I J C T A, 9(9), 2016, pp. 4003-4008

Preparation of Chitosan/Seaweed-ZnO nanorods for better Antibacterial activity

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ABSTRACT

Novel Chitosan/Seaweed-ZnO (CS/SW-ZnO) nanorods were prepared by deacetylation process using chitin, zinc chloride and padina tetrastromatica (PTS) as source materials and sodium hydroxide as precipitant. Appearance of peaks for amine and ZnO in the FT-IR spectra confirmed the presence of ZnO nanoparticles. The surfaces of nanorods were characterized using SEM and TEM analysis. The atomic ratio of 78:21 (Zn:O) was obtained by Energy Dispersive X-ray analysis (EDAX). XRD pattern clearly indicates that prepared chitosan/seaweed-ZnO nanorods structures with range of 15-60 nm. The optimized condition for preparation of complex with dense pack and uniform distribution of rods. The sizes of nanoparticles/ rods were reduced with increase the concentration of sodium hydroxide and Seaweeds (PTS). The antibacterial properties of the CS/SW-ZnO nanorods were tested against Gram positive and Gram negative bacteria species.

Keywords: Deacetylation; Seaweed; Nanorods; FTIR; EDAX; TEM

1. INTRODUCTION

For the past few years, nanoparticles have attracted more interests because of their size-dependent properties compared with those of bulk materials. ZnO nanoparticles are mainly used for semiconductor device with wide band gap of 3.37 eV, large excitation energy of 60meV. Because of excellent chemical active and thermal stable, it has plenty of useful applications such as light-emitting diodes [1] and in textiles as antibacterial agents [2] and UV blocking agents [3]. For synthesis of ZnO nanoparticles and nanorods with good crystallinity, chemical and thermal stability, wet chemistry methods like hydrothermal (using water) and solvothermal (using organic solvent) are most extensively used.

In order to prevent particles agglomeration during synthesis of ZnO nanoparticles using these methods, organic surfactants such as cetyltrimethylammonium bromide, ethylenediamine[4-6], polyethylene glycol [7 & 8], carbamide [9], hydrazine [10] and some solvents such as ethylene glycol [11], ethanol [12] and inorganic metal catalyst potassium iodide [13]were used.

To increase the efficiency of synthesized materials, multifunctional hybrid organic–inorganic materials are prepared for usage in various areas, such as optics, electronics, biology, and biotechnology, because of their superior properties to those of the parent organic or inorganic species. Now a day, specific attention has been given to prepare the biopolymer-based nanocomposites, since that type of materials can serve as functional analogs for naturally occurring materials. Introducing of organic chemicals, solvents or metal catalyst into the reaction system either in the hydrothermal or in the solvothermal process, it complicates the synthesis process and make high production cost, so it is necessary to find out alternate biomaterials to use as a surfactant, catalyst or involving in the chemical reaction.

Chitin, a natural biopolymer and source for chitosan is estimated to be produced annually, as much as cellulose, from the waste of the seafood, particularly shells of crustaceans and shrimp. Recently [14], we

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synthesized micro size rod like chitosan-ZnO complex and in the present investigation, chitosan/seaweed-ZnO nanorods were synthesized in the organics-free atmosphere. The extracted chitin and seaweed (PTS) from crabs were used as a source material as well as surfactant, refluxed with and precipitated by adding sodium hydroxide.

2. EXPERIMENTAL DETAILS

2.1. Materials

$ZnCl_2$ (99.5%), NaOH (99%), HCl (93%) and CH_3COOH (99.5%) were used (AR) grade materials from Alpha Acer, Mumbai. Chitin, the shells of crab were collected from mandapam and apply to demineralization and deproteinization. Seaweed (PTS) padina tetrastromatica was collected from seashore at Rameshwaram. Demineralized water was utilized throughout the experiment.

2.2. Preparation of samples

The chitin (0.25g), 30 ml each of $ZnCl_2$ 15% (W/V) and NaOH 45% (W/V) were taken and the preparation were followed as reported by [14]. The filtered residues were dried in a hot air oven at 130ºC for 2.5 h and this sample was named as CS-ZnO. The same methods were repeating by taking chitin instead of seaweed (0.5g). These samples were designated as SW-ZnO respectively.

