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Original Article

Biosynthesis of Znic oxide nanorods s Using Bacterial Cellulose as a Biotemplate

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Abstract
Fabrication of znic oxide nanorods s by using sol- gel technique by Bacterial cellulose Robbins mediated static fermentation of *Komagataeibacter Xyliunus* The characterizations of znic oxide nanorods using A Fourier transform- infrared spectrum (FTIR) confirmed the presence of ZN-O group while XRD provide the crystalline of znic oxide nanorods s, TEM and SEM confirmed the shape of zinc nanorod in rod shape and the diameter in an average of 214 nm. The thermal analysis of znic oxide nanorods s has been studied by Thermo gravimetric analysis (TGA) show that the bacterial cellulose has been pyrolysis at 643^0C by thermal treatment. Finally, we success to fabricated of ZnO nanorods using ecofriendly method mediated Bacterial cellulose Robbins as a biomaterial to control the shape ZnO NRs.

Key Words: Znic oxide nanorods , bacterial cellulose and, sol – gel technique.

Introduction

Nanotechnology is an advanced technology that contributes with sophisticated technology in many disciplines as environmental, medical science, mechanical and electronic engineering, biology, telecommunication teleology and Metallurgy (Chen et al ., 2007 ;2013) . It has become a hot spot of research in modern material science (Sirelkhatim etal., 2015). Nanotechnology allows to design and control of size, dimension and morphology of material at nanoscale (0 -100 nm) (Wang et al.,2008) . In last decades, there is more interest with one (1D) nanomaterial due to wide applications (Duan et at., 2001; Pan et al., 2001; Whang et al., 2003). Zinc oxide (ZnO) is considered as semiconducting material and piezoelectric material with a direct wide band gap of 3.37eV and has a large excitation binding energy of 60 meV at room temperature (Ozgur et al., 2005; Look, et al ., 2001). Zinc oxide nanoparticle (ZnO NPs) often used as a highly functional metallic nanoparticle (Wang et al.,). Zinc oxide nanoparticle (ZnO NPs) often used as a highly functional metallic nanoparticle .,2014). ZnO nanoparticles have various applications in electronic, optoelectronic, electrochemical and electrome-chanical devices (Heo et al ., 2004; Yi et al .,2005; Huang et al ., 2001) , Such as ultraviolet (UV) laser (Wang et al.,2008) , light- emitting diodes (Parke et al ., 2004), field emission devices

(Wang et al ., 2006), high performance nanosensor (Wei et al ., 2009; Yeh et al., 2009), solar cells (Law et al ., 2005; Levy-Clement et al., 2005),and piezoelectric nanogenerators (Wang et al ., 2006; Wei et al ., 2010). ZnO nanoparticle contribute in many applications including pharmaceutical, cos-metology, catalysis, industrial and biomedical science (Premanathan et al., 2011; Koipaei et al., 2016). One-dimensional metal-oxide nano-structures have been interested in; due their unique electronic and optical properties. One dimension nanostructure has various shapes such as nanotube (Berry et al ., 2005), nanowires (NWs) nanorod (Miao et al ., 2004) and nanofiber (Berry et al .,2004). One-dimensional (1D) semiconductor nanostructures have been of intense interest in both academic research and industrial applications because of their potential as building blocks for other structures (Zhang et al., 2012). Nanostructured ZnO has a high surface area, good biocompatibility, and chemical stability, nontoxic and has a high isoelectric point (IEP) of about 9.5. Therefore, ZnO nanostructure is suitable for absorption of protein with low iso-electric oil point (IEP) due to protein immobilization that depends on the electrostatic interaction. BCF is secreted

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from *Gluconactobacter* (*Acetobacter xylinum*) which has unique properties, such as large surface area, high tensile strength, abundance, high water retention capacity, high crystallinity fine fiber network, biocompatibility, relative simple and low cost [24]. BCF pellicles have ribbon-shape ultrafine nano-fiber with width less than (100nm) (Svenssona et al., 2008; Ross et al., 1991; Ma.et al ., 2010; Klemm et al ., 2001).

