

# Growth of ZnO Nanostructures on Biopolymer Films

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**Abstract:** In the present study, ZnO nanostructures were grown onto biopolymer films by hydrothermal method and physical and thermal properties of the ZnO nanostructures on the biopolymer were examined. Structural and optical characterizations of the bio-nanostructures showed that morphology and thermal properties of the nanostructures changed as a function of pH value. It was found that 1D and 3D architectures having average diameters of 50-250 nm and 5-10  $\mu\text{m}$  in length can be built high-purity onto biopolymer structure. According to tagged graphics (TGA) and derivative thermogravimetric analysis (DTG) results, bio-nanostructures have about four-fold decrease in their degradation rate compare to that of pure biopolymer material. Bio-nanostructures promise a new approach for growing nanostructures that could be used in solar cells and its applications.

**Key words:** Dye sensitized solar cell, ZnO, biopolymer, nanowires, nanorods, nanoflower.

## 1. Introduction

The assembly of molecular or polymeric species of biological origin and inorganic substrates through interactions on the nanometric scale constitutes the basis for the preparation of bio-nanohybrid materials. They are of great interest due to their versatile applications in important areas as diverse as new materials with improved functional and structural properties [1-5]. It must be remarked that the development of bionanomaterials also represents an ecological alternative to conventional polymer materials, as the properties of the biodegradable polymers used ensure that the materials produced are environmentally friendly and renewable. Typical examples of this type of bio-nanomaterials result from the combination of polysaccharides such as starch, cellulose or polylactic acid with microparticulated

solids, which are usually called green nanomaterials or bioplastics [6, 7].

Chitosan has received attention as a material for nanoparticles for decade [8]. It is a partially deacetylated form of chitin, which is a structural polysaccharide found in crustacea, insects, and some fungi, and it has attracted interest as a biocompatible, biodegradable, mucoadhesive, and nontoxic material for use in biomedical applications [9-12]. In addition, chitosan has a special feature of adhering to the mucosal surface and transiently opening the tight junction between epithelial cells [13]. Thus, chitosan nanoparticles are potential bionanohybrid systems and its applications. Recently, special attention has been improved to strategies for synthetic approaches to bio-nano-semiconductors. Nano-zinc oxide is a semiconductor material with various configuration architectures much richer than of any other known nanomaterial [14, 15].

The fundamental properties of II-VI compound

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semiconductor ZnO have been studied for many years, owing to its direct wide band gap, large exciton binding energy, huge magneto optic effect, chemical sensing, piezoelectric and ferroelectric properties, low toxicity, high infrared reflectivity, acoustic characteristics, high electrochemical stability and excellent electronic properties [16, 17]. Moreover, in the past few years, much interesting research was been reported connected with ZnO nano-scale structures with various morphologies such as nanowires, nanorods, nanoflowers and nanotubes have been obtained by different methods [18]. ZnO nanostructures have been attracted much interest due to their exceptional unique optical, electronic, mechanical properties [19, 20]. ZnO nanostructures have also some important advantages. For example, they exhibit both semiconducting and piezoelectric properties can be formed the basis for electromechanically coupled sensors and transducers [21, 22]. Also ZnO nanostructures exhibit the most diverse and abundant configurations of nanostructures such as nanoflowers, nanowires, nanorods, nanotubes, and nanoribbons [23].

The preparation of ZnO nanostructures has been studied by various methods such as metal organic chemical vapor deposition, vapor-liquid-solid, chemical vapor deposition, pulsed laser deposition, electro chemical deposition, hydrothermal process, and template-based methods [24]. Among these techniques, the hydrothermal method is a promising technique because other growth techniques generally require expensive equipments, complex process control, and a high growth temperature [25]. The hydrothermal method can allow growing the ZnO nanocrystals at lower temperature. And, it can be used for large scale production, which are simple, fast, and cheap [26].

In the present study, physical and thermal properties of the ZnO nanostructures synthesized on biopolymer films by hydrothermal method were investigated. The study was mainly focused on the rational synthesis and analysis of novel properties of obtained nanoscale biopolymer films. Under various experimental

conditions, the morphology of the ZnO nanostructures was modulated by varying pH of the solution. The results revealed that ZnO nanostructures on the biopolymer have distinct thermal stability and bio-nanostructures promise a new approach for using in solar cells and its applications.

