

Coating of Medical-Grade PVC Material with ZnO for Antibacterial Application

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Received June 7, 2013; revised July 7, 2013; accepted July 17, 2013

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ABSTRACT

The ZnO sol well-crystallized was prepared by the sol-gel method. The ZnO films were coated on medical-grade PVC surface by the improved organic-inorganic interfacial adhesion method. The physical and photocatalytic properties of the samples were characterized by XRD, SEM, DRS spectra and measured by the photodegradation reaction of Rhodamine B (RhB) and anti-bacteria for *Escherichia coli* (*E. coli*), respectively. The results show that pretreatment of PVC by the mix solution of THF-PVC helps to improve the amount and adhesion strength of ZnO suspension to PVC surface. The photocatalytic and antibacterial properties of the THF-ZnO/PVC film are better than that of the ZnO/PVC and neat PVC. Under UV irradiation, the THF-ZnO/PVC film shows the best antibacterial properties with 99% kill rate of bacteria.

Keywords: ZnO; PVC; Photocatalysis; Antibacterial

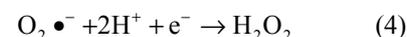
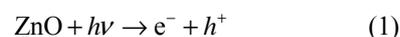
1. Introduction

The increasing use of polymer materials such as polyethylene, polyurethanes, and poly (vinyl chloride) (PVC) in the hospital care has led to a concomitant increase in the incidence of biomaterial-related infections (BRI) [1]. Adhesion of bacteria to biomaterials led to the formation of biofilm on the surface, which plays a crucial role in the pathogenesis of the BRI [1-3]. The growth and production of biofilm protect the bacteria from the host defence mechanisms and external agents as the drug treatments [1,2,4-7], which makes the cure of the bacterial infections quite difficult and requires either higher doses or more potent antibiotics.

In order to efficiently prevent or reduce biofilm formation, many efforts have been done to enhance the antibacterial properties of biomaterials. Some efforts such as modifying the physicochemical properties of biomaterial surface, coating with silver, azidation treatment, antibiotic impregnation into the polymer matrix, have been examined in recent years [8-12].

Recently, coating semiconductor photocatalyst on materials' surface for antibacterial activity has attracted great interest due to the following advantages when

compared with other methods: 1) excellent photocatalytic and antimicrobial activity, 2) nontoxicity and bio-compatibility, 3) strong physicochemical stability and durable antibacterial properties. The antibacterial mechanism of semiconductor photocatalysis is mainly based on its UV photoactive property. Taking ZnO as an example was shown in Equations (1)-(4) [13].



When ZnO was exposed to UV light with the wavelength less than 388 nm, the semiconductor surface generated valence band holes and conduction band electrons as in Equation (1). The holes could react with water or surface hydroxyls ($\text{H}_2\text{O}/\text{OH}^-$) to generate hydroxyl radicals ($\text{HO}\bullet$), while conduction band electrons reacted with adsorbed molecular oxygen (O_2) to generate superoxide radical ($\text{O}_2\bullet^-$). The radicals ($\text{O}_2\bullet^-$ and $\text{HO}\bullet$) can destroy and shrink bacterial cells by reacting with the organism of bacterial cells in the photocatalytic process [14, 15]. Among various oxides semiconductor photocatalysis,

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TiO₂ and ZnO are generally considered to be the most suitable for antibacterial agents [15-18]. TiO₂ film coated on different materials' surface is effective at killing bacteria and viruses under UV irradiation [15,16]. ZnO as antibacterial agents has been reported exhibiting higher antibacterial activity than other metal oxide nanoparticles [19]. It has supposed that ZnO not only kills bacteria under UV irradiation bacteria but also inhibits the bacterial growth under normal visible lighting conditions [20]. To extend the usage of antibacterial agents, many studies have been done to coat ZnO film on many materials' surface that was widely used in life such as glass, ceramic, stainless steel, polymer, and so on. In general, to obtain highly adherent and antibacterial activity of ZnO film, heating the materials that have been modified by ZnO film at high temperature is required. However, one of the main barriers to coat ZnO on polymer is the low heat resistance of polymer. Low heat resistance of polymer disables the routine coating method to be used to modify inorganic ZnO film on polymer.

Recently, organic-inorganic composite membrane by mixing inorganic and organic materials has been supposed to use because of its simplicity, mild conditions and stability [21,22]. In this work, a similar organic-inorganic interfacial adhesion method was used to coat ZnO film on polymer materials. First, suspension of well-crystallized ZnO was prepared by sol-gel at low temperature. Then, to improve the adhesion strength of ZnO to PVC, the mix solution of PVC and THF was used to pretreat the surface of PVC sheet. After pretreated by the mix solution of PVC and THF, PVC sheets were coated with ZnO film by dip-coating with suspension ZnO. The photocatalytic and antibacterial activity of ZnO film was investigated. To evaluate the antibacterial activity after modified by ZnO, the performance of ZnO film was compared with neat PVC under similar operating conditions.

