ZnO sample was studied by SEM images. Figure 3 shows that uncapped ZnO nanoparticles agglomerated with each other and form larger clusters. While starch capped ZnO particles are composed of small granules and show leaf-like morphology. This feature demonstrates nanorods like structure along c axis. SEM images confirm the formation of ZnO nanoparticles with a hexagonal wurtzite structure. It is clear from the pictures that starch capped ZnO having smaller size and nearly uniform size distribution. The XRD results agree with SEM results. Similar results have been reported by Madan et al. and Fakhari et al. [12,13].
The chemical nature and interaction between starch and ZnO were confirmed using FTIR spectra. Table 2 represent various IR peaks and their assignments. The Intensity of IR peaks for starch capped ZnO is higher than the pure ZnO nanoparticles indicating homogeneous formation (as shown in figure 4). The absorption band centered around 3400 cm\(^{-1}\) is attributed O-H stretching mode vibrations. It has been shifted to 3405 cm\(^{-1}\) for starch capped ZnO, exhibiting a coordination link between Zn\(^{2+}\) ions and OH\(^{-}\) ligands [14,15]. Also, strong C=C bond has been found for starch capped ZnO nanoparticles. The band at 1644 cm\(^{-1}\) corresponds to the surface hydroxyl group of H\(_2\)O molecule [9]. However, in starch capped ZnO sample a small narrow band at 1684 cm\(^{-1}\) is ascribed to C=O stretching vibrations [15]. The different bands and their assignments represent the strong binding between starch and ZnO nanoparticles.

![Figure 4 FTIR spectra of ZnO and starch capped ZnO nanoparticles](image)

**Table 2 IR peaks and their Assignments.**

| IR peaks in ZnO (cm\(^{-1}\)) | IR peaks in starch capped ZnO (cm\(^{-1}\)) | Assignments |
|-----------------------------|-------------------------------------------|--------------|
| 400-650                     | 400-650                                   | Zn-O vibration |
| 870 (strong)                | 832 (weak)                                | C-C, CH\(_2\) deformation C=O |
| 1635, 3405                  | 1684,3400                                 | Stretching vibration, O-H bending C=C (carboxylic group) |
| 1543 (weak)                 | 1529 (strong)                             | C-H vibration |
| 2849 (weak)                 | 2851                                      |              |
4. Conclusions
The starch capped ZnO nanoparticles were successfully synthesized by the green synthesis method. X-ray diffraction (XRD) result indicates that the synthesized uncapped and starch capped ZnO nanoparticles have hexagonal wurtzite structure without any impurities and secondary phase. The smaller particle size was found for starch capped ZnO nanoparticles. The existence of functional groups was identified by FTIR spectroscopy. The presences of the various functional groups associated with starch confirm the bonding between ZnO and starch.

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Conflict of Interest: The authors declare that they have no conflict of interest.

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