



Growth of ZnO nanorods on biodegradable poly (lactic acid) (PLA) substrates by low temperature solution method



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ABSTRACT

Plastic materials have found in every aspect of our daily life and the accumulation of plastics in the environment has led to great threat to the planet. Therefore, need for development of biodegradable plastics is essential to replace the petroleum based plastics. In this report, Zinc oxide (ZnO) nanorods were grown on the bio-degradable poly(lactic acid) (PLA) substrates for the first time by using low-temperature solution growth method. Growth of nanorods was carried out on two types of substrates; one is pure PLA substrate and the other one is PLA mixed with ZnO powder. Pure PLA substrates and ZnO powder mixed PLA substrates were prepared by the film casting method. ZnO nanorods growth was carried at different growth temperatures ranging from 50 to 90 °C for the growth duration of 4 hours on both types of substrates. Nanorods growth was observed on the pure PLA substrates with very low density whereas dense nanorods growth was observed on ZnO powder mixed PLA substrates. It was concluded that at a growth temperature of 70 °C, good density and aspect ratio was observed for ZnO nanorods. Absence of ZnO nanorods growth at lower growth temperature is limited by insufficient thermal energy for the decomposition of HMTA and ZnO crystallization. The ZnO nanorods growth is limited by PLA glass transition temperature at higher growth temperatures. The present results will be useful in the preparation of environment friendly active food packaging material with antibacterial properties.

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1. Introduction

In the last decade, plastic bags made of polyethylene (PE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) usage have become common in daily life. These polymers are non-biodegradable and use petroleum as their raw material, and the environment can be contaminated with these bags. Therefore, biodegradable and nontoxic packaging materials have attracted a lot of attention in the research as well as food packaging industry [1–3]. In addition to the above, food contamination due to pathogenic microorganisms is a serious problem in food packaging. Use of active packaging for food conservation, which has antimicrobial and antibacterial agents dispersed on its surface, will be a good solution [4,5]. The metal oxide nanostructures of ZnO, TiO₂, MgO, Fe₂O₃, CuO have been shown effective additives for this purpose [6–8].

Therefore, bio-degradable polymer packaging materials coated with materials which exhibit antibacterial and antimicrobial prop-

erties are essential for both environment friendly and better health. Among many biodegradable polymers, Poly lactic acid (PLA) is chosen in this work due to its bio-compatibility, compostable and easy preparation [9]. Similarly, among many metal oxides, ZnO is chosen in this work due to its multifunctional properties such as antibacterial activity, wound healing, solar cells, sunscreen, and UV sensor, etc. [10].

Few reports were available in the literature on PLA-ZnO nanocomposite films prepared by solvent casting [11,12], melt compounding in a twin screw extruder [13] with good antibacterial activity, along with other useful properties. The main drawback of the above study is, PLA-ZnO nanocomposite films having limited ZnO surface area for an activity such as antibacterial, antimicrobial, anti UV etc., as ZnO is submerged in the PLA matrix. This drawback can be overcome by initiating the growth of ZnO nanorods on the surface of the PLA with the help of ZnO seeds. The growth of ZnO nanorods on the surface of the PLA will enhance the surface area for the activity.

In this report, growth and characterization of ZnO nanorods on the surface of the PLA substrates by the simple cost-effective hydrothermal method was studied.

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2. Experimental

2.1. Pure PLA and ZnO mixed PLA substrates preparation

PLA granules were dissolved in chloroform to get the PLA solution (See [Supplementary information \(SI\), S0](#)). It is considered as pure PLA solution. In the second part, 5 wt% of ZnO powder was mixed with pure PLA solution and considered as ZnO powder mixed PLA solution. Pure PLA and ZnO powder dispersed PLA films were prepared by film casting method [11,12] (SI, S1). Dried films were taken out from the base of film applicator. These standalone films will act as a substrate for the growth of ZnO nanorods in the next section. Hereafter, the stand-alone films are referred as substrates. The films prepared from pure PLA and ZnO mixed PLA solutions were named as substrate-1 and substrate-2 respectively.

2.2. Synthesis of ZnO nanorods

Growth procedure for the ZnO nanorods is similar to the reported literature [14,15]. Equimolar aqueous solution of Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylene tetramine (HMTA, $C_6H_{12}N_4$) were mixed under continuous stirring and stirring process is continued for 1 h for uniform mixing. The resulting solution was taken in screw reagent bottle and substrates 1 and 2 were placed over the solution (SI,S2). The screw reagent bottle containing the growth solution and substrates were placed inside the hot air oven for about 4 h at different growth temperatures of 50, 60, 70, 80 and 90 °C for the growth of ZnO nanorods (SI,S3). After the 4 h of growth, substrates were taken out from the solution, rinsed with de-ionized water, and dried with blower. Further, resulting substrates were characterized for their physical appearance, morphology, crystallinity and optical properties (SI, S4).

