Carbohydrate Polymers 87 (2012) 1065–1072

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Optical, bactericidal and water repellent properties of electrospun nano-composite membranes of cellulose acetate and ZnO

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ARTICLE INFO

Article history:
Received 19 May 2011
Accepted 13 August 2011
Available online 19 August 2011

Keywords:
Nanocomposites
Nanoparticles
Fibers
Defects
Hydrophobic
Bactericidal

ABSTRACT

In this report, ZnO nanoparticles embedded cellulose acetate (CA) fibrous membrane with multifunctional properties have been prepared through electrospinning method. The morphology of the electrospun composite membrane was analyzed by Scanning Electron Microscope (SEM). It was found that the polymer concentration in the solution has a significant effect on the morphology of the fibers. The optical property of the sample was tested using Photo Luminescence (PL) spectra. There is no significant change in the emission features of cellulose acetate with the addition of ZnO. The anti-bacterial property of the sample was studied using disc diffusion method. The wettability of the pure and composite fibrous membrane was also studied by measuring the contact angle of water on the membrane. It was observed that the embedded ZnO in the CA was responsible for the hydrophobic nature of the surface.

1. Introduction

Over the past few years, there has been a tremendous growth of research activities to explore electrospinning to develop fibers in the micro and nanometer range using various types of materials or polymers. The nanofibers produced by electrospinning have several remarkable advantages like high aspect ratio, flexibility and high tensile strength. It has attracted the attention of researchers as it is cost effective and simple technique (Sundaray et al., 2004; Li & Xia, 2004; Andreas & Joachim, 2007). Different types of nanomaterials were successfully incorporated into various polymer matrices owing to their unusual combination of optical, mechanical and bactericidal properties (Di et al., 2009; Li et al., 2008a, 2008b; Nah et al., 2008; Prakash et al., 2010; Seoudi, Abd, & Shabaka, 2008; Xinghua, Changlu, Hongyu, Xiliang, & Jian, 2004; Xupin, Bowen, Weimin, & Xianlin, 2010). The properties of these nanocomposites are strongly dependent on the size, dispersion efficiency and morphology of the sample. The in situ growth of nanoparticles in polymer matrixes is attracting increasing interest in terms of practical applications and synthetic challenges. A major obstacle in these processes is the presence of aggregates and inhomogeneous distribution of nanoparticles (Grant & Dmitry, 2009; Julian, 2006; Michael, Anish, & Phillip, 2006).

Electrospun bionanocomposites has been a recent focus of researchers and has a huge impact in diverse areas such as tissue engineering, bone replacement/repair, dental applications, wound healing and controlled drug delivery (Jing et al., 2003; Pim-on, Nuttaporn, & Pitt, 2008; Schneider, Wang, Kaplan, Garlick, & Egles, 2009; Shafei & Abou-Okeil, 2011; Wenguo et al., 2010). Cellulose and its derivatives are widely used as versatile materials because of its low cost and its processability into different forms. Unlike starch, it has low water solubility; therefore it allows better control over scaffold design, textile, filtering, etc. However, their applications are still limited due to the lack of antimicrobial activity. Recently, it has been found that these limitations can be overcome by the incorporation of antimicrobial nanoparticles into it (Won, Ji, Taek, & Won, 2004; Won, Ji, & Won, 2006). ZnO is a direct wide band gap semiconductor (E_g = 3.4 eV). The high exciton binding energy (~60 meV) of this material ensures that it is a promising candidate for stable room temperature luminescent and lasing devices. Moreover, ZnO is a bactericide and inhibits both Gram positive and Gram negative bacteria (Dai, Chen, Wang, Zhou, & Hu, 2003; Tam et al., 2008).

Microbial contamination is a life-threatening issue in food industry, synthetic textiles, packaging, healthcare care products (Li et al., 2008a, 2008b). Among the various kinds of pathogenic microorganisms, *Staphylococcus* and *E. coli* are closely related species that commonly cause a wide variety of infections and

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doi:10.1016/j.carbpol.2011.08.030

diseases (Ales et al., 2009; Enjuoo et al., 2010). Therefore, the development of antimicrobial surface coating has attracted increased attention to prevent the microbial contamination (Perelshtein et al., 2009). The use of inorganic antimicrobial agents has gained importance because of their ability to withstand adverse processing condition as compared to organic antimicrobial agents (Yiguang et al., 2009; Yuvaraj, Kaushik, & Narasimha, 2010). The ability to prepare nanobiocomposites of cellulose acetate and ZnO, paves a way to develop new biocidal agents.