3. RESULTS AND DISCUSSION

3.1. SEM analysis

SEM image of Chitosan/ Seaweed -ZnO nanoparticles/rods dried at 130ºC are shown in Fig. 1(a-b). The sample prepared with 15% $ZnCl_2$ and 45% NaOH (CS/ZnO) obviously shows in various types of particles, sheets and rods in (Fig 1a). The same observations also noted in the Seaweed/ZnO (SW/ZnO) sample, but it has equal distribution of particles and smaller size of nanorods (Fig.1b). It was also noted from the image, which formed ZnO nanorods are uniformly accommodated in a particular place.

3.2. FT-IR spectroscopy

FT-IR spectral studies of Chitosan/Seaweed-ZnO nanorods are shown in the Fig. 2. The absorption peak appeared at 1629 cm^{-1} which is attributed to (N-H) bending vibration of amine group, confirm the presence of $–NH_2$ group [15] in the CS-ZnO sample (Fig. 2a). The stretching vibration of –OH and $–NH_2$ groups at 3439 cm^{-1} indicates the hydrogen bonding. Zinc oxide bond formation is confirmed by the peaks appeared at 476 cm^{-1} [16].

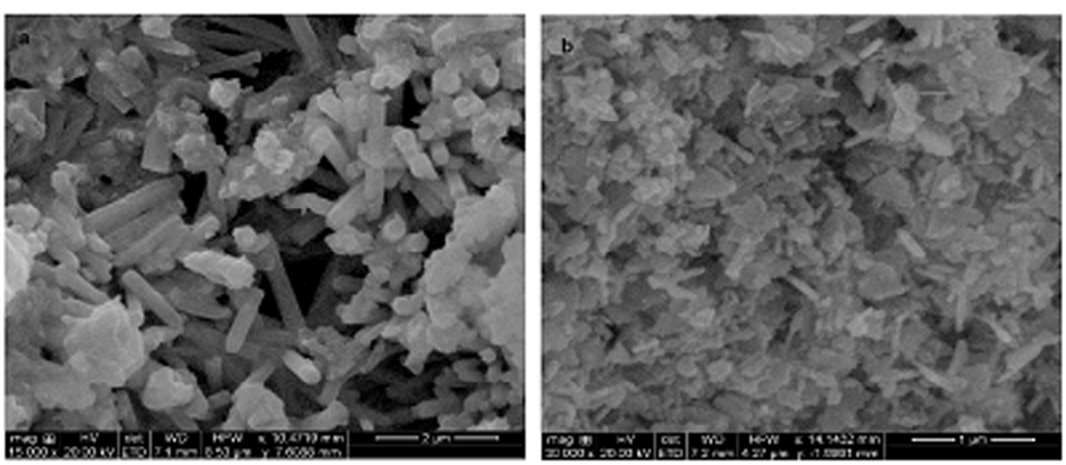

Figure 1: SEM image of Chitosan/Seaweed-ZnO nanorods (a) CS-ZnO and (b) SW-ZnO

The polysachaaride of seaweed/ZnO (SW-ZnO), a high intensity sharp 3493 cm^{-1} and broad (1632 & 1442 cm^{-1}) peaks were noticed [11]. A new band at 2359 cm^{-1} which is attributed to the C-N asymmetric stretching vibration [17] was appeared (Fig.2b). The absorption band range (1800 cm^{-1} – 1300 cm^{-1}) consists of $-NH_2$ deformation was appeared in distorted condition. This is clearly evidence in the formation of ZnO bonded with chitosan and seaweed [18] ZnO bond [19] was showed at 436 cm^{-1} [20 & 21]. Basic peaks of chitosan polymer at 1193 cm^{-1}, 1073 cm^{-1} and 1022 cm^{-1} were noticed [22].

