

Short Communication

## Electrochemical Synthesis of ZnO Nanoparticles and preparation of Pea Starch/ZnO composite for Active Food Packaging Application

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ZnO nanoparticles were synthesized using a facile electrochemical technique in large-scale production. Nanocomposite films designed based on pea starch (PS) incorporated with ZnO nanoparticles were successfully prepared and characterized. Biopolymer films with high UV absorption and enhanced resistance to sunlight were obtained by samples incorporated with ZnO nanoparticles in concentrations between 1 and 5 wt%. 5% ZnO content incorporated nanocomposite matrix was the least permeable to water vapor. The interplay between the ZnO and the polymer matrix structure may have contributed to the significant decrease in water solubility of the PS/ZnO nanocomposite. The PS/ZnO (5 wt%) nanocomposite film has the best antimicrobial activity among the films tested. Cyclic voltammetry analysis of the samples indicated higher conductivity of the PS/ZnO nanocomposite which can result in the enhancement of the antibacterial properties of starch-based polymer through the electrostatic discharge between ZnO nanoparticles and bacteria. Biopolymer film incorporated with ZnO nanoparticles exhibited excellent antibacterial activity and has the potential to be used to properly preserve the packaged foods by employing it as an active food packaging material.

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**Keywords:** ZnO nanoparticles powder; Electrochemical technique; PS/ZnO biopolymer films; Antibacterial activity

### 1. INTRODUCTION

Food poisoning is referred to as any type of illness caused by the consumption of contaminated food, which may be caused by either bacteria, viruses, parasites, or toxic substances [1]. Typically, improper maintenance of food is a common cause of food poisoning that may result in medical expenses

and affect trade and economy. Therefore, the packaging industry has an incredible part in the betterment of human life and health.

At present, the largest part of materials utilized in packaging industries is constructed from petroleum-based plastic materials due to the relatively convenient use, low cost, and high durability. However, due to the increasing price of oil and the non-biodegradable nature of plastic materials, many researches have shifted their focus to develop biodegradable packaging materials with the use of alternative material to plastic-like biodegradable materials. [2, 3]. Thus, renewable-based strategies may lead to a sharp decline in non-renewable source consumption and greenhouse gas emissions. Among the natural polymers in packaging materials, a futuristic candidate is starch as it is a renewable resource that is generally low-cost and readily available [4]. Because of poor processing, barrier, mechanical properties of bio-composite materials, and expensive production cost in comparison to the commonly used plastic films, not much use has been made of the bio-composite based packaging materials in the packaging industry. Researches are being done to enhance the mechanical, gas barrier and physical attributes of the composite by homogenously blending the biopolymer with various fillers [5-8]. ZnO among many other nanofillers is a suitable option to be used as a reinforcement in a polymer matrix because of its extensive surface area, high surface energy, optical transparency plus mechanical and thermal properties [9-16]. Also, nanosized ZnO has exhibited antimicrobial features and potential to be used in preserving food. To decrease the problems in the environment and enhance the function of food packaging materials, it is crucial to develop bio-nanocomposite materials. In this study, a simple and robust technique has been used for the large-scale synthesis of ZnO nanoparticles powder by an electrochemical method. ZnO nanoparticles were used as fillers to prepare pea starch (PS)/ZnO biopolymer matrix. The films underwent characterization for their electrical barrier, and antibacterial features.

## 2. MATERIALS AND METHOD

To synthesis of ZnO nanoparticles by electrochemical process, 250 ml of the electrolyte solution was put in 300 ml electrochemical cell. The electrolyte mixtures have been prepared by mixing choline chloride:ethylene glycol (1:2 molar ratio), 0.01M  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and 1.5 mL/L  $\text{H}_2\text{O}_2$ . Conductivity and pH of the electrolyte solution were attuned using KCl and 1 M NaOH, respectively. Zn electrodes were immersed in the electrolytic cell. The distance between the anode and cathode electrodes was approximately 2 cm. The electrodes were connected to the DC power source. The voltage and time were kept at 5V for 1 h at room temperature, respectively. Finally, the aqueous solution was subjected to a centrifugal force at 7000 rpm at 5 °C for 20 min. The white yield attained was further rinsed with DI water dried at 90 °C for one day.