The self-cleaning effect caused by superhydrophobicity is needed for many applications such as self cleaning, anti-fouling coatings, etc. Till date, various methods have been adopted by researchers to produce superhydrophobic surfaces (Tarwal & Patil, 2010). Therefore, developing a simple approach to fabricate the superhydrophobic surface without further coating of low surface energy material is important and scientifically challenging.

In this study, we report the successful preparation and optimization of ZnO embedded CA membrane and also characterization of this biocomposite membrane based on the optical, bactericidal and water repellent properties.

2. Experimental details

2.1. Materials

Cellulose acetate (CA, M_W = 25,000) was purchased from Aldrich. Zinc acetate dehydrate, Dimethyl formamide (DMF) and acetone were purchased from Sisco Research Laboratories–India.

2.2. Experimental procedure

Initially 0.2 mol of zinc acetate dihydrate was dissolved in mixture of DMF/acetone in the ratio of 4:1. Then the cellulose acetate (14 wt%) was added in to the sol solution and stirred for 5 h to achieve the homogeneous solution which is finally considered as a precursor solution for electrospinning. The concentration of the CA solution was varied between 6 and 14 wt%. The electrospinning process was performed in a similar way as reported in our previous work (Anitha, John Thiruvadigal, & Natarajan, 2011). The flow rate was kept constant at 0.4 mL/h. The distance between the electrodes was about 12 cm. The collected composite membrane was dried initially at 80 °C for 6 h.

2.3. Measurements and characterization

The Scanning Electron Microscopy (SEM) (Quanta 200 FEG) was used to analyze the sample morphology and Energy Dispersive X-ray Spectroscopy analysis (EDS) gave the chemical composition of the sample. The functional groups present in the sample were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) (Bruker Tensor Instrument). Photo Luminescence study was performed using SPECTRAQ Fluorolog spectrophotometer. Measurement of contact angle of water was performed using Axisymmetric Drop Shape Analysis (ADSA)-Easy Drop Goniometer (KRUSS, DSA II GmbH, Germany).

2.4. Antibacterial activity studies

Antibacterial tests were carried out on Gram positive bacteria Methicillin-Resistant *S. auereus* (MRSA) and Gram negative bacteria *Escherichia coli*, *Klebsiella pneumoniae*, *Citrobacter freundii* using Kirby–Bauer disk diffusion method. The bacterial cultures were maintained in Nutrient agar slopes at 4 °C and sub cultured on Nutrient agar plates. The isolated colonies of the respective bacterial strains adjusted to 1–2 × 10^7 cfu/ml by 0.5 Mcfarland standards. The culture was inoculated on Muller–Hinton agar plates. CA membrane disc were placed aseptically on the Muller-Hinton agar medium which was already swabbed with the test organism. The experiment was carried out for both CA membranes, with and without ZnO nanoparticles. The plates were incubated at 37 °C for 24 h to observe the inhibition zone.

3. Results and discussion

3.1. Morphological investigation

3.1.1. SEM analysis

It is well known that the morphology of the electrospun fibers are strongly dependent on the number of processing parameters such as polymer concentration, voltage, distance between the electrode, etc. The influence of the various polymer concentrations (6, 8, 10, 12 and 14 wt%) in the solution on the morphology of fibers were examined by SEM as shown in Fig. 1(a–e), respectively. At lower concentrations, beads are formed along the fiber which is generally considered as defects. These beads may decrease the effective surface area of the fibers. The number of beads formed is reduced as we go from 6 to 12 wt% and the beads completely disappeared in the case of 14 wt% of the solution. However, there is a considerable increase in the fiber diameter. The average diameter of the optimized fiber was found to be 170 ± 40 nm. The increased polymer concentration in the solution helps to prepare the uniform defect free fiber because at higher polymer concentrations, sufficient chain entanglements serve to stabilize the jet by inhibiting its breakup (Anitha et al., 2011).

EDS analysis was used to identify the composition of the fibers as shown in Fig. 1f. The elemental analysis reveals the presence of ZnO in the fibers. The Al peak in the spectrum comes from the aluminum foil which served as substrate. The carbon peak originates from the polymer part of the fibers.