3.3. XRD diffractrometry

Fig. 3 (a-b) shows the XRD pattern of chitosan/seaweed-ZnO nanoparticles. The nano-sized hexagonal structure phase of ZnO reported in JCPDS card (No. 36-1451, a = 0.3249 nm, c = 0.5206 nm). The particle size was calculated using Scherer ($D = .94\lambda/\ \beta\ \cos\theta$) equation varies from 15-60 nm which was mainly

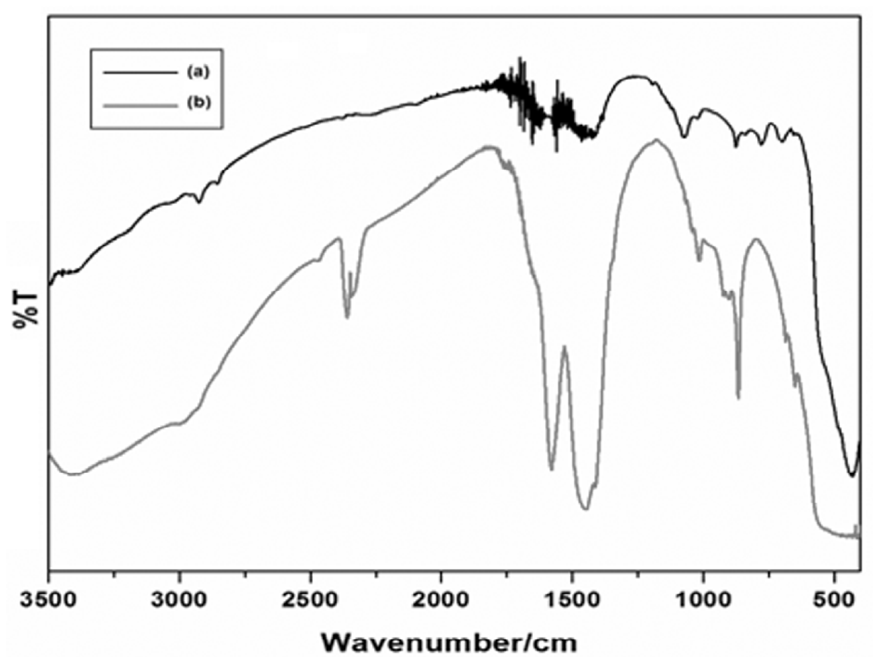

Figure 2: FT-IR spectra of Chitosan/Seaweed-ZnO nanorods (a) CS-ZnO and (b) SW-ZnO

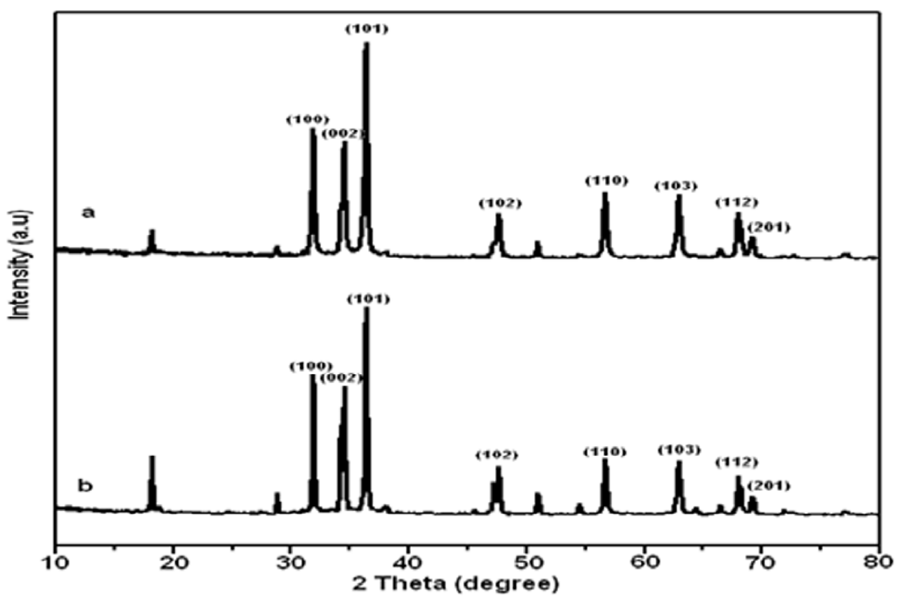

Figure 3: XRD pattern of Chitosan/Seaweed-ZnO nanorods (a) CS-ZnO and (b) SW-ZnO

depends on seaweed (PTS) and NaOH concentration. The calculated nanosize of ZnO good agreement with characteristic of nano-sized particles reported in literature [23].

3.4. EDX Analysis

EDX analyses of Chitosan/Seaweed-ZnO nanoparticles/rods are shown in (Fig.4). The atomic ratio of (Zn/O) was calculated from sample show the atomic ratio of 78:21 for CS-ZnO sample. The atomic ratio Zn:O to be expected 1:1 is believed to have originated from the absorption of excessive zinc ions on the surface of the nanoparticles [24 & 25]. Based on the stoichiometric composition and chemical purity of these samples, the nanorods are obtained in good quality [26].

