International Journal of Biological Macromolecules 104 (2017) 1833–1836

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Wet chemical synthesis of chitosan capped ZnO:Na nanoparticles for luminescence applications

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ARTICLE INFO

Article history:
Received 12 November 2016
Received in revised form 30 January 2017
Accepted 7 February 2017
Available online 9 February 2017

Keywords:
Chitosan
ZnO nanoparticles
Imaging
Photoluminescence
Biomedical applications

ABSTRACT

The structural and optical properties of nanomaterials exhibit severe changes when capped with organic polymers. In this work we focus on the effect of chitosan capping on ZnO:Na nanoparticles synthesized by wet chemical method. The main characteristics analyzed are x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL). Hexagonal crystal formation of nanoparticles was confirmed from the XRD and the lattice strain was estimated from the Williamson Hall (WH) plot. Various bonds present in the synthesized sample were analyzed using FTIR. Capping results in the reduction in grain size thereby enhancement in the PL intensity. The yellow emission is in well agreement with the Commission International d'Eclairage (CIE) diagram.

1. Introduction

Zinc oxide is a well-known oxide phosphor having significant role in the optical and biomedical field of modern research. When doped with suitable elements ZnO finds important applications in light emitting diode [1], transparent conducting oxides [2], photo catalyst [3] etc. The stability and nontoxic nature of this oxide phosphor lead them to be used as a labeling agent in bio imaging [4] and as an antibacterial element [5]. The wide band gap, luminescence efficiency and the drastic changes in properties in the nano regime of ZnO leads to the effective execution of these applications. Doping with different activators will help us to utilize this blue phosphor to the wide range applications of optoelectronic field. Green and red emitting ZnO was reported very often, but there are only few reports on the yellow emitting ZnO, which is resultant of Na doping [6,7].

During material synthesis, especially in colloidal mixing, capping agents are used to prevent the excess growth and agglomeration of nanoparticles. These stabilized resultant particles show boosted structural and optical properties. For ZnO, there are previous reports on the effect of capping agents like polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), triethanolamine (TEA) etc. These are synthetic capping elements and have minimum use in biological area. So in the present scenario, usage of natural polymers is of high relevance due its remarkable applications.

Chitosan is a highly basic natural polysaccharide found in the shells of crustaceans, molluscans and cell walls of some fungi. It is a non toxic, biocompatible and biodegradable polymer found in various medicines and have used in the agricultural area also. ZnO capped with chitosan is an interesting material of research due to its applications like UV protector [8], anti-microbial activity [9] etc. Chitosan conjugated with folic acid have high attraction towards the cancer cells bearing the folate receptors. So the ZnO-chitosan-folic acid complexes have found very good applications in the tumor-targeted bio imaging and drug delivery [10]. The main synthesis technique employed are sol-gel [11], chemical precipitation [12], hydrothermal [13] etc.

This is the first time report of chitosan capped ZnO:Na nanoparticles which is a yellow phosphor. Pure ZnO gives blue emission, which is the least eye sensitive colour. Hence yellow is preferable for luminescence applications in medical field being more eye sensitive and having less scattering than blue. Both chitosan capping and doping with Na will not affect the biocompatibility of ZnO. But chitosan capping enhances the purity and intensity of yellow emission in ZnO:Na nanoparticles which help them useful in biomedical applications. We have employed the wet chemical method for the synthesis and the characterization techniques used are x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL).

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http://dx.doi.org/10.1016/j.ijbiomac.2017.02.027
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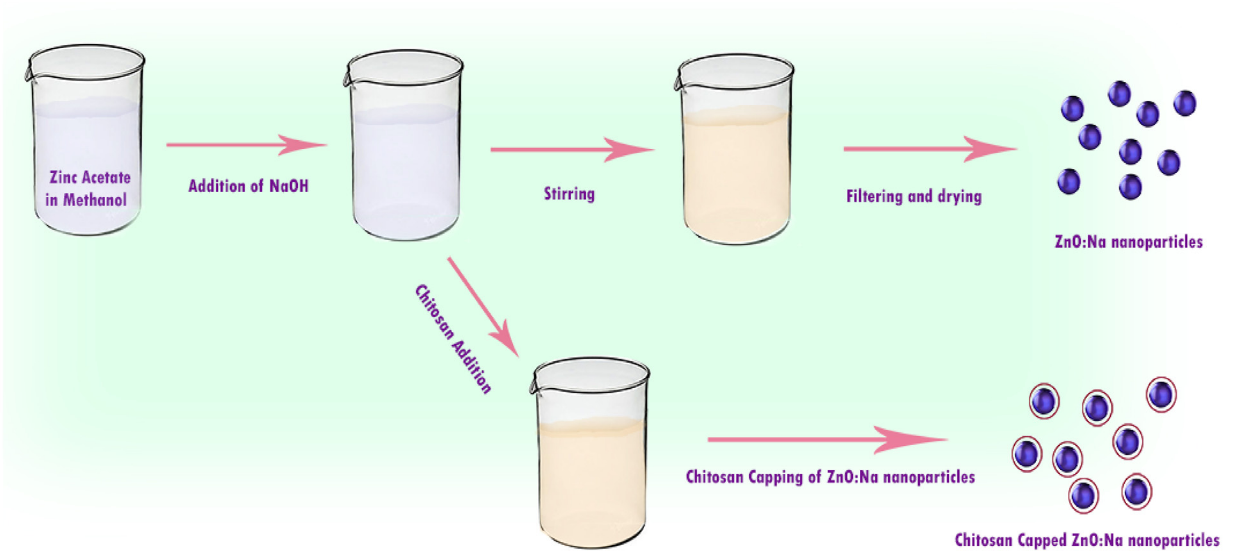