In the presented work, *bacterial cellulose* was used as biotemplate to synthesiz ZnO nanorod using the sol-gel technique. Synthesized ZnO nanorods were structurally characterized using SEM, TEM, FTIR and XRD analyses.

Material and methods

Chemicals

Zinc acetate hydrate (Zn $(CH3COO)_2$. $2H_2O$) were obtained from oxford (India).,NaCl , yeast extract , glucose ,Na_2HPO_4, NaOH, Citric acid were supplied from SAS chemical CO, (MUMBAI). All solutions were prepared using double deionized distilled water.

Biosynthesis and purification of the Bacterial Cellulose

Komagataeibacter Xyliunus (ATCC 10245) was incubated statically in Hestrin and Schramm (HS) medium(Schramm et al ., 1954) containing 20g/L D-glucose, 5g/L yeast extract, 5g/L peptone, and 2.7 g/L Na_2HPO_4 and 1.15 g/L citric acid in deionized water (DI). The pH of the medium was adjusted to 6.0-6.2 using 10% NaOH or 0.1M HCl. Three days old starter culture was disturbed with the ratio 1:10 in 500 mL flask containing HS medium, then incubated at 30 °C for 5-7 days. The *Bacterial Cellulose Ribbons* (BC) were harvested after 5 days. Harvested BC Ribbons were boiled in deionized water (DI) at 70 0C for 3 hours, then in 2% NaOH followed by deionized distilled water and dried at 70 °C prior to use.

Synthesis of ZnO Nanorods

ZnO nanorod was synthesized using sol–gel method. 1.5 g of Zn $(CH3COO)_2.2H_2O$ was dissolved in 15 mL of ultrapure water (milli -Q water, USA) (18 M Ω) containing (100 mg/ml-1) of BCF, stirred for 30 min. and heated at 60oC for 2 hrs. Then, placed in the oven for calcination at 700 ^oC; where the temperature increases gradually with the rate of 4^oC per minute for 3 hours; annealing the ZnO nanorods gradually; and then further characterized.

ZnO Nanorods Characterization

The crystalline nature and grain size of ZnO nanorods was carried out by X- ray diffraction (XRD) pattern at 25-280C with a D8 Advance X – ray diffractometer (Bruker – Germany) with a nickel (Ni) filtered using CuKα (λ= 1.54184 A0) radiations as an X-ray source. A Fourier transform-infrared spectrum (FTIR) of sample is registered using Nicolet 6700 (Thermo scientific–USA). The thermal analysis was measured using Thermo gravimetric analysis (TGA) TGA -50 (Shimadzu, Japan) Morphology and size of ZnO nanoparticle were examined by Scanning Electron Microscope (SEM, JSM- 690, JEOL, Inc., Tokyo, Japan) and Field Emission Transmission Electron Microscopy (FETEM, JSM- 2100F, JEOL Inc.) at an accelerating voltage of 15Kv and 200 Kv.

Results and Discussion

Structure characterization of the biosynthesized BC and ZnO nanorods

FT-IR spectroscopy

Result obtained in Figure (1) showed that the FT-IR spectrum of BC have a strong absorption peak at 3396.1cm^{-1} representing the OH group. Broad band of 3394 cm^{-1} indicates the presence of more hydrogen bonding pattern. Our results correlate with the findings of (Slusaraka et al ., 2008) who indicated that *Acetobacter Xylinum* grown in HS medium produced cellulose showing IR spectrum in the region of 3400cm-1. The strong absorption peak at 1638cm-1 confirms the presence of carboxylic acid group (COOH) in the cellulose structure. The bands at 715 cm-1 show the possibilities C-O-C functionalities present in the BC. According to Jung et al. (Jung et al .,2010) who reported that the IR spectrum of BC produced in molasses medium is observed in the region of 3240 cm-1 , attributing to the presence of more quantities of cellulose Iα. Our results (Figure 1A) indicated that the transmittance peak near to 3240 cm-1is achieved, indicating that cellulose Iα is abundantly present in the BC produced in HS medium. Figure (2) showed the FT-IR spectra of ZnO nanostructure prepared using BC as bio - template by sol-gel method. There is a strong peak at 493.5cm-1 indicated ZnO nanoparticle formation and weak broad peak at 3438.2 cm-1 corresponding to the hydroxyl group. The result obtained (Figure 2) indicated that the hydroxyl groups have a strong interaction with Zn^{2+}(Li et al., 2009) .While, the disappearance of peak at 1638cm-1 as a result of thermal treatment and BC pyrolysis Overall, results confirmed the formation of ZnO nanorod shaped (Que et al ., 2005) .