3. Results and discussion

The physical appearance of the substrates 1 and 2 before and after the growth of ZnO nanorods was photographed with a camera

(SI,S5). White film is clearly seen on the surface of both the substrates, which tentatively confirms the formation of ZnO film [16,17]. Growth of nanorods were observed on the substrate-1 in the growth temperature window of 60–90 °C but with very low density, no proper alignment, and some nanorods are just lying on the substrate (SI,S6). This low density growth and improper alignment of the nanorods may be due to the absence of ZnO seeds.

3.1. SEM analysis

Morphology of the films deposited on the substrate-2 at different growth temperatures of 50–80°C for a growth duration of 4 h are shown in the Fig. 1(a)–(d). Growth of nanorods was not observed at a lower growth temperature of 50 °C and below. The absence of growth in nanorods may be due to the insufficient thermal energy for the decomposition of HMTA which in turn affect the ZnO nucleation as well as nanorod growth [14,18]. This can be seen in the Fig. 1(a). ZnO Nanorods growth was observed throughout the substrate at the growth temperatures of 60 °C–80 °C (SI,S8). The density of obtained nanorods depends on the availability of the ZnO seeds on the surface of the substrate. Length of the nanorods is increasing with the increase of growth temperature and can be seen in Fig. 1(c)–(d). This increase in the length of the nanorods with temperature is due to the sufficient thermal energy available for the decomposition of HMTA and also increased nucleation of ZnO [14,18]. The density of the nanorods was reduced at a growth temperature of 80 °C and above.

To find out the limit for upper growth temperature, nanorods growth was performed at 90 °C for growth duration of 4 h on substrate-2. Fig. 2(a)–(b) shows poor nanorods density along with many voids on the surface of the substrate. This is because of the softening of substrate well above the glass transition temperature and the nanorods were ejected from the nucleation sites. This can be evidenced by a lot of voids which were results of ejection of nanorods (SI,S8). Finally, it was concluded that the growth temperature of 70 °C was optimum for good density and aspect ratio of ZnO nanorods.

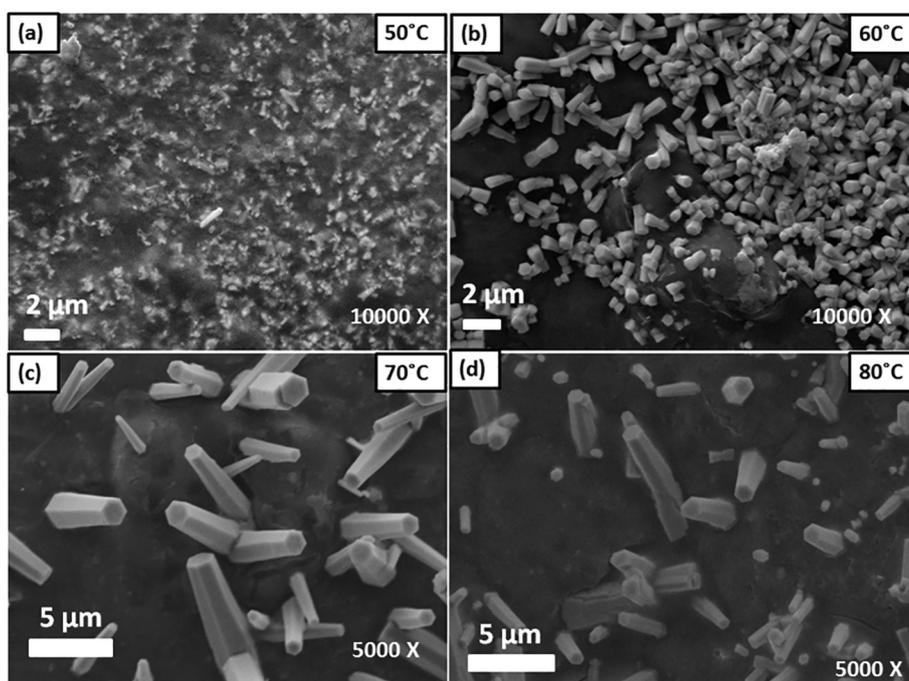


Fig. 1. SEM images of the ZnO nanorods grown on substrate-2 for 4 h growth duration at (a) 50 °C, (b) 60 °C, (c) 70 °C and (d) 80 °C.