Fig. 1. Schematic representation of the synthesis of ZnO:Na nanoparticles by wet chemical method.

2. Experimental

2.1. Materials

All reagents were of analytical grade and used as such without further purification. Zinc acetate and Sodium hydroxide pellets were procured from Merck with 98% purity, and Chitosan(DDA-80 to 85) was purchased from Koyo Chemical Ltd.,Japan.

2.2. Preparation of chitosan capped ZnO:Na nanoparticles

0.1 M zinc acetate prepared in 50 ml methanol was used as the precursor for the synthesis of ZnO nanophosphor. 0.175 M sodium hydroxide (NaOH) was added to the above solution for Na incorporation. The solution was magnetically stirred for one and half hour at room temperature, centrifugally filtered and dried using a hot air oven. The resultant white product was grinded using agate mortar and pestle to get the fine powder of the ZnO:Na nano phosphor. Capping was done by adding 4 mg of chitosan after NaOH, during the mixing procedure. A schematic representation of the experimental procedure is portrayed in Fig. 1.

2.3. Characterization

The crystallographic analysis was done using Bruker AXS D8 advance X-ray diffractometer (Cu-Kα radiation λ = 1.5406A°) by recording the data in the range 20° to 65° with a step size of 0.02°. FTIR Spectrophotometer was used for the identification of vibrational bands [Scanning range: 400–4000 cm^{-1}]. Photoluminescence emissions were recognized using Horiba Flouromax-4C Spectrofluorometer keeping excitation slit width at 1 nm, emission slit width at 3 nm and integration time as 0.1s.

3. Results and discussion

3.1. Characterization of the chitosan capped ZnO:Na nanoparticles

The x-ray diffraction (XRD) pattern for the uncapped and chitosan capped ZnO:Na is depicted in Fig. 2.a. From the figure it is confirmed that the samples agree with the JCPDS file 89-0510, having hexagonal crystal structure. The two impurity peaks [denoted as δ] in the uncapped ZnO is from the zinc hydroxide phase present in the synthesized sample [JCPDS: 38-0356]. On chitosan capping, the diffraction peaks get broadened thereby decreasing the crystallite size. Also, the impurity peaks due to hydroxide are eliminated on capping and a better crystalline structure is obtained. The minute peaks around 25° in the XRD spectrum is due to diffraction from chitosan [14]. The average grain size of the synthesized ZnO:Na nanoparticles was estimated using the Debye – Scherrer formula,

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where λ, β and θ respectively denote the wavelength of x-rays used, full width at half maximum of the diffracting peak and glancing angle.

The lattice parameters (a, c) were calculated from the inter planar distance (d_{hkl}) using the following expression

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Where (hkl) denotes the miller indices of the corresponding planes. The grain size and lattice parameters for the synthesized samples are tabulated in Table 1.

There is a chance of introduction of strain (ξ) in the crystal lattice on synthesis and it is associated with the grain size and glancing angle by the following relation [15]

$$\beta\cos\theta = \frac{0.9\lambda}{D} + 2\xi sin\theta$$

Fig. 2b is the Williamson-Hall (WH) plot, representing the above relation of grain size and lattice strain. It is a plot between 2sinθ and βcosθ in which the slope gives the strain in lattice and the y intercept leads to the grain size. In the present case, the plot for uncapped ZnO:Na represent a straight line having lesser slope than the capped one indicating an increase in lattice strain on chitosan capping. The reduction in grain size with capping is also observable from the plot, because higher the y intercept value lower the grain size and vice versa.

FTIR spectra for the capped & uncapped ZnO:Na nanoparticles along with chitosan is portrayed in Fig. 3. The absorption peaks shown in the spectra denotes the various vibrational bands present in the synthesized sample. There is shift in the absorption peak values and intensity on chitosan capping as presented in Table 2.