XRD structure characterization of ZnO nanorod

Results obtained in Figure (3) showed X-ray Diffraction (XRD) patterns of ZnO nanorod. The peaks at 2 θ = 31.746, 34.395, 36.226, 47.526, 56.549, 62.832, 67.893 and 69.028 were assigned to (100), (002), (101), (110), (103), (200), (112) and (201) of ZnO nanorod All peaks were indicated polycrystalline Wurtzite structure (Zincite, JCPDS

no.: 79-2205). No characteristic peaks of any impurities were detected indicating the quality of the prepared ZnO nanorod. The XRD pattern is identical to the hexagonal phase with Wurtzite structure with space group (C6V=P63mc) and unit cell parameter a= b= c=3.248Å and c = 5.2ÅThe average crystal sizes of ZnO nanorod obtained with calcinating temperature at 700 °C for 180 min. The average crystallite size (d) of ZnO nanowire was estimated by Scherer's equation (Patterson et al., 1939).

$$d=k\lambda/\beta \cos\theta$$

Where k = 0.9 is the shape factor, ß is the measured FWHM (Full Width at Half Maximum), θ is the Bragg angle of the peak, λ is the XRD wavelength. The average crystal size of ZnO nanowire was found to be 214 nm (Figure 2).

Thermal properties of ZnO nanorods

Figure (4) showed the Thermo Gravimetric Analysis (TGA) of synthesized ZnO using BC nanofiber biotemplate. Results obtained in Fig. (3) explained the reaction of Zinc acetate dehydrate during the pyrolysis process of the BC ribbons. Three weight losses were observed during the thermal degradation curve of BC. The first steps showed a weight loss between 61oC and 287 oC, where physically adsorbed zinc ions with hydrogen bonded linked to water molecules were lost at the first stage due to the dehydration of BC and Zinc acetate dehydrate. The second stage has a weight loss that can be explained by the decomposition of zinc acetate. The third stage occurs between 300 C^0 and 530 C^0 with calcination of the ZnO nanorod. The exothermic peak at 643C^0 could be attributed to the termination of the pyrolysis process and preliminary crystallization of the ZnO nanorod. Thus, overall, the fabrication process of ZnO nanorods has two steps: one is the adsorption of zinc ions onto the BC fibers and the second is the removal of BC templates at high temperature (700 ^OC under atmospheric air (Su et al., 2009).

Morphologylogical studies of ZnO nanorods

SEM image obtained in Figure (5) showed the bacterial cellulose (BC) after suspension with ultrapure water for 10 min. BC have ribbons shape and were produced from *Komagataeibacter Xyliunus* in the static fermenation culture. Micrographs of thread like cellulosic microfibrils appears and the bacterial cells entangled in its fibrils are tightly packed with conferred morphological feautres similar to that of pure micrphological cellulose. SEM of ZnO nanorods presented in Figure (6) indicated that there is no impurities on the surface it is is smooth. Figure (7) showed the TEM image that confirms the structure of BC ribbons, while in Figure (8), TEM analysis of ZnO nanorod confirmed its rod shape with a diameter of 214 nm.

Conclusion and recommendation

A facile approach has been proposed to prepare ZnO nanorods with ecofriendly green technology using the sol-gel technique; which is considered as the best method to control the dimension, as well as, the shape of nanomaterial. The advantage of BC as a matrix network can be used as good biomaterial template to prepare 1-D nanostructure. This approach provides an environment-friendly, simple and efficient technique for the preparation of well-structured shaped of ZnO nanorod. Moreover, this method could be used to prepare other nanoscale metal oxide from the thermal decomposition process. In the future, we recommend proceeding further using the advantages of using ZnO nanorod in the field of cancer therapy due to its reactive oxygen species or as a biosensor due its electric conduction.