3.1.2. TEM analysis

TEM analysis was used to analysis the dispersion efficiency of nanoparticles in polymer matrix directly as shown in Fig. 2. The corresponding SAED patterns of fiber are shown inset in the same figure. From the image, it is clearly revealed that the ZnO particles are well dispersed throughout the cellulose acetate fibers without the presence of agglomeration.

3.2. XRD analysis

The XRD pattern of CA and ZnO embedded cellulose acetate are shown in Fig. 3. The CA fibers exhibit the diffuse charactertics pattern of an amorphous phase with the typical peak around 23°. The observed peaks in the range of 30–50° could be indexed as the wurtzite structure of ZnO which is well matched with standard diffraction data (JCPDS: 36-145). No additional peaks are detected and which indicates the formation of ZnO in the CA fibers (Youliang, Dongmei, Jian, & Guangtian, 2006).

3.3. FTIR analysis

The results of the FTIR analysis was used to analysis the interaction between ZnO and cellulose acetate. Fig. 4a and b shows the FTIR spectra of pure CA and CA/ZnO composite fibrous membrane, respectively. The main characteristics bands of CA were assigned as follows: The characteristic absorption peak at 3500 cm^{-1} can be attributed the presence of hydroxyl group and the peaks at 1743, 1270 and 1050 cm^{-1} corresponding to the stretching of C–O group, ether group and –C–O–bond of the –CH_2–OH group, respectively (Saowakon, Manashuen, Jochen, Pitt, & Tipaporn, 2010).

In Fig. 4b, in addition to the characteristics peak of CA, a new peak around 477 cm^{-1} is assigned to the Zn–O vibration which