## 2. Experiments

### 2.1 Preparation of Methacrylated Chitosan Films

A 3% w/v solution of chitosan was prepared in 3% aqueous acetic acid. The reaction was carried out at 75 °C in a 100 mL of flame dried three-necked round-bottom flask, equipped with a nitrogen inlet and a dropping funnel. A solution of 0.1 M ceric ammonium nitrate in 10 mL of 1N nitric acid was added followed by 4.5 g of methyl methacrylate (MMA) dropped into the well-stirred reaction mixture. After 8 h, the reaction was stopped and the product was precipitated in sodium hydroxide solution with vigorous stirring. The precipitate was washed with distilled water several times and filtered. The homopolymer was extracted from the grafted product using acetone as solvent in a soxhlet extractor. The grafted chitosan was dissolved in 2% aqueous acetic acid with continuous stirring for 2-3 days. The solution was cast on disposable polypropylene molds and heated at 45-50 °C for 48 h. The film was neutralized with 2% sodium hydroxide solution and extensively washed with distilled water.

### 2.2 Preparation of ZnO Nanostructures onto Methacrylated Chitosan Films

ZnO nanostructures were grown on methacrylated chitosan films by hydrothermal method using ammonia as the base source. The biopolymer films were cleaned carefully for 2 min. by dipping each in acetone, de-ionized water, methanol and de-ionized water sequentially. After cleaning, 10 mM  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (aq) solution was prepared and its pH was set to 10.0, 10.6 and 11.0 using ammonia solution. Then, the methacrylated chitosan films were

immersed into the solution and then heated to 120 °C for 6 h. After the growth step, the substrate was rinsed using de-ionized water and dried by flowing nitrogen and nanostructured ZnO-biopolymer films were obtained.

### 2.3 Characterization of Nanostructures

The crystal structures of the self assembled ZnO 1-D and 3-D architectures were analyzed by X-ray diffraction (XRD) (Pananalyticae, XPERT-PRO) with Cu-K $\alpha$  radiation of 1.54 Å, within the 2 $\theta$  angle ranging from 20-80, and the absorption and transmittance measurements were carried out by UV-VIS Lambda 2S spectrometer (Perkin-Elmer). The composition and surface morphologies of ZnO-biopolymer films were studied with scanning electron microscopy (SEM) (Hitachi S8000). Thermal decomposition temperatures of ZnO-biopolymer films were measured by Simultaneous TGA-DTA Instrument (SEIKO). Bonding analysis of the ZnO-biopolymer films were studied by FTIR spectra (Perkin Elmer).

## 3. Results and Discussion

In the present study, a possible chemical reaction mechanism and a new method for the self assembly of ZnO nanowire, nanorod and nanoflower shaped semiconductors were grown on biopolymer films. By adjusting the experimental parameters, ZnO nanostructures with different morphology and sizes were obtained. The surface morphology of the ZnO nanostructures was found to be depended on reaction temperature, duration, molar ratio, and pH of the solution. It was shown only as dependent solution pH with ammonia as the base source.

The ZnO crystal synthesis on the biopolymer film surfaces in the long-chain-assisted route was based on heterogeneous nucleation and subsequent growth. At the lowest pH value, pH~10 of the Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution, the decomposition of the Zn(OH)<sub>4</sub><sup>2-</sup> complex dissolved and led to super saturation beyond ZnO

