GREEN SYNTHESIS OF COBALT (5%, 10% AND 15%) DOPED ZNO NANOCOMPOSITES BY USING FLOWER EXTRACT OF HIBISCUS ROSA SINENSIS AND THEIR BIOSENSOR ACTIVITY.

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A B S T R A C T

In the present study states a green approach for the synthesis of Cobalt (5%, 10% and 15%) ZnO nanocomposites by employing a flower extract of hibiscus rosa sinensis. The resultant nanocomposite was characterized by using UV-Visible spectroscopy, Fourier Transform Infrared Spectroscopy, X –ray diffraction and Transmission Electron Microscopy. The average crystalline size of 5% Co doped ZnO nanocomposite was 21-25 nm, which is in good agreement with TEM images. The band gap of Co doped ZnO was found to be 3.34 eV.

Further Co doped ZnO –Chitosan composite was modified for enzyme immobilization and Urea bio sensing.

Keywords: CZO, green synthesis, urea biosensor

1. Introduction

Nanotechnology is one of the most active areas of research in modern material science. This field has been emerging out day by day making an impact in sphere of life human life and creating new advancement in the life sciences. Nanocrystalline particles have tremendous application in the field of biomolecular detection, antimicrobials [1], catalysts and biosensors.

Green synthesis of nanoparticles makes use of environmental friendly, non toxic and safe reagent. Phytomining is the use of hyper accumulating plant to extract a metal from biomass to return an economic profit [2].

ZnO has been the most commonly and extensively studied material in the field of nano science and technology. It is because of the unique characteristics of this material, Such as high isoelectric point (9.5), high band gap energy (3.37eV), low cost, high stability, high binding energy of 60 meV [3-4]. Due to these tremendous properties, ZnO nanoparticles have been extensively used in light-emitting diodes, laser diodes, solar cells, microelectronic, surface acoustic wave devices, hydrogen-storage devices, transparent electrodes, transparent thin-film transistors, antibacterial coating, UV protectors, targeted drug delivery and sensors [5-8].

Chitosan (CS) is a low cost, biocompatible, high molecular weight branched polymer with unique physical and chemical properties. The important advantages are biodegradability, non toxicity, electrolytic properties and polymer modification [9].

The aim of present study is to synthesized Co doped Zinc oxide nanocomposite by using flower extract green synthesis route. The transition metal doping is expected to improve the optical, electrical and structural properties over their individual component. A biosensor was developed to sense urea. The response of urease immobilized on CH/Co doped ZnO/Au working electrode towards the detection of urea.

2. Materials and methods

2.1 Reagents

Cobalt (II) nitrate hexahydrate (Co $(NO_3)_2.6H_2O$) and zinc nitrate hexahydrate (Zn $(NO_3)_2.6H_2O$) were purchased from Sigma- Aldrich. The Urea was obtained from Qualigens fine chemicals, Mumbai. Urease enzyme was obtained from Loba chemie. All other chemicals were used of analytical grade.

The PBS (0.05M, pH 7.0) was prepared freshly before each experiment.

2.2 Preparation of flower extract

The petals of Hibiscus rosa-sinensis were collected directly from the plant. The ample amount of Hibiscus rosa-sinensis petals were taken and thoroughly washed with distilled water and dried it for five days under shadow. After it gets properly air dried, the dried petals were cutted and grinded to powder by using mixer.

The flower extract was prepared by placing 4.5 g dried fine powder of Hibiscus rosa-sinensis flower in 250 ml glass beaker along with 100 ml distilled water. The mixture was then boiled for 1.5 hours until the colour of aqueous solution changes reddish on magnetic stirrer. The extract was cooled at room temperature and filtered using Whatmann filter paper. The extract was stored in refrigerator.

2.3 Synthesis of Cobalt doped Zinc Oxide nanocomposites

The extract of flower was used for the synthesis of Cobalt doped zinc oxide nanocomposite. The 30 ml Hibiscus rosa-sinensis flower extract was taken and boiled at 60-80^0 C using magnetic stirrer. To this add 3g of zinc nitrate and cobalt nitrate (5%, 10% and 15%). The solution was stirred for 4 h maintaining the temperature at 90° C. After this time, the temperature was reduced to 30° C. The solution was stirred for 24 h till colour of solution become yellow. Further annealing of remnants was carried out in muffle furnace at 350° C for 1 h. The white powder was obtained.