Conflict of Interest Statement: The author declares no conflicts of interest.

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Fig(1) the FT-IR of bacterial cellulose using static culture of Komagataeibacter Xyliunus.

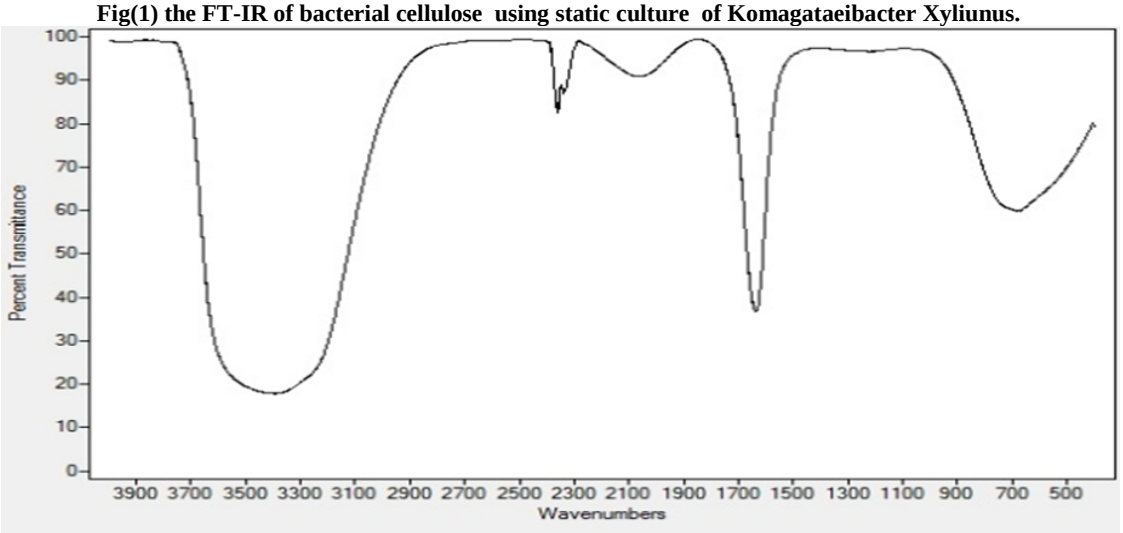