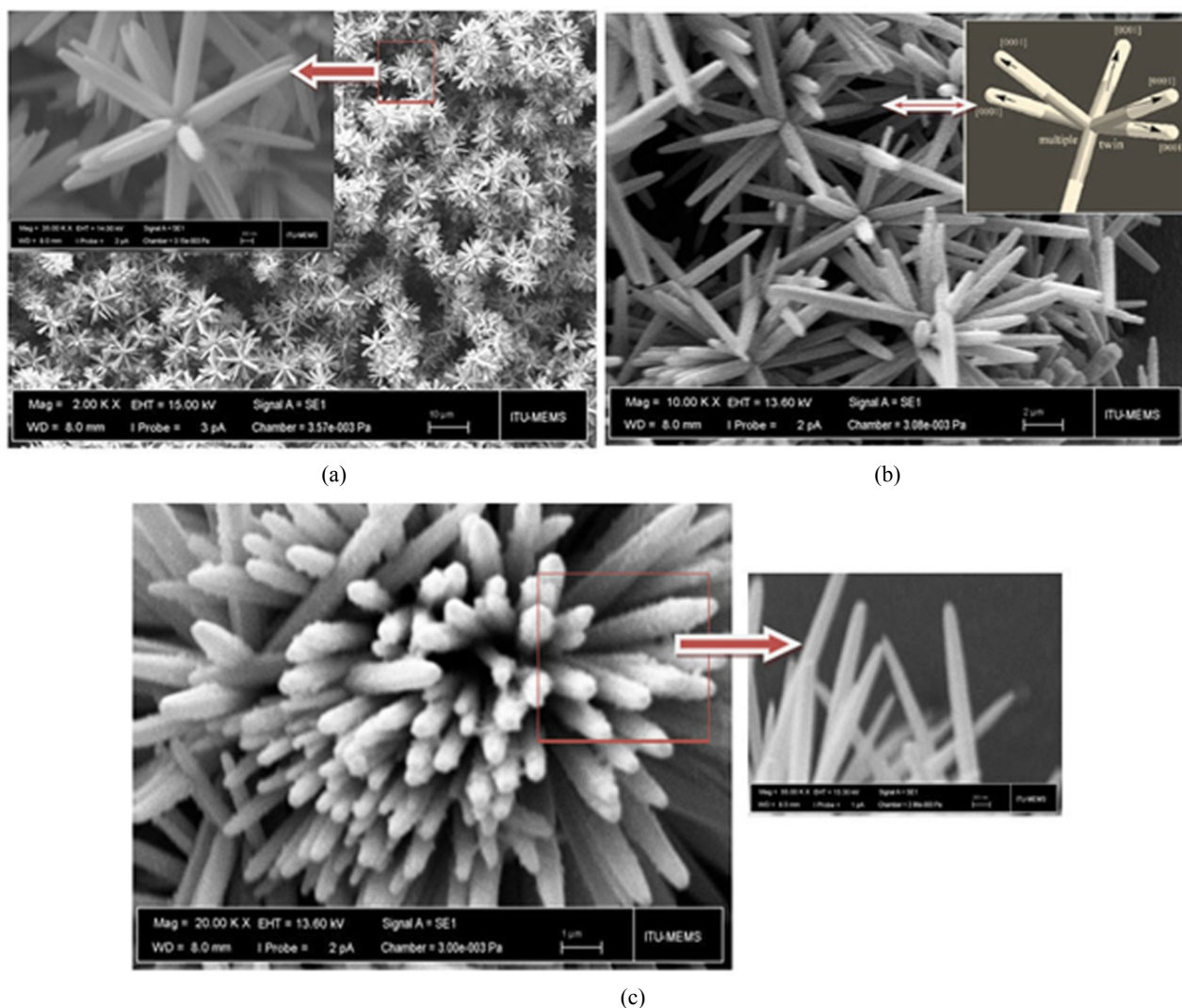
solubility. By increasing pH, the Zn(OH)<sub>4</sub><sup>2-</sup> ion decomposition occurred at the interface between biopolymer film surface and solution, when the concentration of Zn<sup>2+</sup> and OH<sup>-</sup> exceeded super saturation, seed form and ZnO crystals nucleate heterogeneously on the negatively charged biopolymer film surface, and finally grown from the ZnO nucleus as flower like structures. With an increase in the pH of Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution from 10.0 to 10.6, the surface energy of the nanosized 3D-ZnO nanostructures increased to some extent, thus restricting the growth rate of 1D-ZnO nanostructures along the preferred c-axis direction. As a result, the morphology of ZnO nanostructures turned from nanoflowers to nanorods. Similarly, increasing the pH value of the solution from 10.6 to 11.0, nanowire structures were obtained.

SEM images with different magnification (Fig. 1a) showed that ZnO nanocrystals with flower-like shapes were obtained uniformly on the biopolymer surface. The diameters of the ZnO nanoflowers were measured as varying between 50 nm and 250 nm size of flowers like structures.

For the solution with pH of 10.6, ZnO nanorod structures were obtained in the diameters ranging from 40 nm to 400 nm and lengths of about 5  $\mu$ m as shown in Fig. 1b. Magnified image showed that flower-shaped structures were constituted by the accumulation of several hundreds of sharp-tipped hexagonal ZnO nanorods. All the nanorods were seen as originated from a single centre arranging them in a spherical shape exhibiting flower-like morphologies. The rod tip appeared sharp with wide hexagonal-bases.