2.4 Preparation of Co doped ZnO/Chit/Au plate electrode

Chitosan (100 mg) was dissolved in 50 ml of 0.2M acetic acid by stirring at room temperature for about 3h, and then sol gel derived Co doped ZnO nanoparticles were dissolved in 20 ml of chitosan solution with stirring for 30 minutes. Finally, a viscous solution of Chit-nano Co doped ZnO was obtained. The Chit-nano Co doped ZnO solution was deposited onto the surface of Au plate by spin coating technique. The prepared Chit-nano Co doped ZnO /Au electrode was kept dry for 6h. Further it was rinsed repeatedly with 0.05M phosphate buffer.

2.5 Fabrication of bioelectrode

The Urease an enzyme was immobilized onto surface of Chit-nano Co doped ZnO /Au electrode. The Urease enzyme 10 µL solution prepared in phosphate buffer (pH 7.0, 0.05M) was placed over Co doped ZnO/Chit/Au plate electrode. The bioelectrode was washed with buffer solution, dried and stored at 4^{0}C when not in used.

3. Results and discussion

3.1 X-ray diffraction

The powder x-ray diffraction methods are used to study the structural properties and the phase purity of the samples. Fig.1 shows the XRD pattern of the synthesized Co-doped ZnO nanocomposites which are annealed at 350^{0}C. The intense diffraction peaks of Co doped ZnO appears at 31.60^0, 34.41^0, 36.33^0, 40.66^0, 47.51^0, 55.66^0, 61.66^0, 67.60^0, which correspond to (100), (002), (101), (102), (110), (103), (200), (112) respectively. All the diffraction peaks, which have been labeled with (hkl) planes, were matches with JCPDS data card: (36-1451). The detected peaks are certainly indexed as ZnO hexagonal wurtzite structure verified by PDF Code: 36-145.

The (101) peaks shows variation in the intensity at 36.33^0 Bragg's angle. The grain size of nanocomposite was determined using the Debye Scherrer equation**.**

$$D = K\lambda / \beta \cos\theta$$

Where K is constant equal to 0.94, D and λ are the particle size in manometer and wavelength of the radiation (1.54056 Å for Cu Kα radiation) respectively. β and θ are the peak width at half-maximum intensity (FWHM) and peak position. The average crystallite size of 5% Co doped ZnO is found to be 21-25 nm.

The particles size for Co doped ZnO was found to be lower than pure ZnO (26.93 nm). It was found that the decrease in the particle size was attributed to disorders created by the cobalt ions in the ZnO lattice structure. From the study it was assumed that for a smaller amount of Co, its ions substitute well with Zn ions. Furthermore the peak positions were shifted to higher 2θ values indicating possible contraction of the ZnO unit cell [10].

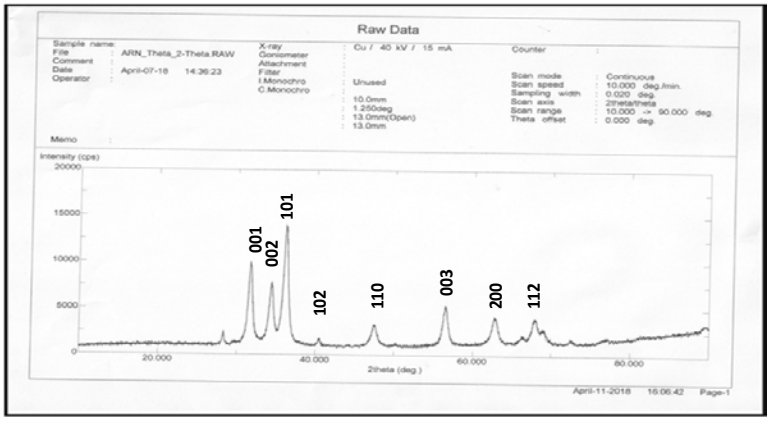

Fig. 1: XRD pattern of 5% Co doped ZnO nanocomposite

3.2 FTIR Spectroscopy

The FTIR spectrum was recorded using KBr solid pellet technique. Fig. 2 Shows the FTIR spectra of Co doped ZnO. The weak absorption peaks at 3213 cm^{-1} attributed to the O–H stretching vibrations. This is related to the absorbed water on the surface of nanomaterial. Another intense absorption peak at 586.39 cm^{-1} is related to the stretching vibrations of the Zn–O bond. Some absorption band near 509 cm^{-1} was also found. This is related to the vibration of the Zn–O bond.