3.5. TEM analysis

The nanostructure of chitosan/seaweed-ZnO nanoparticles/rods were analyzed by TEM analysis is shown in Fig. 5. This image reveals that the product consists of nanorods and hexagonal nanoparticles with the

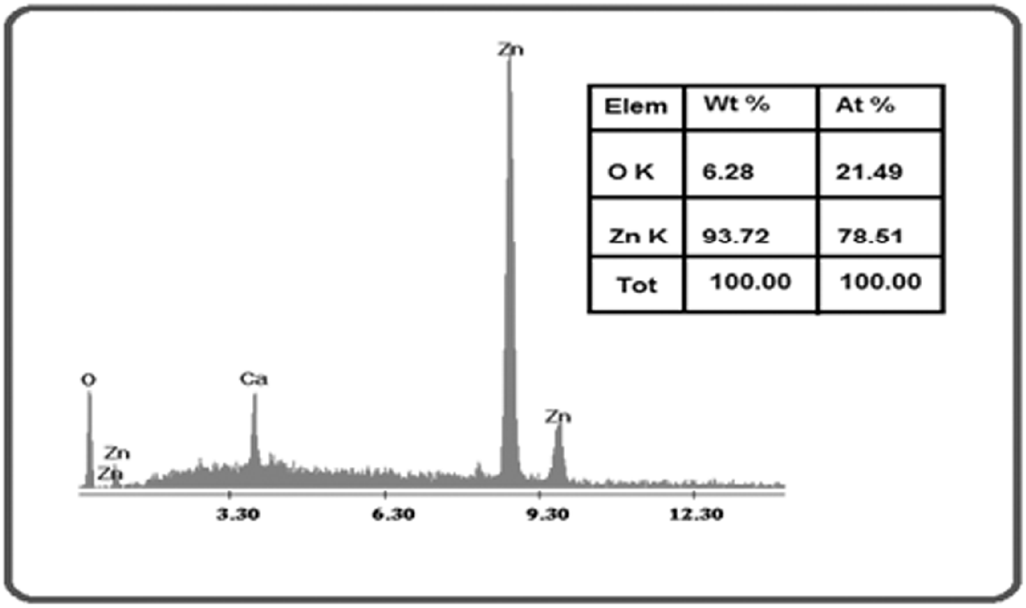

Figure 4: EDX patterns of Chitosan-ZnO nanorods (a) CS-ZnO.

