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## Synthesis of ZnO Nanoparticles using Carboxymethyl Cellulose Hydrogel

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### ABSTRACT

A new approach has been proposed to synthesis pure ZnO nanoparticles from zinc nitrate hexa-hydrate precursor and sodium carboxymethyl cellulose capping agent. The resulting nanoparticles were characterized by X-ray Diffraction (XRD), Fourier Transform Infra-red (FTIR) spectroscopy, photoluminescence spectroscopy and Field Emission Scanning Electron Microscopy (FESEM). The XRD results showed that particle size is in the range of few nanometers with hexagonal wurtzite structure. Photoluminescence and FESEM results suggested that the adopted method can be successfully utilized for the preparation of size controlled nanocrystalline ZnO powder.

**Key words:** ZnO nanoparticles, sodium carboxymethyl cellulose, XRD

### INTRODUCTION

Synthesis of size, shape and dimension controlled metal oxide nanostructures has evoked extensive research interests due to their unique chemical, optical and electronic properties. Zinc Oxide (ZnO) is one of the II-IV versatile n-type semiconductor materials having a wide range of properties like good transparency, high electron mobility, strong room temperature luminescence, direct-band gap of 3.37 eV and large exciton binding energy of 60 meV (Wirunmongkol *et al.*, 2013). Zinc Oxide is a very interesting multifunctional material for its applications in solar cells (Matsubara *et al.*, 2003), sensors (Choopun *et al.*, 2007), displays, varistors, piezoelectric devices, antibacterial treatment (Tam *et al.*, 2008), photodiodes, food additives and so on (Chandramouleeswaran *et al.*, 2007; Kim *et al.*, 2010).

In the recent past, synthesis of zinc oxide nanoparticles have been attempted in different methods like Chemical Vapor Deposition (CVD) (Purica *et al.*, 2002), hydrothermal process (Baruah and Dutta, 2009; Chen *et al.*, 2011), sol-gel method (Hashem *et al.*, 2013; Chen *et al.*, 2011), Pulsed laser deposition (Kim *et al.*, 2010), direct precipitation methods (Chen *et al.*, 2011), conventional sputter deposition techniques (Choopun *et al.*, 2007) used to synthesize nanoparticles of various size and morphology. In comparison, the synthesis of ZnO nanoparticles using hydrogel process is simple, efficient, cost effective, large-scale production and does not required any sophisticated experimental condition.

Hydrogel is a network of polymer chains that are hydrophilic, sometimes found as a colloidal gel in which water is the dispersion medium. Hydrogels are highly water absorbent, soluble under physiological conditions of temperature, pH and ionic strength (Hashem *et al.*, 2013).

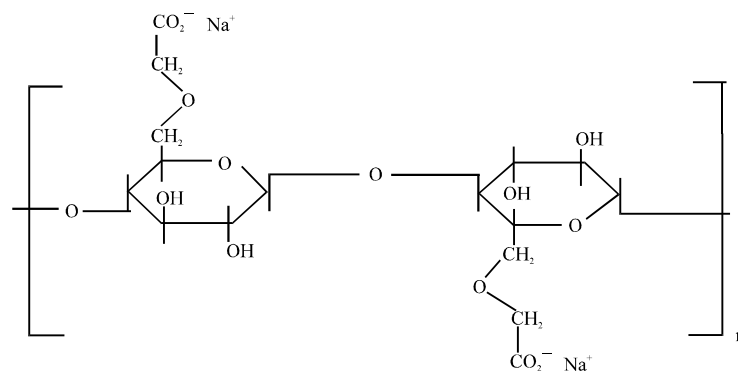


Fig. 1: Chemical structure of NaCMC

Cellulose is a polymer chain composed of repeating cellobiose units, which in turn are composed of two anhydroglucose units. If hydrogen in each anhydroglucose unit is replaced with  $\text{CH}_2\text{COONa}$ , it gives sodium carboxymethyl cellulose (CMC) (Biswal and Singh, 2004). The chemical structure of CMC is shown in Fig. 1, where  $n$  represents the degree of polymerization. Characteristic of CMC depends on degree of substitution. It acts as stabilizer, binder, lubricant, gelling agent etc (Shao *et al.*, 2008; Baruah and Dutta, 2009). In our study, CMC is used as a capping agent in order to reduce agglomeration. To the best of our knowledge, we are the first to focus on synthesis of ZnO nano crystals using CMC as a capping agent.

## EXPERIMENTAL METHOD

**Materials used:** Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and Sodium Carboxymethyl Cellulose (NaCMC), were used as a base material for synthesis.