2. Materials and Methods

2.1. Material

Medical-grade PVC sheets were purchased from Tyco Healthcare International Trading (Shanghai) Co., Ltd., and were washed with absolute alcohol before use. *Escherichia coli* were cultured at 37°C in Luria-Bertani (LB) medium (pH 7.0) containing tryptone 1%, yeast extract 0.5%, sodium chloride 1%. When tested, the bacterial concentration was adjusted to the required concentration (10⁴ - 10⁵ cfu/ml). Other reagents were of analytical grade and used as received.

2.2. Preparation of ZnO Sol

Zn(Ac)₂·2H₂O was dissolved in methanol to obtained a 0.075 M solution of Zn (Ac). Ammonia was dropped into

the solution to adjust the pH to 8 and then stirred the solution at 65°C for 2 h to obtain ZnO sol.

2.3. Coating ZnO on PVC Surface

The ZnO film was prepared by dip-coating method with ZnO suspension as precursor. The PVC sheets (1.5 × 4.5 cm) were pre-immersed in THF-PVC solution for 10s. Immediately, the PVC samples were dipped into ZnO colloidal sol and were slowly pulled out of the sol at a speed of 1200 mm/h in an ambient atmosphere. The ZnO gel film on PVC were dried in an oven at 60°C for 30 min and then were dried at 120°C for 2 h. After seven such coating steps, the transparent ZnO film on PVC were obtained. The PVC sheets without pretreatment were coated with ZnO under similar operating conditions for comparison. For ease of presentation, the ZnO film with pretreatment were labelled as THF-ZnO/PVC and that without pretreatment were labelled as ZnO/PVC.

2.4. Structure and Morphology Characterizations

The crystal structure of the sample was characterized by X-ray diffraction (XRD) (Bruker D8 Advance powder diffractometer). The scanning electron microscopy (SEM) was performed on a Philips XL30 ESEM system. The UV-Vis spectra were obtained in the diffuse reflection mode using a Carry 500 spectrometer at a resolution of 2 nm. The spectra of the PVC, ZnO/PVC and THF-ZnO/PVC sheets were recorded in the ultraviolet and visible in the wavelength range from 250 to 800 nm.

2.5. Photocatalytic and Antibacterial Property

2.5.1. Photocatalytic Activity

The photocatalytic activities of PVC, ZnO/PVC and THF-ZnO/PVC were determined by monitoring the degradation of organic dye Rhodamine B (RhB). A quartz tube reactor with condenser pipe was used and four 4W-UV lamps with wavelength at 365 nm were fixed around the reactor. The PVC sheets (1.5 × 4.5 cm) were immersed in 20 ml aqueous solution of RhB (1 × 10⁻⁵ mol/dm³) and kept for 12 h in black prior to irradiation. The concentration of RhB at different irradiation times was monitored by Varian UV-260 spectrometer.

2.5.2. Bacterial Adhesion

The neat PVC, ZnO/PVC and THF-ZnO/PVC sheets were immersed in the aqueous solution of *Escherichia coli* (*E. coli*), and kept at 37°C for 24 h. The sheets were taken out and rinsed gently with sterile phosphate buffered saline (PBS) to remove the non-adherent bacteria. Then, the bacteria adhered on the sheets were eluted into 5 ml of sterile PBS in an ultrasonic cleaner for 5 min. The number of the eluted bacteria was then determined

by colony counts (CFU). The adherent number was expressed by the ratio of the total adherent bacterial to the area of the measured sample.

2.5.3. Antibacterial Property

ZnO/PVC sheets (2.5×2.5 cm) were placed on sterile plates, and then 0.5 ml broth inoculated with 10^4 cfu/ml of *E. coli* was added onto the surfaces. The samples were irradiated with an 8 W UV lamp (with wavelength at 365 nm) for 150 min. After irradiated, the sheets were rinsed with sterile phosphate buffered saline (PBS) and the number of viable bacteria was determined by colony counts (CFU). The blank PVC sample was also test for comparison. The antibacterial property of PVC, ZnO/PVC and THF-ZnO/PVC was valued by the kill percentage, a ratio of the dead number of the bacterial to the initial number of the bacterial.