The SEM images in Fig. 1c indicated a high density and homogeneous distribution of the ZnO nanowires when pH of the solution was 11.0. Aligned ZnO nanowires were found on the randomly distributed ZnO thin films (Fig. 1c).

Higher magnification image showed that the form diameter of each ZnO nanowire has little variation



**Fig. 1** SEM image of biopolymer/ZnO nanostructure: (a) nanoflowers, (b) nanorods and (c) nanowires.

bottom to top and there were two typical diameters among those nanowires. The similar diameters around 50 nm and the rest about 200 nm in diameter can be regarded as the combination of two thinner nanowires.

The lengths of the synthesized nanowires were approximately 10 micrometers. Side-on image showed that well-aligned nanowires grew vertically on the biopolymer films. In addition, they were in high density and randomly distributed over most of the substrate.

The crystalline structure, purity and composition of ZnO nanostructures were analyzed with XRD and the results are shown in Fig. 2. As can be seen from the figures, all the diffraction peaks were consistent

with the values of the standard (JCPDS card No. 36-1451).

This result along with the SEM images confirmed that the nanostructures on biopolymer films displayed pure hexagonal ZnO structure with high crystallinity. Peaks at  $2\theta \approx 31.64^\circ$ ,  $34.46^\circ$  and  $36.23^\circ$  were attributed to (100), (002), (101) and (102) ZnO planes, respectively. While (101) diffraction peak displayed dominant intensity for the ZnO nanostructures sample as seen in Fig. 2, the enhanced (100), (002) and (102) diffraction peak showed low intensity. X-ray diffraction measurement showed that the films have highly preferred (002) c-axis orientation and high quality crystal structures.

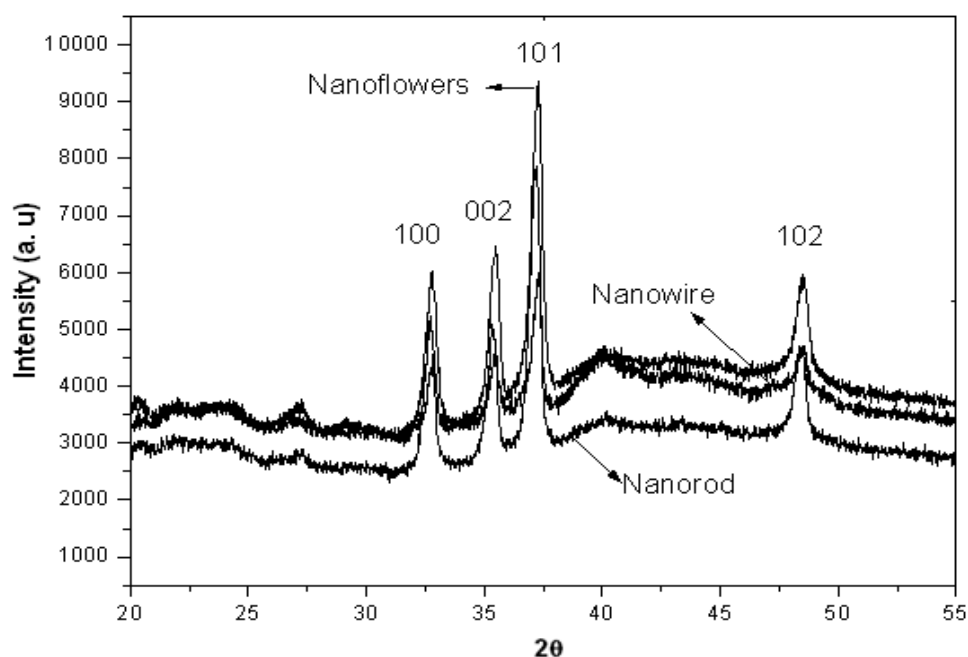


Fig. 2 X-ray diffraction patterns of biopolymer/ZnO nanostructure.

FTIR spectrum of ZnO nanostructures on biopolymer is shown in Figure 3. There was a broad band with very low intensity at  $3,375\text{ cm}^{-1}$  corresponding to the vibration mode of water OH group indicating the presence of small amount of water

adsorbed on the ZnO nanostructure surface and also OH groups of chitosan. The band at  $1,725\text{ cm}^{-1}$  was attributed to C=O bending of ester groups of chitosan. A strong band at  $561\text{ cm}^{-1}$  was attributed to the Zn-O stretching band.