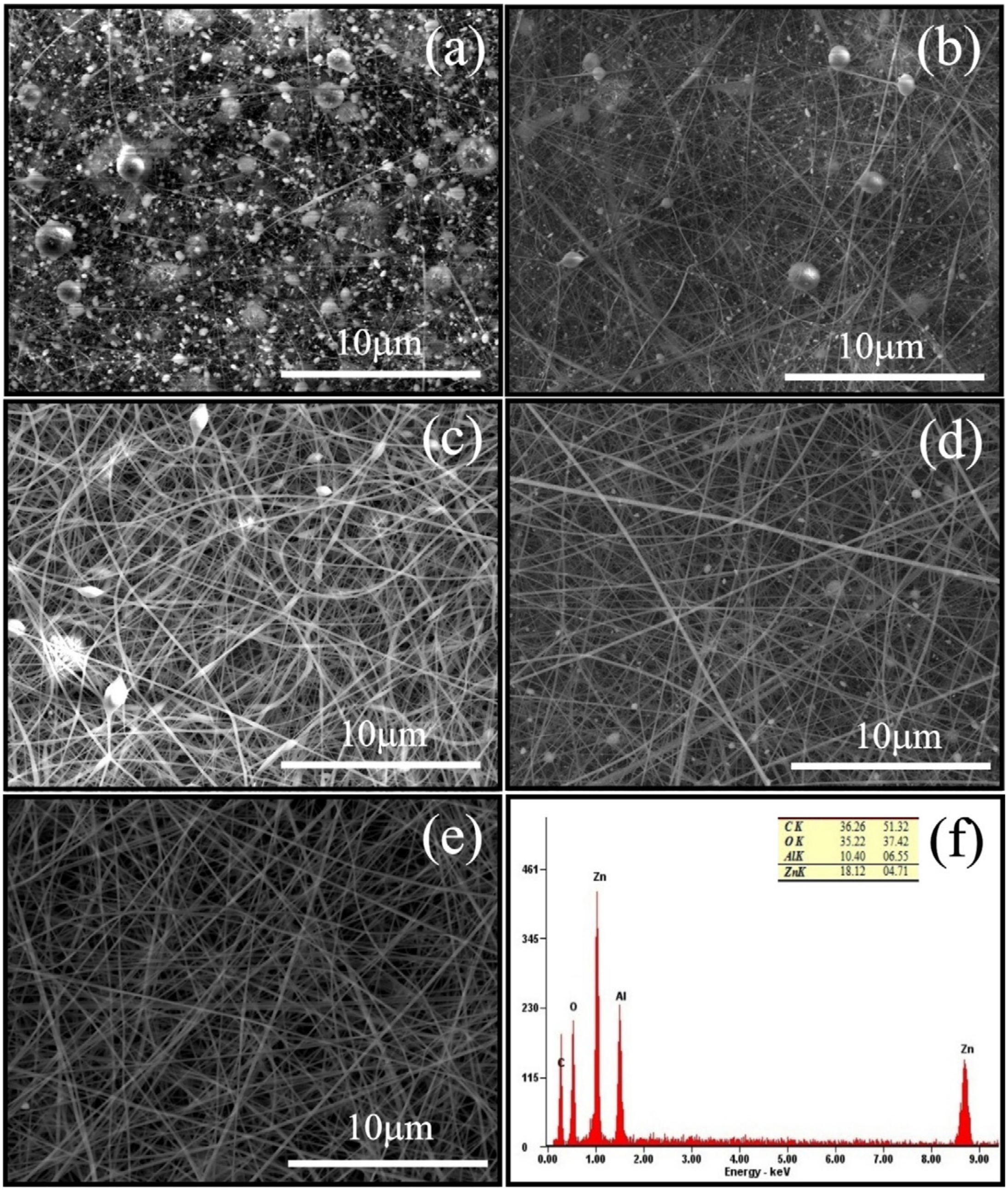

Fig. 1. SEM image of the ZnO embedded CA membrane with varied polymer concentration (a) 6 wt% (b) 8 wt% (c) 10 wt% (d) 12 wt% (e) 14 wt% (f) Energy Dispersive X-ray spectra analysis (EDAX).

further confirms the formation of ZnO. By comparing the IR spectra of ZnO/CA composite fibrous membrane with that of pure CA fibrous membrane, the characteristics peak of –OH group was shifted to 3471 cm^{-1} from 3450 cm^{-1} as shown in figure. Similar shift are observed for the peaks located at 1743, 1370 and 1050 cm^{-1}. The observed shifts in the peaks may be described due to the formation of hydrogen bonding between ZnO and CA (Xiaomeng, Changlu, & Yichun, 2007).

3.4. PL studies

In order to investigate the quality and purity of the sample, PL spectrum was recorded for both CA and CA/ZnO composite fibrous membrane shown in Fig. 5a and b, respectively. It is well known that a typical spectrum of ZnO has two major characteristic peaks: a UV near-band-edge (NBE) whose peak emission is around 380 nm and deep-level (DL) emission in the visible region (Li et al., 2004; Lin, Yun, Huibin, Paul, & Ziyu, 2002; Periyasamy, Narayan, Hak, & Douk, 2004). In the PL spectrum of CA/ZnO composites membrane exhibits both characteristics bands of CA and ZnO and the characteristics peaks remained the same as observed in their single component. However, there is no significant change in the observed emission spectra. It clearly indicates that the emission features of cellulose acetate are not significantly affected by the embedded ZnO nanoparticles. In addition to this, yet another interesting observation is that visible emission was quenched in the observed spectra which may be the result of the surface passivation of ZnO with CA (Jan-Peter, Tobias, Lars, Ilja, & Jurgen, 2008).

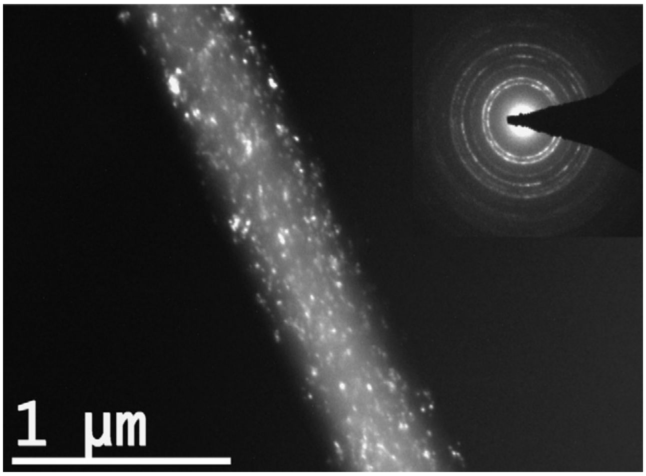

Fig. 2. TEM image of the composite fiber and SAED patterns (inset in the left top of the Fig.). The ZnO nanoparticles are clearly seen in surface of the fibers.