Various concentrations of synthesized nano ZnO (0, 1, 3 and 5 wt%) were mixed with distilled water. The nano ZnO was dissolved completely by constantly mixing for approximately 45 min and heating at 70 C. After which the solution was kept in an ultrasonic bath for 25 min, later brought down to room temperature and employed to make 5wt% aqueous PS. The plasticizers added were a combination of sorbitol and glycerol (3:1) at 40% (w/w) of total solid. Heating at 55 C and holding for

45 min was done to gelatinize the starch nanocomposite. On completely gelatinizing the starch, the solution was brought down to room temperature. A portion (90 g starch) of the dispersion was set as mold onto Perspex plates (10 cm×10 cm). Drying of the films took place at 24 °C and 50% relative humidity (RH) for a day. The same plasticizer was used to prepare control films without ZnO nanofillers. After drying, the films were dried removed manually and conditioning in a desiccator at approximately 25 °C and 52% relative humidity to analyse further.

The samples were characterized by FE scanning electron microscopy (FESEM, FEI Sirion 200) and transmission electron microscopy (TEM, Philips CM12, FEI, CO) analyses.

UV-vis spectra of the PS/ZnO bionanocomposite films were obtained by a UV-vis spectrophotometer.

The water vapour permeability (WVP) of films was studied based on the standard method of ASTM E96-95 with slight modification.

The test cups were filled with water up to 1.5 cm underneath the film. Water vapor transmission rate (WVTR) was estimated from the slopes of the steady-state amount of water vapor transmission through the film versus time curve. The WVP of the films was calculated in g m/m<sup>2</sup>Pa s as follows:

$$WVP = (WVTR \times L) / \Delta p \quad (1)$$

where WVTR is the measured water vapour transmission rate (g/m<sup>2</sup>s) through a film, L is the mean the film thickness (m), and  $\Delta p$  is the partial water vapor pressure difference (Pa) across the film. Based on the study by Maizura et al., the determination of the water solubility (WS) test on the edible films was done [17]. 3 cm x 5 cm rectangular pieces of the films were placed with P2O5 in a desiccator for a day. Then, the samples were kept in beakers filled with 90 mL of DI water and stirred using an agitator at ambient temperature. The soaked samples were removed using a filter paper, dried at 60 C in an oven to maintain the weight of the sample. The WS of films was determined as follow:

$$WS(\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (2)$$

where  $w_f$  and  $w_i$  are the final and initial weight of the film, respectively.