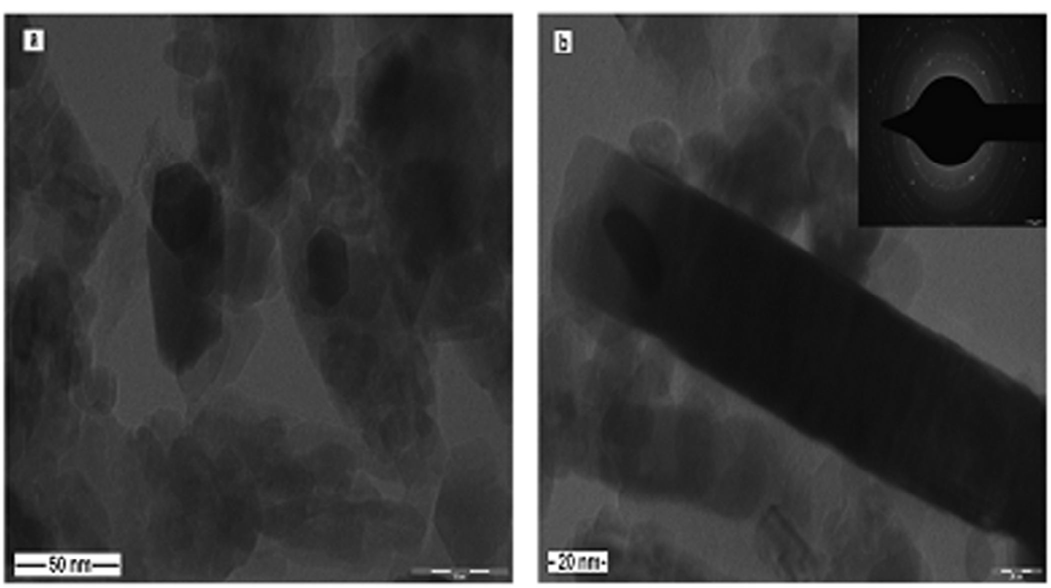

Figure 5: TEM image of Chitosan/Seaweed-ZnO nanorods (a) CS-ZnO and (b) SW-ZnO

average size of 50 nm (Fig. 5a). A nanoparticle with 100 nm widths was shown in the (Fig. 5b) which is in good correlation to Scherer formula based on the XRD pattern.

3.6. Antibacterial Activity

Biological activity requires the interactions with microorganism, this type interaction is subjective by molecular size, functional group and metal ion. Figure 6 shows the zone of inhibition values of CS-ZnO and SW-ZnO nanorods using S. aureus, and E. coli bacteria. When compared with pure chitosan, the zone of inhibition for S. aureus on CS-ZnO/ SW-ZnO nanorods are increased 54 to 60 mm and E.Coli bacteria is increased to 42 mm to 45 mm, respectively.

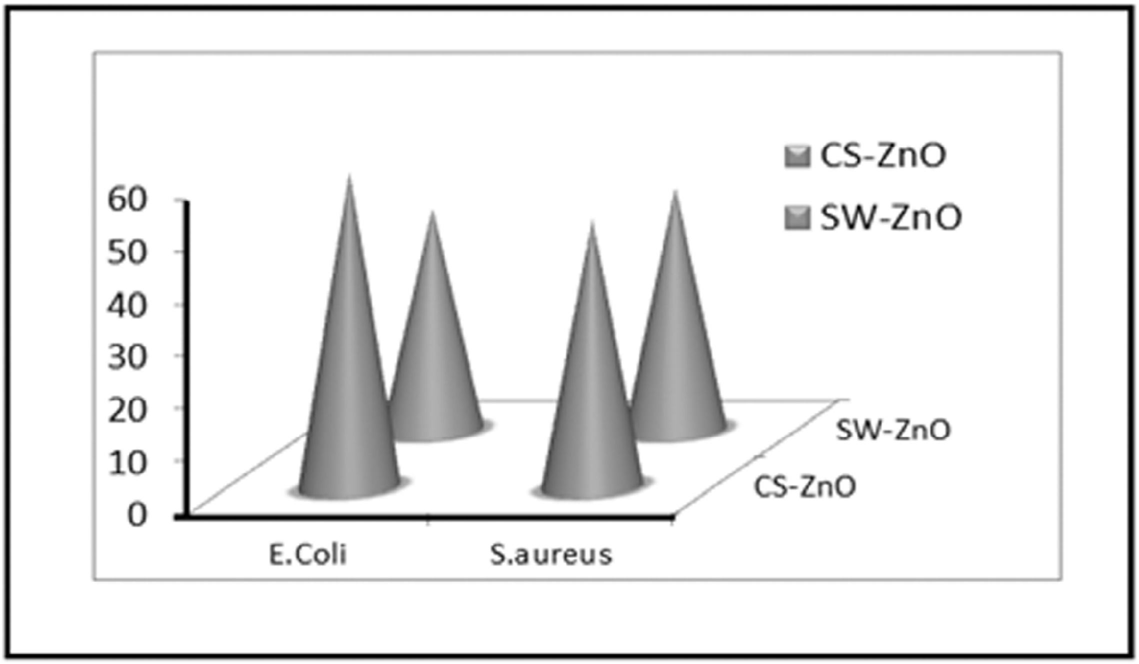

Figure 6: Antibacterial activity of Chitosan/Seaweed-ZnO nanorods against E.Coli and S.aureus bacteria (a) CS-ZnO and (b) SW-ZnO

4. CONCLUSIONS

To conclude, the novel chitosan/seaweed-ZnO nanorods were prepared by eco-friendly hydrothermal deacetylation process was confirmed by FTIR spectra. XRD data showed that the obtained chitosan-ZnO nanorods were composed of hexagonal wurtzite phase. The individual particle size is evidenced nanoscale from the SEM and TEM images. The as-prepared nanorods are used for antibacterial activity against E.coli bacteria to get better antibacterial activity.

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