Fig (2) the FT-IR spectra of ZnO after synthesize by sol gel technique

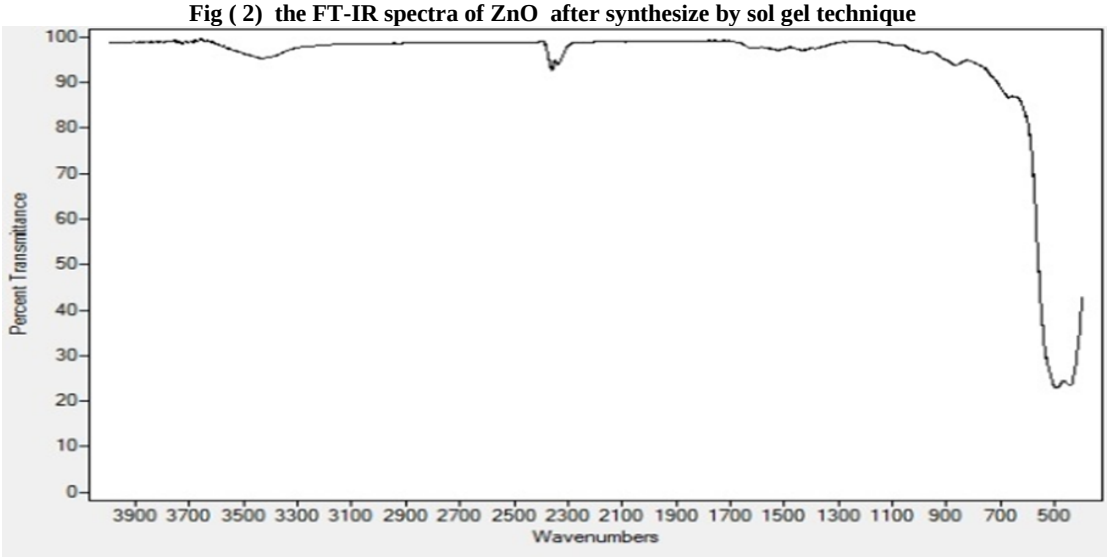


Fig (3) shows XRD patterns of ZnO nanorod

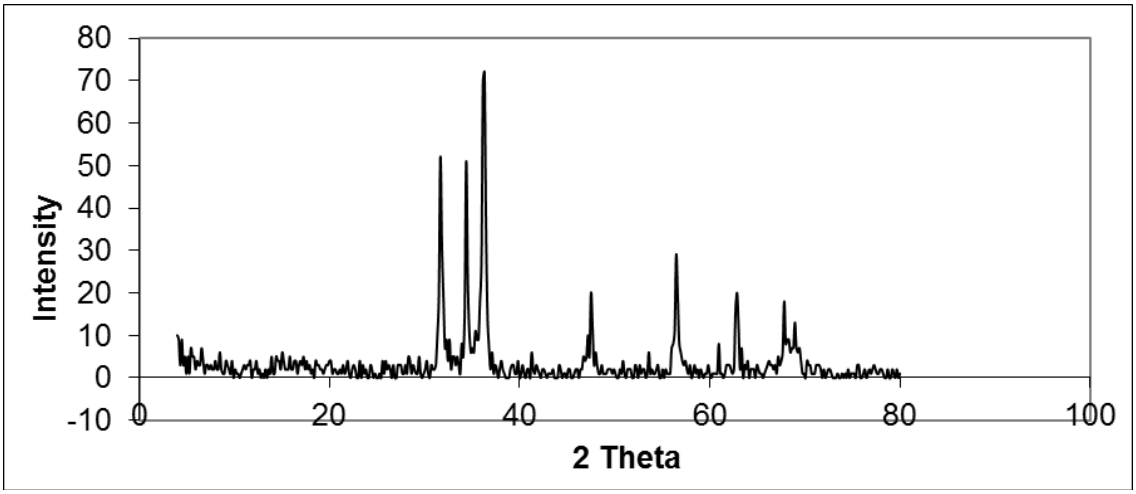


Fig (4) shows the curves of Thermogravimetric analysis (TGA) ZnO/BC nanofiber