**Synthesis method:** To synthesize ZnO nanoparticles, zinc nitrate hexahydrate was used as starting material and NaCMC as a capping agent. The molar ratio of NaCMC to  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  taken for synthesis was 1:3. Initially, 4.68 g of zinc nitrate hexahydrate was dissolved in 20 mL of deionized water with constant stirring. 1.56 g of NaCMC was added to zinc nitrate solution, which was under constant stirring and heating. With the addition of NaCMC to zinc nitrate solution a viscous solution was obtained, which was transferred to a ceramic crucible. It was kept in the muffle furnace for drying at  $350^\circ\text{C}$  for 30 min, where an exothermic reaction has occurred. As a result of exothermic reaction the solution was transformed into a powder. The powder was then calcinated at  $520^\circ\text{C}$ , to get crystalline nanoparticle. The powder was removed from the furnace and grinded with a mortar to get ultrafine nanoparticles.

The ZnO nanoparticles were characterized by infrared spectroscopy (FTIR) to determine composition and molecular structure, the particle morphologies were investigated by Field Emission Scanning Electron Microscope (FE-SEM, 670 1 F, JEOL, Japan) and the crystallographic structure of the sample was examined using powder X-ray and Diffractometry (XRD). The particle size was estimated using Debye-Scherrer equation. The photoluminescence spectra of the sample was measured using spectrofluorometer (JASCO FP 8200) with the excitation wavelength of 325 nm at room temperature.

## RESULTS AND DISCUSSION

The X-ray diffraction pattern of ZnO nanoparticles recorded using  $\text{Cu K}\alpha$  radiation is shown in Fig. 2. A definite line broadening of the XRD peaks indicates that the prepared material consists

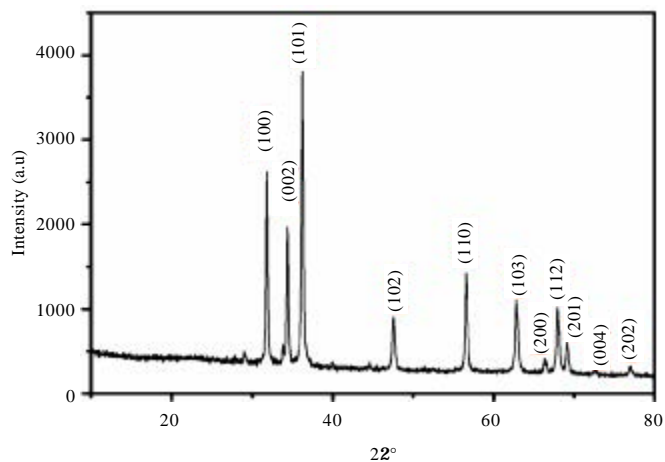


Fig. 2: X-ray diffraction pattern of as synthesized ZnO nanoparticle

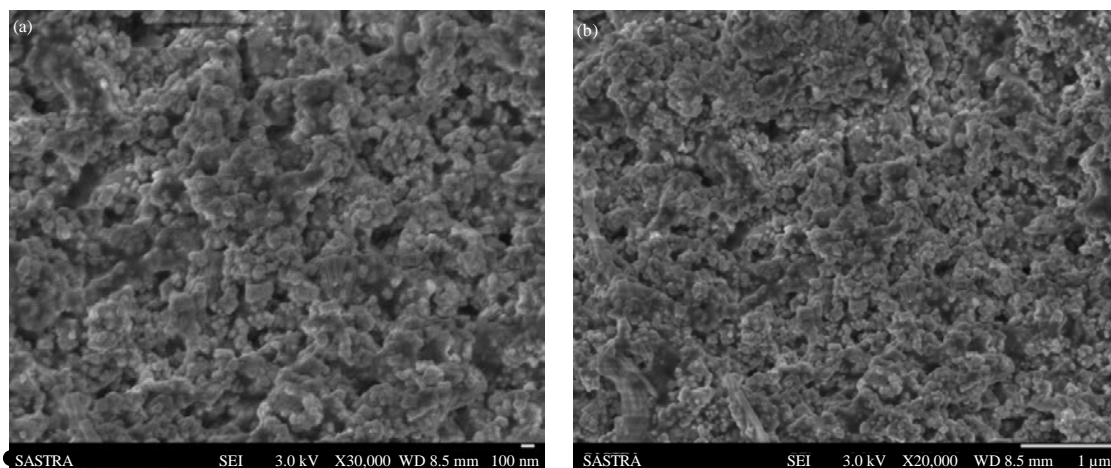


Fig. 3(a-b): Typical FE-SEM photographs of synthesized ZnO nanoparticles at two different magnifications, (a) 30,000X and (b) 20,000X showing the particles with spherical morphology

of nanoscale ranged particles. X-ray diffraction studies confirmed that the synthesized materials were ZnO with wurtzite phase and all the diffraction peaks agreed with the JCPDS data (Kim *et al.*, 2010).

The average grain size of the particle was calculated using Debye-Scherrer equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where,  $K = 0.9$  is Debye-scherrer constant,  $\beta$  is the full width at the half-maximum (FWHM) and  $\theta$  is the diffraction angle.