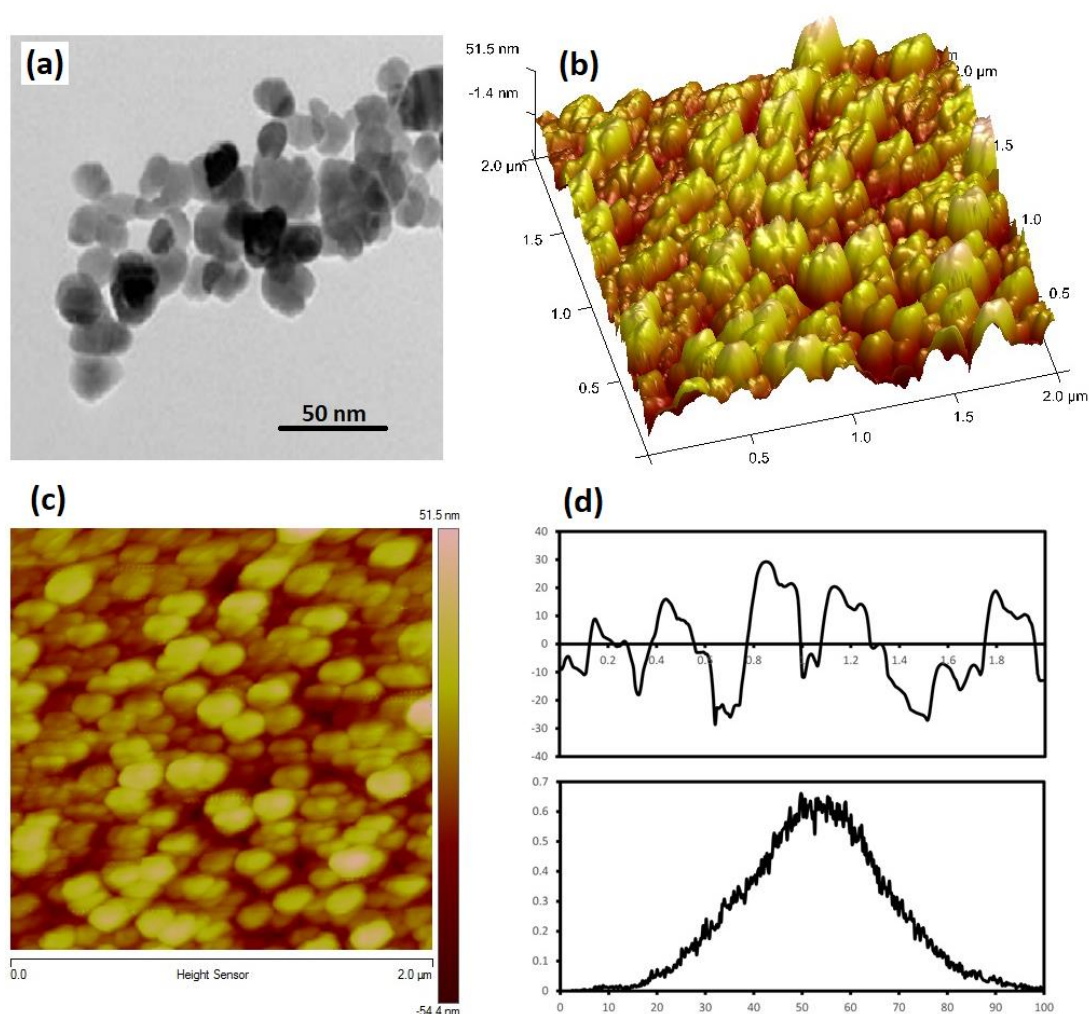
Ponce et al. described the agar diffusion method to assess the antimicrobial activity of PS/ZnO films [18]. The antimicrobial effects of the film against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were determined by the usage of inhibition in a solid media zone. Mueller Hinton (Merck, Darmstadt, Germany) agar plates were rubbed with 100 mL of inoculum with approximately 10<sup>6</sup>–10<sup>7</sup>CFU/mL of tested bacteria. Disc-shaped film samples were placed on these discs. Incubation of these plates took place at 37 °C in a subsequent manner for a day under mild shaking. The diameter of the inhibition zone of the bacterial growth around the film was used to calculate the antimicrobial activity of the films.

The highest conducting electrolyte was sandwiched between two carbon electrodes using Perspex plates. CHI600D electrochemical analyzer was used to analyze CV study of PS/ZnO nanocomposite. Biopolymers were then evaluated at scan rate of 10 mVs<sup>-1</sup> from –1 to +1 V with sample interval of 0.001 V.

### 3. RESULTS AND DISCUSSION

Figure 1a illustrates the TEM micrographs of ZnO nanoparticles with 20 and 60 nm diameters. The figure 2b and c clearly show 3D and 2D AFM images of the as-grown products which present particle-shaped structures. The length distribution of the ZnO nanoparticles indicates that most nanoparticles have diameters between 20 and 60 nm (figure d).

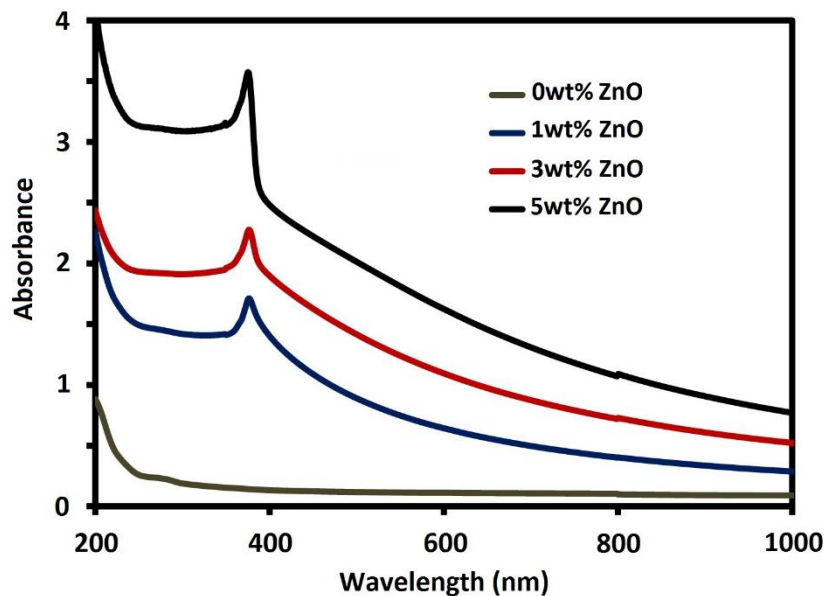
Figure 2 shows the UV-vis absorption results in the form of spectrum for PS/ZnO nanocomposites with varying levels of nano ZnO. Low absorbance is seen for PS composite film and the highest value for absorbance is seen at approximately 3.2 for 5wt% nano ZnO reinforced composite, both in the UV range. The inherent capability of nano ZnO to be absorbed in the UV region may have attributed to the highest value of absorbance.