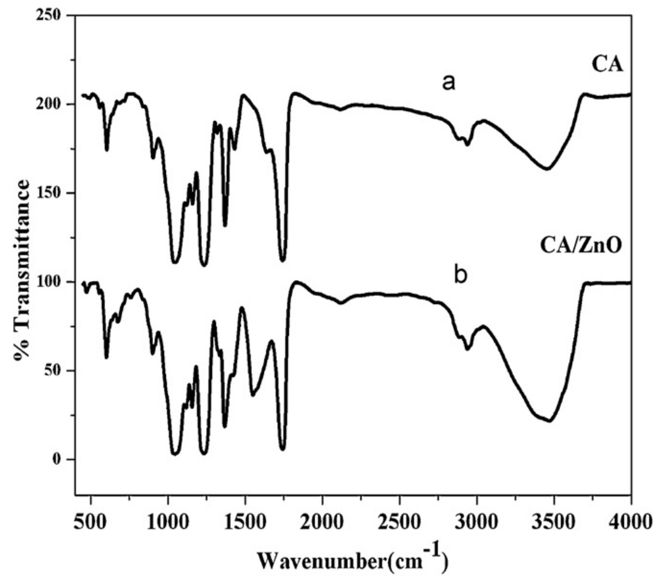

Fig. 4. FTIR spectra of (a) pure CA fibrous membrane (b) ZnO embedded CA fibrous membrane.

3.5. Bactericidal properties

The antimicrobial properties of the fibrous CA (Fig. 6a) and ZnO impregnated CA (Fig. 6b) were evaluated against both Gram positive and Gram negative bacteria under normal lighting condition. Here, Kirby Bauer technique was adopted to evaluate the antimicrobial activity. The bare CA fibrous membrane was used as a control. According to the results obtained, no detectable inhibition Zones were seen for the bare CA. Conversely, the significant Zones were observed for ZnO embedded CA. The diameters of the zone of inhibition around the membranes after one day were measured to be 27 mm, 22 mm, 14 mm for Methicillin-resistant *S. aureus* (MRSA), *E. coli* and *Citrobacter freundii*, respectively. However, no antibacterial activity was shown against *K. pneumoniae*. It is seen that the composite membrane had a stronger influence on MRSA than *E. coli*. Such results are in a good agreement with the previously reported literature (Roya & Majid, 2010; Yanmin et al., 2008). The nature

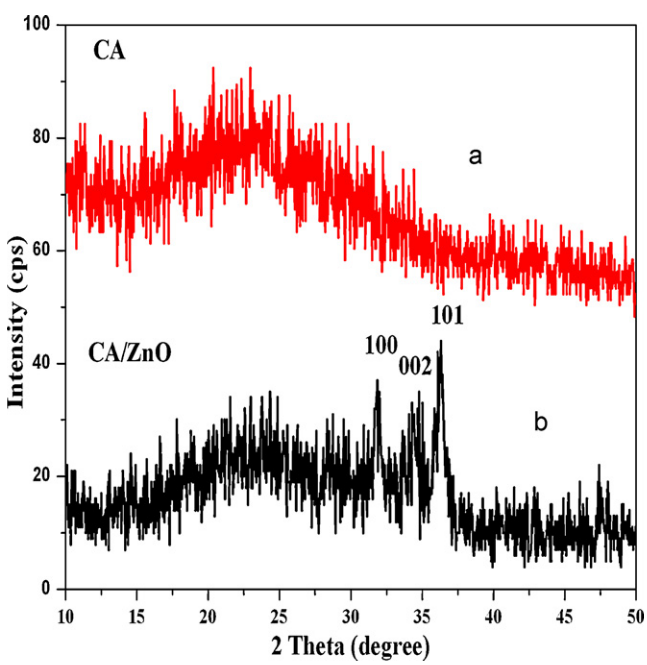

Fig. 3. XRD pattern of (a) Cellulose acetate fibrous membrane (b) ZnO embedded cellulose acetate fibrous membrane.