The FESEM pictures at two different magnification of synthesized ZnO nanoparticles is shown in Fig. 3. These pictures confirm the formation of ZnO nanoparticles and it suggest that the

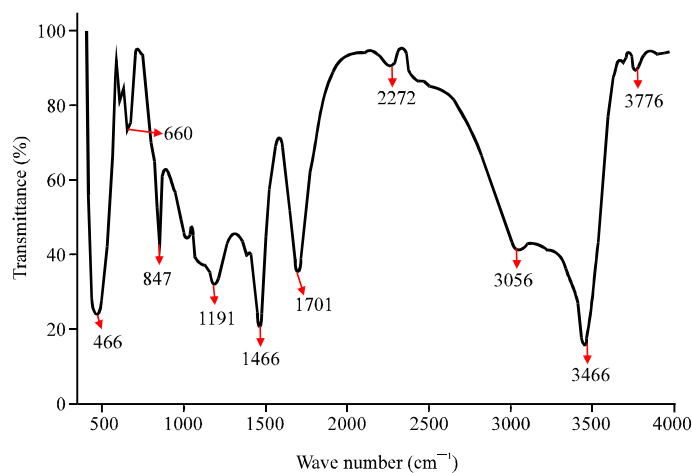


Fig. 4: Typical FTIR spectra of the synthesized ZnO nanoparticles, in which the peaks below  $500\text{ cm}^{-1}$  confirmed the presence of ZnO

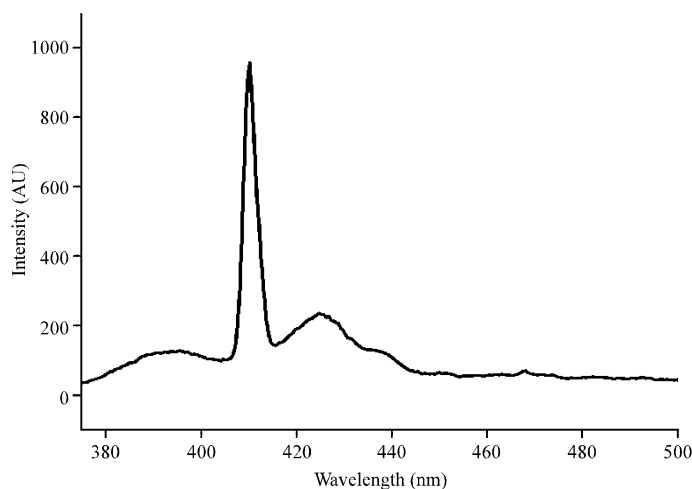


Fig. 5: PL spectra of ZnO with the excitation wavelength of 325 nm at room temperature

nanoparticles have spherical morphology. From the figures, it also can be seen that the size of the nanoparticle was less than 39 nm which was in good agreement with the grain size (26 nm) calculated from the Debye-Scherrer formula.

The FTIR of the ZnO nanoparticles is shown in Fig. 4. The observed main peaks below  $500\text{ cm}^{-1}$  corresponds to (Zn-O) confirms the formation of ZnO. A peak near  $1466\text{ cm}^{-1}$  is due to  $\text{NO}_3$  bonding which might be due to the absorption of nitric acid group on the ZnO powder surface and a peak at  $2272\text{ cm}^{-1}$  might be due to carboxylic acid. A peak between  $3010$  and  $3100\text{ cm}^{-1}$  is due to C-H stretching. The absorption peaks above  $3000\text{ cm}^{-1}$  are due to unsaturation (Nehru *et al.*, 2012; Talam *et al.*, 2012).

The room temperature photoluminescence (PL) spectra of ZnO nanoparticles is shown in Fig. 5. The spectrum of ZnO exhibits UV emission at 395 nm and sharp emission at 410 nm. These

are attributed to (near-band-gap edge emission) radiative recombination between the electrons in the conduction band and holes in the valance band and oxygen vacancies (Talam *et al.*, 2012; Yu *et al.*, 2009):

$$E_g = \frac{hc}{\lambda} \quad (2)$$

The bandgap of synthesized ZnO nanoparticles calculated using bandgap Eq. 2 was 3.14 eV, which was less when compared with the actual bandgap of ZnO (3.37 eV).

## CONCLUSION

ZnO nanoparticles were successfully synthesized by Hydrogel method. The crystallinity of the nanoparticles were confirmed from the high intensity peaks of XRD. The average grain size was calculated to be 26 nm by Debye-Scherrer equation. FESEM images showed that the nanoparticles had spherical morphology. In addition to this, FTIR analysis confirmed the formation ZnO. From these results it is clear that the adopted method can be successfully utilized for the preparation of size controlled ZnO nanoparticles.

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