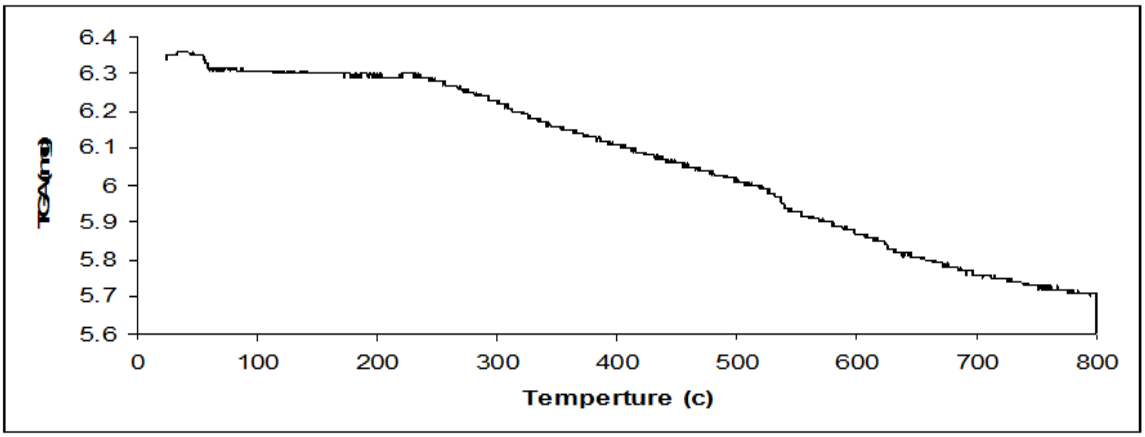


Fig (5) the Scanning electron microscope of bacterial cellulose

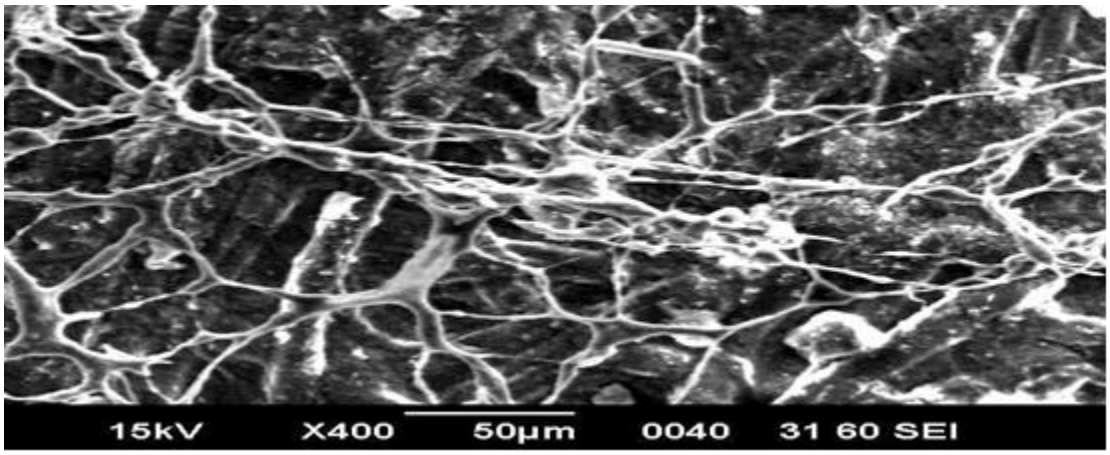
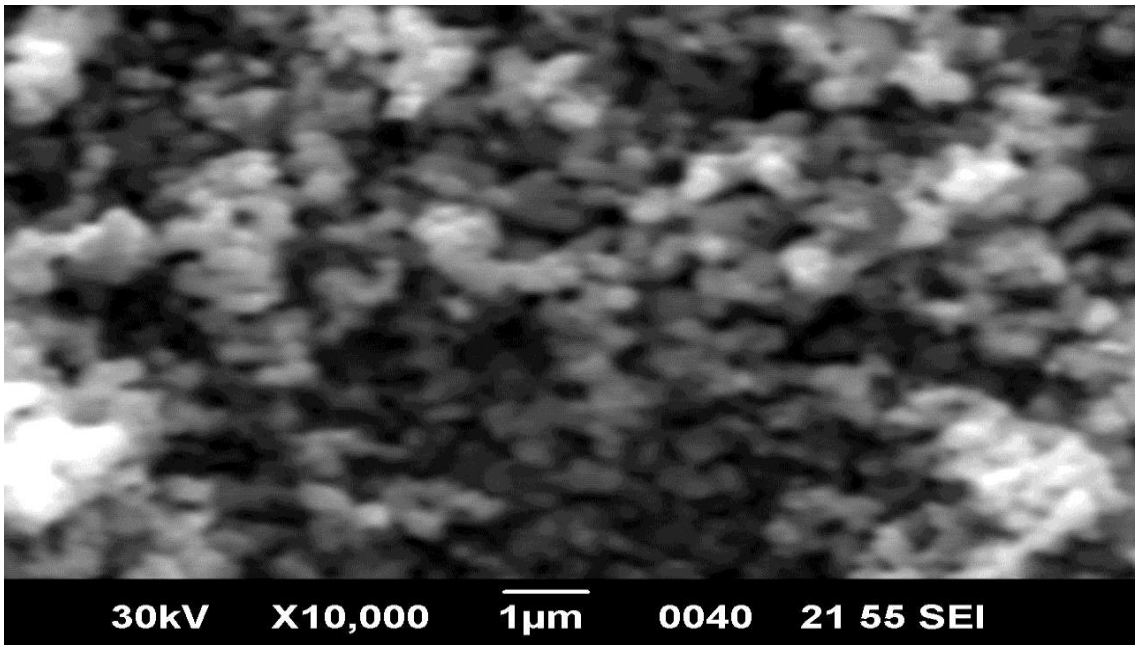
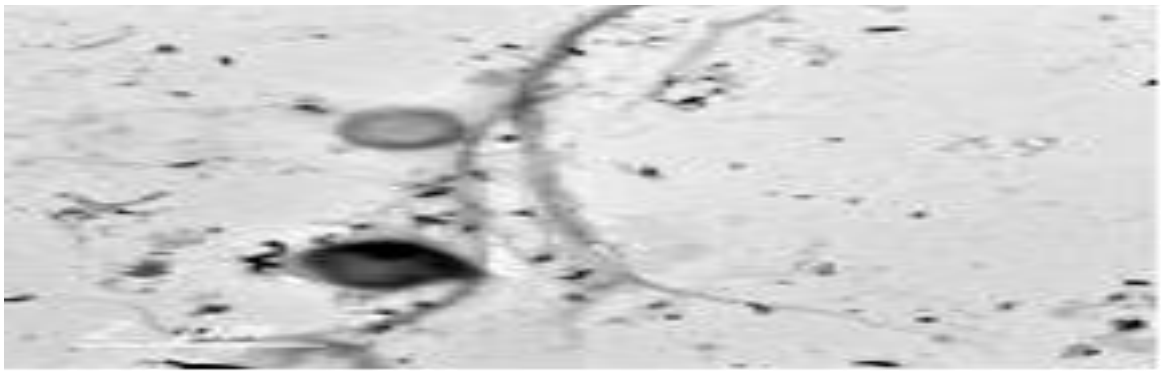