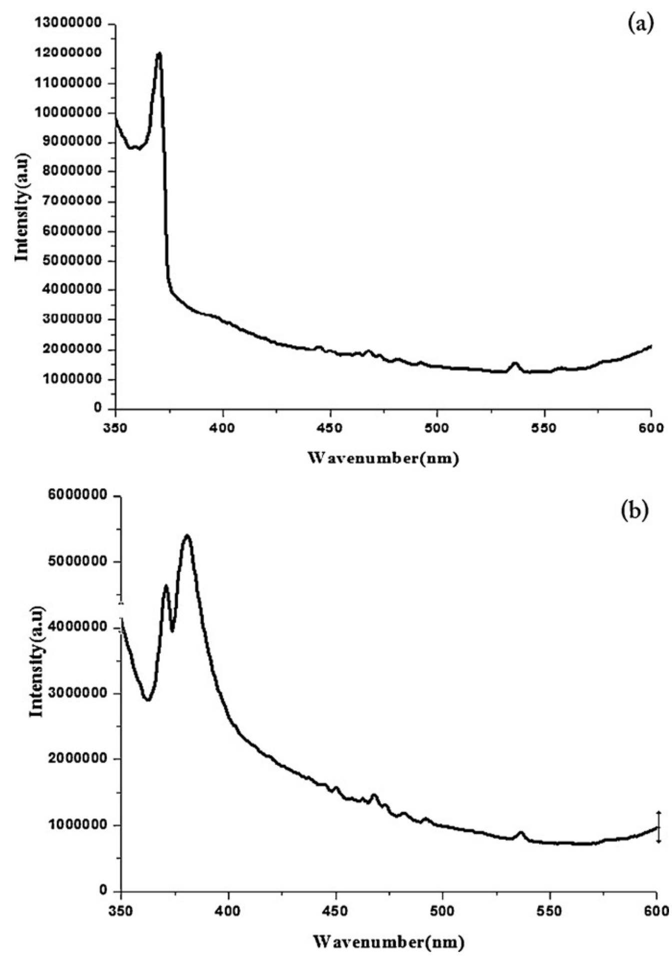

Fig. 5. PL Spectra of (a) pure CA fibrous membrane (b) ZnO embedded CA fibrous membrane.

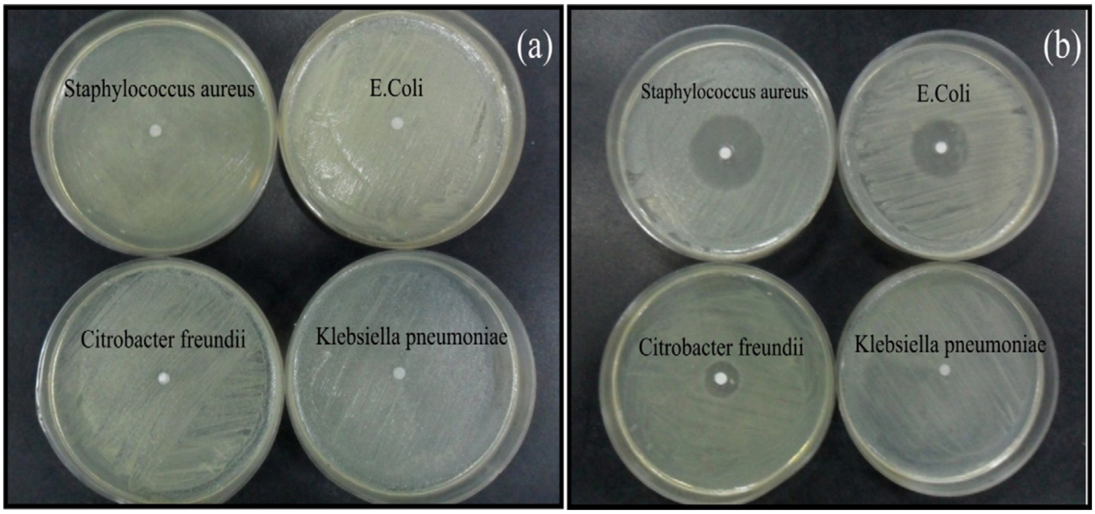

Fig. 6. Images of bactericidal effect of (a) pure fibrous CA membrane and (b) ZnO embedded CA fibrous membrane against Gram-positive methicillin-resistant *Staphylococcus aureus* (MRSA) and Gram-negative *E. coli*, *Citrobacter freundii*, *Klebsiella pneumoniae*.

of cell wall structure is one of the possible reasons for observed difference in sensitivity.