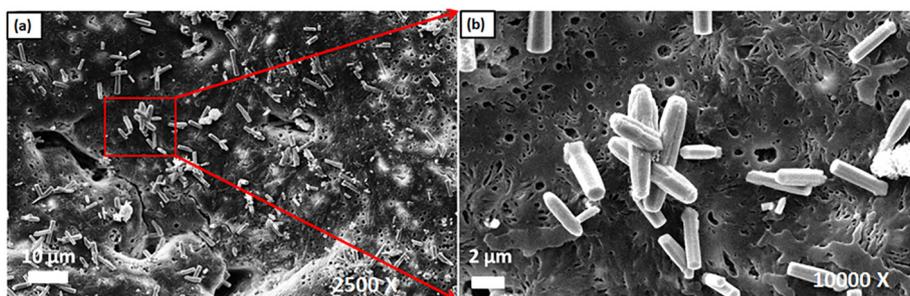


Fig. 2. ZnO nanorods growth at 90 °C for 4 h on substrate-2, (a) at low magnification, (b) magnified region of red square in the Fig. 2(a).

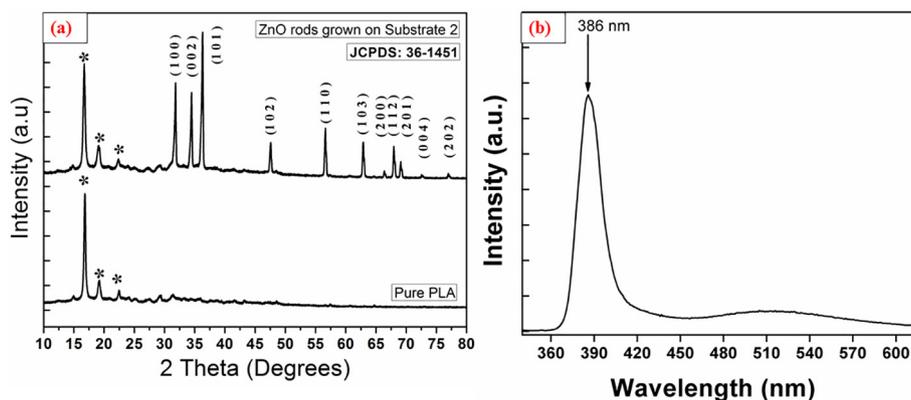


Fig. 3. (a) XRD pattern of pure PLA film and ZnO nanorods film grown on substrate-2 at 70 °C, (b) PL spectra of ZnO nanorods film grown on substrate-2 at 70 °C.

3.2. XRD analysis

Further, crystallinity of the ZnO nanorod films grown on substrate-2 at a growth temperature of 70 °C were studied by X-ray diffraction. Fig. 3(a) shows the XRD pattern of ZnO nanorod film. The major diffraction peaks at 16.68°, 19.06°, 22.33° were related to the pure PLA peaks and indexed with a star symbol. The diffraction peaks at 31.86°, 34.54°, 36.36°, 47.65°, 56.68°, 62.92°, 68.03° were indexed as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) planes of ZnO, thus confirms the crystalline nature of the films [19]. This is well coincides with the JCPDS card no 36-1451 and also with the reported literature [19].

3.3. Photoluminescence analysis

Further, optical properties of as-grown ZnO nanorods were measured at room temperature and the corresponding spectrum is shown in the Fig. 3(b). Two luminescence bands have been observed in the PL spectrum. Intense PL peak was observed in the range 360–420 nm with center at 386 nm (3.2 eV) corresponds to near band edge emission [20]. This near band edge emission band in the UV region arising from the recombination of electrons in the conduction band and holes in the valence band [20]. Second broad visible luminescence band observed in the range 460–580 nm is corresponds to defect-related deep level emissions, such as oxygen vacancies and Zinc interstitials [20].

4. Conclusions

In summary, ZnO nanorods were successfully grown on bio-degradable PLA substrates for the first time by using simple low-temperature solution growth method. ZnO nanorods growth was

not observed at lower growth temperatures of 50 °C and below as well as at higher growth temperatures of 80 °C and above. Optimum ZnO nanorods growth was observed at a growth temperature of 70 °C. Crystalline nature of the obtained ZnO nanorods film was confirmed with the XRD. Room temperature PL spectra of these nanorods film exhibited a sharp UV emission peak at 386 nm. Further, ZnO nanorods growth on bio-degradable PLA substrates can be easily extended to large area substrates since the growth method is simple, inexpensive. ZnO nanorods growth on the large area can be used as active packaging material in the food industry in the future due to the antibacterial properties of ZnO nanorods.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.126807>.

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