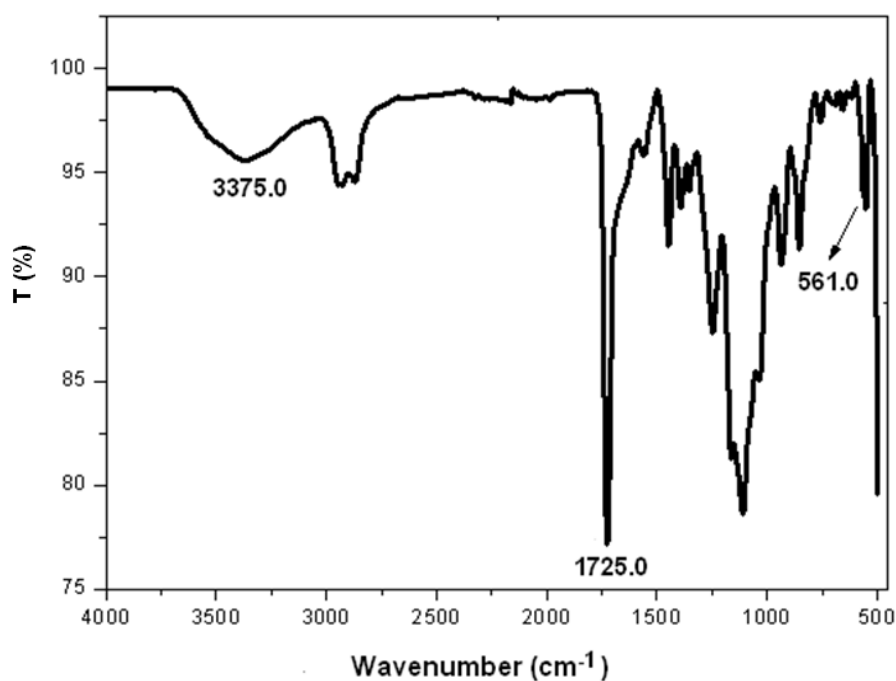


Fig. 3 FTIR spectra of biopolymer/ZnO nanostructure.

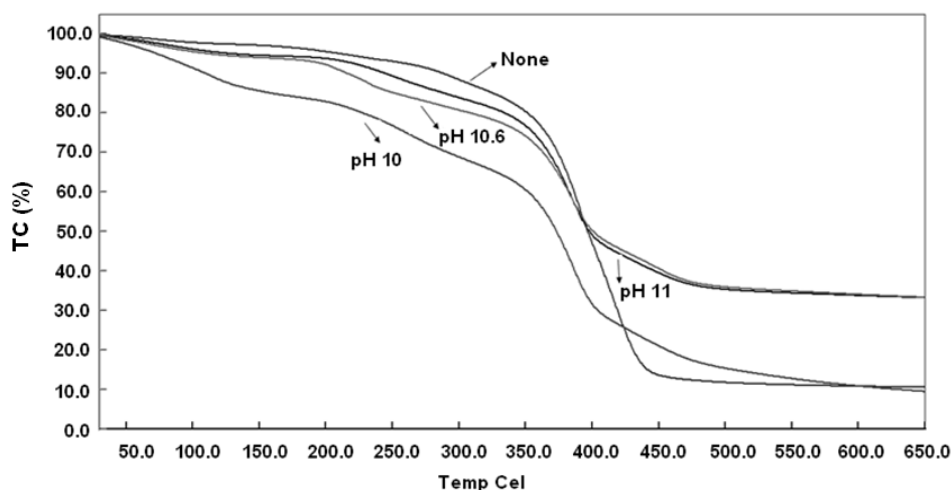


Fig. 4 TGA thermograms of biopolymer/ZnO nanostructure.

Thermal stabilities of the methacrylated chitosan and ZnO nanowire, nanorod and nanoflower semiconductors were studied by TGA. Fig. 4 showed the TGA thermograms of methacrylated chitosan and ZnO nano structures. As it can be seen from the TGA trace, the mid-point degradation temperature was found to be lower for the ZnO nanoflower than nanorod and nanowire. Therefore, it can be stated that ZnO nanoflower structure has the lowest thermal stability relative to the methacrylated chitosan and compared to other nanostructures. This lowest thermal stability of the nanostructure may be attributed to a minimized interaction between ZnO nanoflower and polymer

matrix of methacrylated chitosan which then leads to restricted molecular mobility of the polymer chains. The lower interaction is mainly attributed to three dimensional structure of ZnO nanoflowers compared to one dimensional structure of ZnO nanorods and nanowire. Moreover, the peak maximum temperature values from the first derivative (DTG) of weight loss (Fig. 5) was found to be higher for the methacrylated chitosan with a rate of decomposition, compared to all other nanostructures grown.