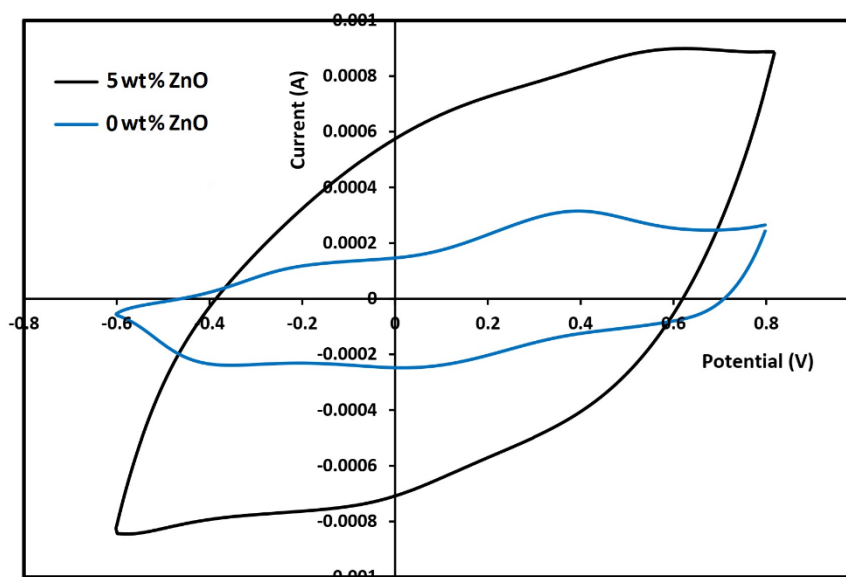
**Figure 1.** (a) HRTEM of ZnO nanoparticles and AFM images (b) 3D and (c) 2D image, and (d) particle size distribution of zinc nanoparticles.

The strong existence of the highly excited crystal facets of (0002) and (10  $\bar{1}$ 1) in the UV near band-edge regime may have attributed to the intense UV photocatalysis. Also, the enhancement of the

levels of photocatalysis can be done with small diameter structures [19, 20]. To add further, the structural defects of nano ZnO may have attributed to the higher optical absorption in the visible regime (400–700 nm) of the PS/ZnO sample [20]. PS/ZnO nanocomposites may provide effective protection against UV light and can be used as UV-shielding materials.



**Figure 2.** UV–vis absorption spectra for PS/ZnO nanocomposites with different concentrations of ZnO nanoparticles at room temperature.