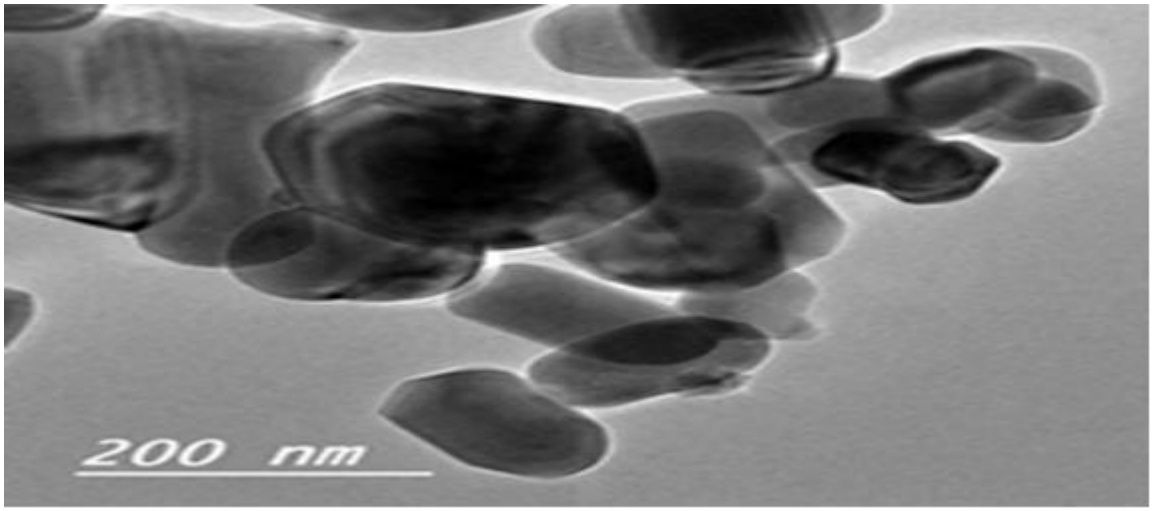
Fig (6) the Scanning electron microscope of ZnO nanorod



Fig(8) The transmission electron of bacterial cellulose



Fig(8) The transmission electron microscope of znic oxide nanorods



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