The *S. aureus* is composed of multi layers of peptidoglycan which has plenty of pores that could render them more susceptible to the intracellular transduction by the nanoparticles leading to cell disruption (Inphonlek, Pimpha, & Sunintaboon, 2010; Xiaofang et al., 2010). In contrast, the cell wall of *E. coli* is relatively thin mainly consisting of peptidoglycan and an outer layer of lipopolysaccharide, lipoprotein, and phospholipids, which would be less prone to the attack of the nanoparticles. Therefore, the nanoparticles had higher antibacterial activity against *S. aureus* than *E. coli* (Jean-Paul, Richard, Stepan, Maria, & Kevin, 2009; Zhongbing et al., 2008). To date, several mechanisms have been postulated for the antimicrobial property of ZnO nanoparticles (Guy et al., 2009; Lingling, Yunhong, Yulong, Malcolm, & David, 2007; Nadanathangam, Sampath, Kathe, Varadarajan, & Virendra, 2006; Rizwan, Amrita, Soon-Il, Young-Soon, & Hyung-Shik, 2010). However, much remains unknown mechanism will be the subject of future research. The reason for such an observation in composite fibrous membrane under normal lighting condition is not totally clear yet. A thorough survey of literature till date, have made us assume that the antimicrobial effects of composite membrane might be associated with the presence of an electrostatic attraction between the positively charged nanoparticles and the negatively charged bacteria (Harris & Richards, 2004; Jingyuan et al., 2010; Peter, Rosalyn, George, & Kenneth, 2002; Sivakumar et al., 2010).

It is a well known fact that, both Gram positive and Gram negative bacteria have negative charge. The peptidoglycan layer of Gram positive bacterium is rich in Teichoic acids, which are negatively charged due to presence of phosphate in their structure. On the other hand, the highly-charged lipopolysaccharides, which are the major constituents of the outer membrane of Gram negative bacterium, impart a strong negative charge to surface of the bacterial cells (Roberta et al., 2006; Hirotaka, Takuya, & Hiroyauki, 2009).

The work of Vimala et al. (2010) which is related to our report, is considered for a comparative account. They demonstrated that the presence of pores in fiber structure is one of the reasons for superior antibacterial activity. The fact that the porous structure absorbs large quantity of water, enormous amount of silver nanoparticles, as a result, is released in to the media. These results cannot be applied to the current work, since the result of WCA measurements confirmed the hydrophobic nature of the prepared sample.

The surface area in contact with the microorganisms determines the antibacterial activity. As the electrospun fibers have large surface area, broad range of probable reaction with surface of the cell wall is possible, when compared to one-dimensional nanostructures prepared using any other physical/chemical methods. Moreover, this method produces nanoparticles which are homogenous and monodispersed. The absence of aggregation of the particles is one of the most distinguishing features of this method. Other chemical methods used for synthesis of nanoparticles in polymers lead to aggregation of particles resulting in decreased antibacterial activity. Yet another factor which is responsible for high antibacterial activity is the enhanced dispersion stability of ZnO nanoparticles in the CA fibers.

3.6. Wettability studies

Contact angle measurement was carried out to evaluate the wetting properties of the fibrous membrane. Most of the previous studies focused on the preparation of hydrophobic and super hydrophobic surface by appropriate surface modification of the sample (Ding, Ogawa, Kim, Fujimoto, & Shiratori, 2008; Patra, Sarkar, Bera, Ghosh, & Paul, 2009; Tarwal and Patil, 2010). Still, it is difficult to achieve the super hydrophobic surface without chemical modification of the sample. Fig. 7a and b shows the contact angle of a water droplet on the fibrous membrane for duration of 30 s.

In the case of pure CA fibrous membrane, the measured contact angle was found to be 47° initially and the contact angle decreases rapidly from 47° to 31°. The observed hydrophobicity of ZnO embedded CA is about 124°, which is much higher than that of the pure CA fibers. The value of the WCA does not change significantly from that observed initial value. From the observed result, it was concluded that the wetting property of the CA has changed from hydrophilic to hydrophobic when ZnO was impregnated into it.

Trapping of more air under water droplets falling on the fibers could be a result of the surface roughness of the fibers caused by electrospinning as well as the presence of nano ZnO. On comparison with the work by Bin Ding, where fabrication of superhydrophobic cellulose acetate (WCA of 132°) was done using simple sol–gel coating of decyltrimethoxysilanet and tetraethylorthosilicate (Bin et al., 2006), ZnO impregnated cellulose acetate fibrous showed not only the superhydrophobic nature(WCA 124°) but also a good bactericidal property.