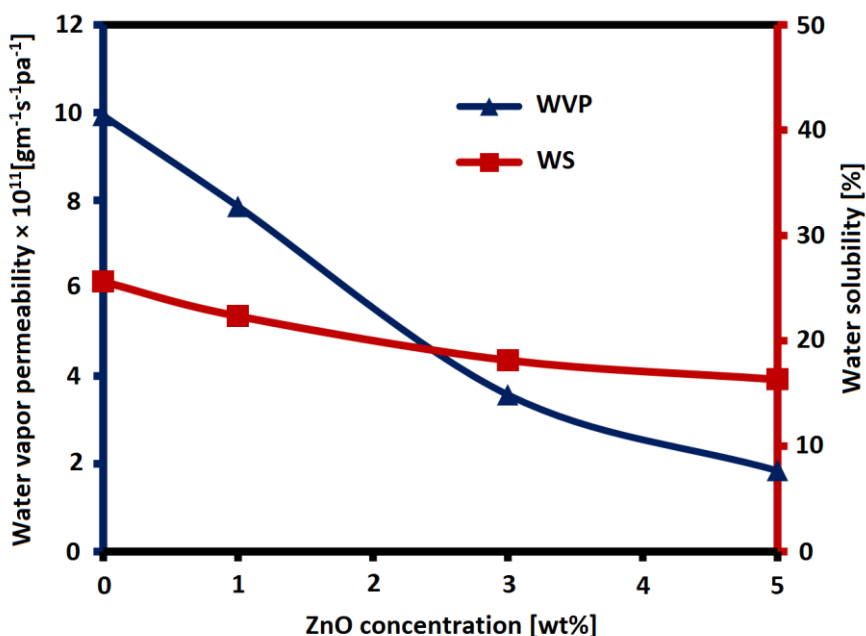


**Figure 3.** Cyclic voltammogram of Pea Starch biopolymer incorporated by 0 and 5 wt% ZnO nanoparticles.

Cyclic voltammetry (CV) study was conducted to evaluate the capacitance of PS biopolymer incorporated by 0 and 5 wt% ZnO nanoparticles [21]. The capacitive behavior of biopolymer comprising of ionic liquid–based polymer electrolyte is compared to that of ionic liquid–free polymer electrolyte as

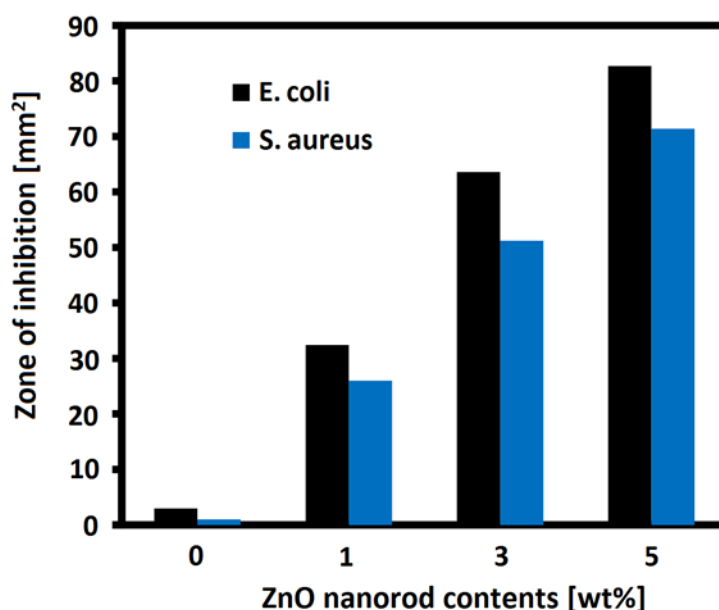
illustrated in Figures 3. Figure 3 depicts CV profile of biocomposite with 0 wt% ZnO nanoparticles and the CV of PS biocomposite containing the most conducting biopolymer membrane (5 wt% ZnO). The redox processes are not detected in this potential region [22]. This observation confirms the enhancement of electrochemical properties in PS biocomposite incorporated with ZnO nanoparticles. Furthermore, the higher conductivity of biopolymer incorporated with ZnO nanostructures (Fig. 3) indicates more charge carriers in the nanocomposites which can be the reason for the enhancement of the antibacterial properties of starch-based polymer through the electrostatic discharge between ZnO nanoparticles and bacteria [23]. Therefore, the PS/ZnO nanocomposites have the potential to be used to properly preserve the packaged foods by employing it as an antibacterial food packaging material.

Figure 4 illustrates the determination of the water vapor barrier property of the films by the WVP. The higher water-resistance of the nano ZnO in comparison to the resistance of the matrix may have attributed to the crucial decrement in WVP in after the formation of composite with nano ZnO. Thus, the inclusion of ZnO makes it tedious for the water vapor molecules to pass, described based on Nielsen's simple model of tortuosity [24]. The model articulates that each layer of the nanoparticle is at right angle orientation to the diffusion pathway, and thus indicates that the gas molecules should pass through a longer diffusive path to decrease the permeability coefficient [25].