As shown in Table 1, all ZnO-biopolymer nanostructures have a slower degradation rate, modest mid-point degradation temperature and a relatively

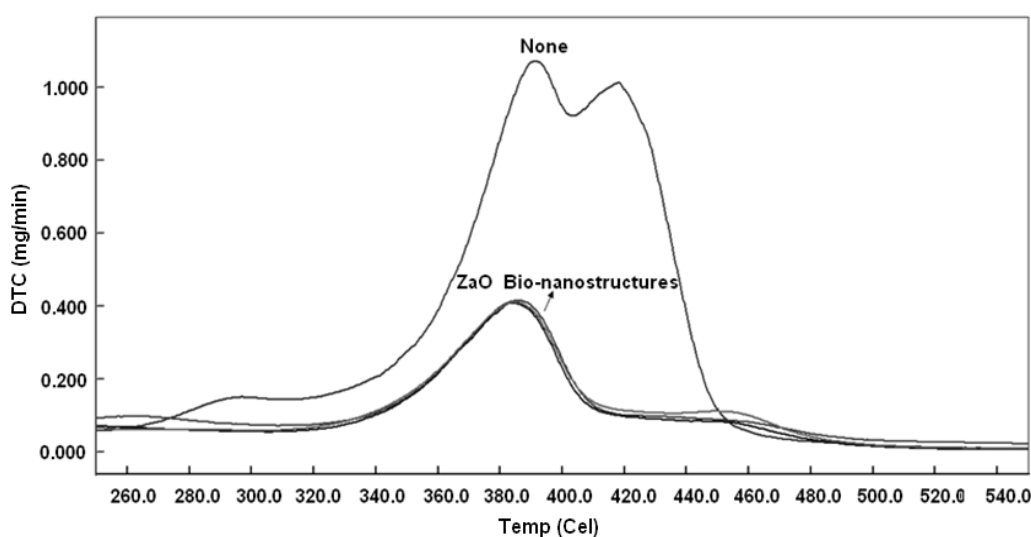


Fig. 5 DTG spectra of biopolymer/ZnO nanostructure.

**Table 1** Degradation rates of methacrylated chitosan, ZnO nanorod, ZnO nanowire and ZnO nanoflower.

Materials	The peak maximum temperature (°C)	Maximum rate of weight loss (mg/min) (at °C)
Methacrylated chitosan	391	1.072 at 391
ZnO nanorod	384	0.411 at 384
ZnO nanowire	384	0.408 at 384
ZnO nanoflower	386	0.415 at 386

broad peak at its maximum weight loss. Methacrylated chitosan has a 2.6 times higher degradation rate and relatively broad peak at its maximum weight loss as well as modest midpoint degradation temperature.

Our study demonstrated that all ZnO-biopolymer nanostructures have a higher thermal stability with a higher char yield compared to the methacrylated chitosan. This enhancement in thermal stability of the nano structures may be attributed to confinement of biopolymer chains between the ZnO layers, which restricts molecular mobility of polymer chains thus resulting in a strong ZnO-biopolymer structure which inhibits heat transfer through nanostructures and slows down the escape of the volatile degraded products from the interlayer galleries.

#### 4. Conclusions

In the present study, ZnO nanostructures were successfully carried out on biopolymer by hydrothermal method. Structural and optical characterizations of nanostructures showed that morphology and thermal properties of ZnO nanostructures on biopolymer changed as a function of pH value. Improved thermal properties of the ZnO-biopolymer nanostructures promise a new way for growing nanostructures that could be used in nano-optoelectronic applications.

Further work on the optimization of ZnO-biopolymer nanostructures may lead to an extension of the proposed cost-effective and efficient technique for fabrication of nanoscale devices and nanosystem applications for solar cell applications. It is anticipated that the results from the presented study will be used to explore new phenomena and materials behaviours in order to synthesize nanometer sized

electronic and optoelectronic device in the near future.

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