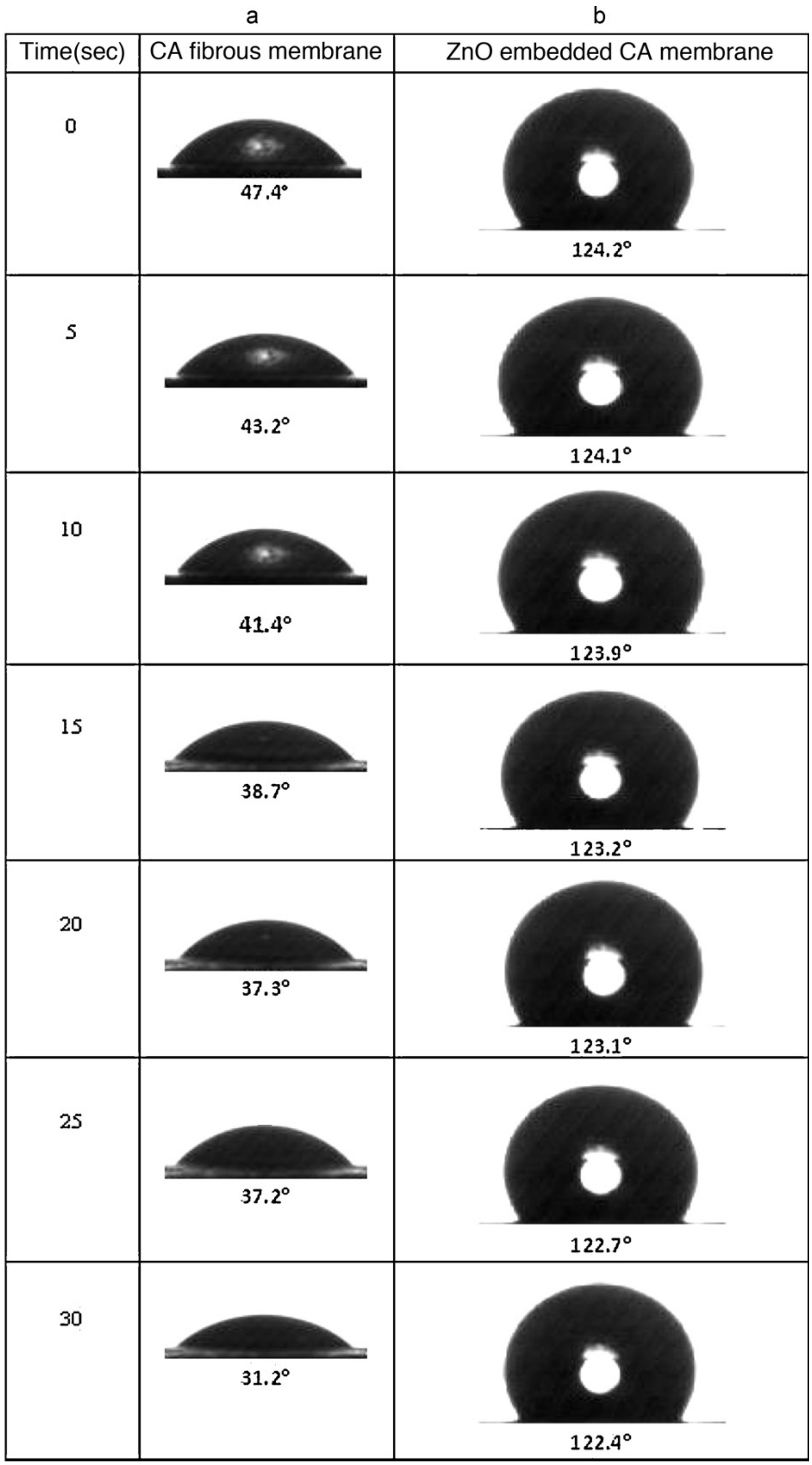

Fig. 7. The optical photograph of water droplet on (a) pure and (b) ZnO embedded CA fibrous membrane.

4. Conclusion

ZnO embedded cellulose acetate fibrous membrane has been prepared by electrospinning method. From the analysis of FTIR spectra, it could be concluded that the formation of hydrogen bond between ZnO and CA. The ZnO embedded fibrous membrane showed a better water repellent property than pure CA membrane. The sample exhibited strong antibacterial activity against the *S. aureus*, *E. coli* and *Citrobacter*. Moreover, the wettability of the surface can be changed from hydrophilic to hydrophobic. Our simple method provides a new approach to fabricate the hydrophobic surface without need for further surface treatment. Therefore, the electrospinning technique could be considered as the best suited method for synthesis of composite fibrous membrane, since agglomeration of nanoparticles is prevented and the contact area between the surface and the microorganisms is increased.

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