**Figure 4.** Water vapor permeability and water solubility of PS/ZnO nanocomposite films

The WS of PS/ZnO nanocomposite films is shown in Figure 4. The PS/ZnO nanocomposite matrix undoubtedly decreases the solubility of the composites. This conclusion may be ascribed to the interplay between ZnO and the polymer matrix structure. When the concentration of ZnO nanoparticles increase in biocomposite films, more H bonds in the ZnO and the matrix components are formed [26, 27]. Therefore, water molecules do not overlap effectively with nanocomposite compared to nonfiller composite films.



**Figure 5.** Concentration effects of ZnO nanoparticle on antimicrobial activity of PS/ZnO nanocomposite films

Although few mechanisms have been suggested to clarify the variations in the antimicrobial activity of ZnO against Gram-negative and -positive bacteria, slight hesitation is still present. Thus, further studies need to be performed to explain the sensitivity of these microorganisms to ZnO nanostructures. The antibacterial activities of PS film and PS/ZnO nanocomposite have been tested against *S. aureus* and *E. coli*. As shown in Figure 5, all nanocomposite films incorporated with ZnO nanoparticles indicate strong antibacterial activity with the increase in ZnO nanoparticle concentration. The results demonstrate that the PS/ZnO (5 wt%) nanocomposite film has the best antimicrobial activity among the films tested. Furthermore, *E. coli* has a higher sensitivity to PS/ZnO nanocomposite than *S. aureus*. The higher resistance of *S. aureus* to ZnO nanoparticles than that of *E. coli* may be attributed to the variations among these two bacteria in terms of the intracellular antioxidant contents, like carotenoid pigments inside *S. aureus* [28].

**Table 1.** Overview of inhibition zone of biopolymer films incorporated with ZnO nanostructures

Biopolymer materials	Incorporated materials	Inhibition zone (mm <sup>2</sup> )		Ref.
		<i>S. aureus</i>	<i>E. coli</i> .	
Corn starch	Mentha pulegium oil	83	76	[29]
Alginate	Cinnamon Essential Oil	48	45	[30]
	Nanoemulsions			
Poly(vinyl chloride)-based Film	ZnO nanoparticles	58	63	[31]
Soluble soybean polysaccharide	TiO <sub>2</sub> nanoparticles	71	53	[32]
Pea starch	ZnO nanoparticles	72	83	Present work

Excellent antimicrobial activity of ZnO nanostructures against *S. aureus* and *E. coli* and the corresponding mechanism of action have also been demonstrated by other researchers. Table 1 indicates inhibition zone of biopolymer films incorporated with nanostructures according to previous researches [29-32]. The functional activity of nanostructures is strongly influenced by their sizes [33]. Thus, the antimicrobial activity of ZnO nanoparticles on *E. coli* and *S. aureus* can be enhanced with the aspect ratio of nanofillers. This phenomenon can be related to the surface area/volume ratio, which concludes in the increased reactivity of the ZnO surface in nm size [34]. Given that the H<sub>2</sub>O<sub>2</sub> generation relies more on the ZnO surface area, the larger surface area will conclude in more reactive oxygen species on the ZnO surface, thereby resulting in better antibacterial activity and higher aspect ratio. The presence of H<sub>2</sub>O<sub>2</sub> leads to a reduction in bacterial growth, which can be a dominant mechanism for antibacterial behavior [35].

#### 4. CONCLUSIONS

We reported a novel gas synthesis approach that can produce ZnO nanoparticles at a rapid rate of 100 nm/s in only 15 s. PS/ZnO nanocomposites were synthesized by reinforcing ZnO nanoparticles into plasticized starch. PS/ZnO nanocomposites exhibited strong UV light absorption in the region between 290 and 370 nm even at low ZnO nanoparticle concentrations. The strong interplay between the ZnO nanofiller and PS matrix was attributed to the enhancement of biopolymer features. Furthermore, ZnO nanofiller significantly enhanced the water vapor barrier compared to the PS matrix. The antibacterial activities of ZnO nanostructures were assessed by estimating the reduction ratio of bacteria treated with ZnO. PS/ZnO biopolymer films indicated an excellent antimicrobial activity against *S. aureus* and *E. coli*.

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