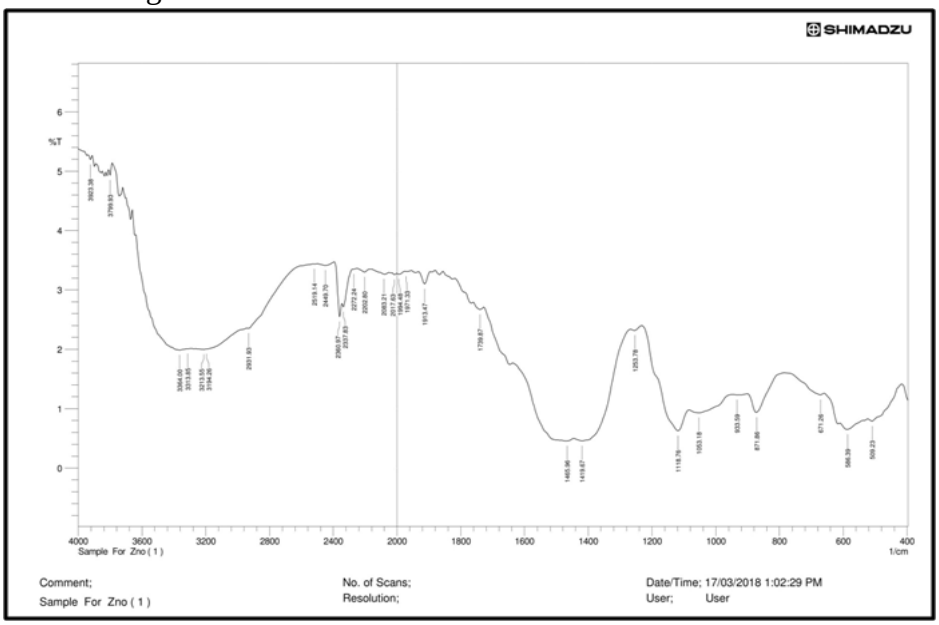

Fig. 4: FTIR spectra of 5% Co doped ZnO nanocomposite

3.3 UV- Visible Spectroscopy

The UV spectra of Co doped ZnO was examined using (Shimdzu- 1800) UV-Visible Spectrophotometer in the visible range. Fig.3 represent the absorption spectra of Co doped ZnO (CZO) at 371.0 nm in the visible range between 200 - 800 nm of wavelength, which indicate the formation of Co doped ZnO nanoparticle by green synthetic route. The band gap energy was calculated on the basis of maximum absorption band of Co doped ZnO. From the UV-Visible spectra, it was found that absorption band at 371.0 nm for Co doped ZnO nanocomposite.

The band gap energy is calculated according to following equation [11]**.**

$$E_{bg} = 1240/\lambda$$

Where E_{bg} is the band gap energy and λmax is the wavelength (371.0 nm) of the nanocomposite. The energy band gap (E_{bg}) for Co doped ZnO was found to be 3.34 eV which is lesser than pure ZnO (3.37 eV) Moreover, the absorption spectra is changed owing to incorporation of Co^{2+} ions into the ZnO crystallographic planes.

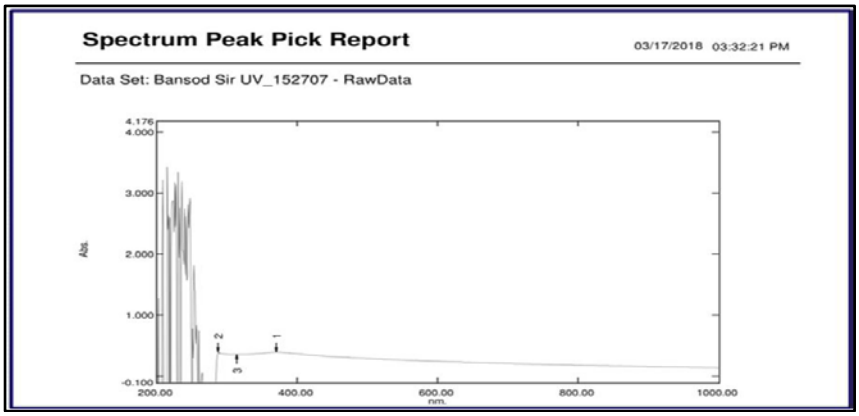

Fig. 3: UV-Visible Spectra of 5% Co doped ZnO nanocomposite.

3.4 Transmission electron microscopy

The size and morphology of 5% Co doped ZnO nanocomposite were analyzed by TEM as showed in fig. 4. The TEM images 5% Co doped ZnO nanocomposite shows a globular morphology and high density growth with some agglomeration.

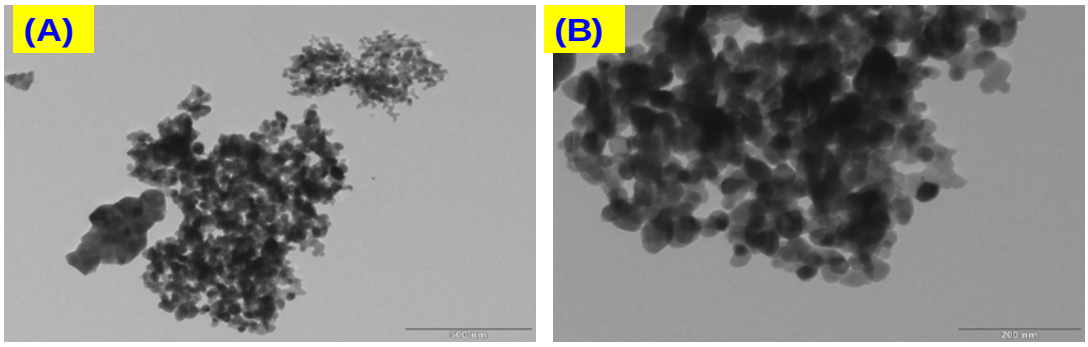

Fig.4: TEM Spectra of 5% Co doped ZnO nanocomposite

3.5 Electrochemical studies

The cyclic voltammetric (CV) studies (Fig.5) of CH/Co doped ZnO (CZO)/Au plate have been carried out in PBS (0.05 pH 7.0,1% KCl) containing 5mM $[Fe(CN)_6]^{-3/-4}$. The magnitude of current response of CH/Co doped ZnO(CZO)/Au plate (Curve a) is higher than that of bare Au plate (curve c). It revealing that Co doped ZnO nanocomposite have increased electro active surface area of electrode resulting in enhanced electron transport between the electrode and electrolytic medium. However (curve b) shows magnitude of current response decreases after immobilization of urease enzyme onto CH/Co doped ZnO (CZO)/Au plate. This may perhaps due to insulating characteristics of urease enzyme.

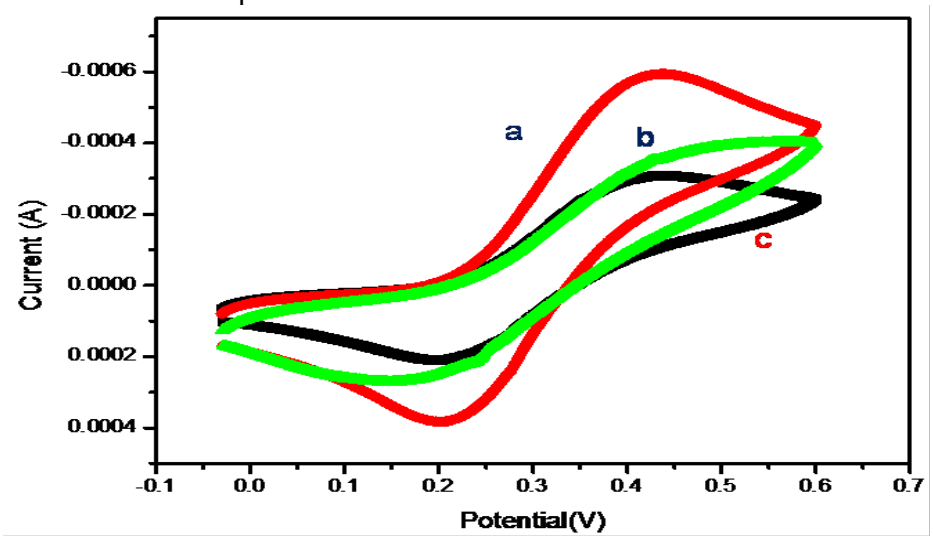

Fig. 5: CV studies of a) CH/Co doped ZnO/Au plate b) Urs/CH/Co doped ZnO/Au plate c) bare Au plate

4. Conclusion

In summary, Co doped ZnO nanocomposites were successfully synthesized by facile green synthetic route. The detailed characterization viz. UV-Visible, IR XRD and TEM confirmed that the nanocomposites were grown in high density with particle size 21-25 nm. The urea biosensor was fabricated by immobilizing Urs onto CH/Co doped ZnO/Au plate. It shows excellent sensitivity with respect to urea analyte.

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6. References

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