3. Results and Discussion

3.1. Structure and Morphology

The ZnO nanoparticles were prepared by simple sol-gel method. The size analysis of ZnO sol indicated that most of ZnO colloid particles are located in the range of 50 - 70 nm (**Figure 1**). ZnO colloid particles were dried into powder at 120°C for X-ray diffraction (XRD) analysis. Several obvious peaks are observed at 2θ values at 31.6, 34.3, 36.1, 47.3, 56.4, 62.5 and 67.7, which correspond to wurtzite structure of hexagonal ZnO [23] (**Figure 2**). No other phases are observed in the patterns, indicating that the sample that prepared by this method are pure wurtzite ZnO.

Figure 3 shows the SEM images of neat PVC, ZnO/PVC and THF-ZnO/PVC. The neat PVC surface is smooth with little flaws. After coated only with ZnO colloid, the morphology of ZnO/PVC become rougher and a small ZnO nanostructure sheet spread on the ZnO/PVC surface. However, when PVC were pretreated by THF-PVC solution and subsequently coated with ZnO

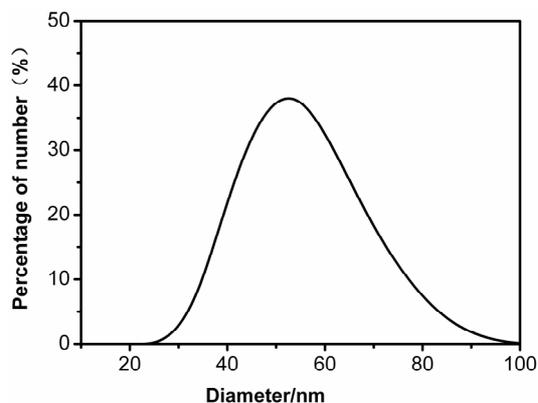


Figure 1. Size distribution of ZnO colloid particles.

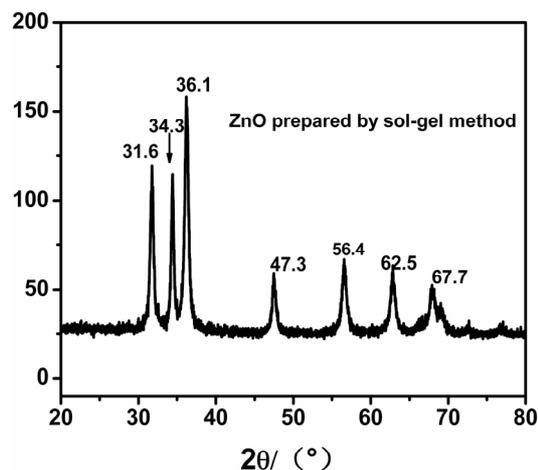


Figure 2. XRD spectra of ZnO.

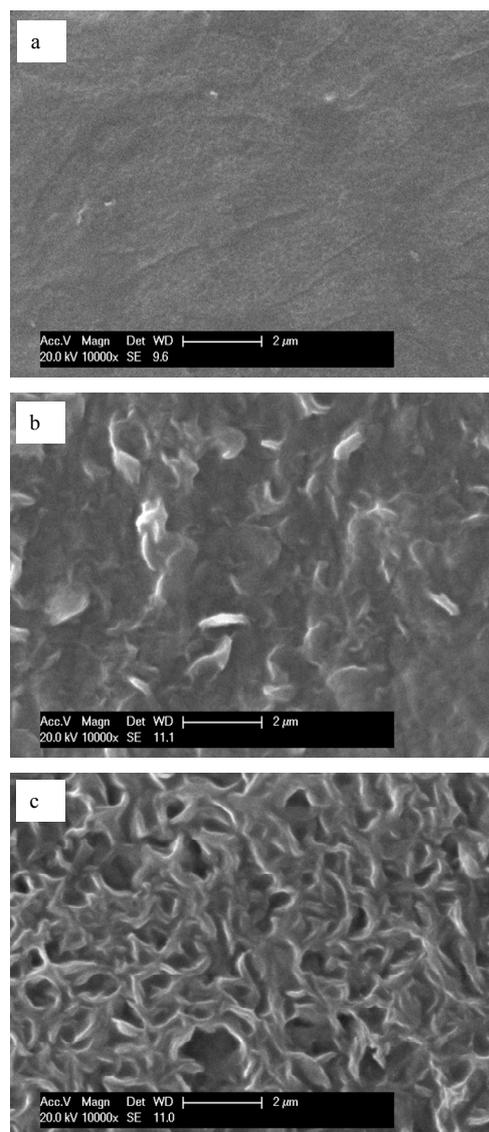


Figure 3. SEM images of different PVC surface; a) neat PVC; b) ZnO/PVC; THF-ZnO/PVC.

colloid, many ZnO nanostructure sheets stacked on THF-ZnO/PVC surface closely and the surface of THF-ZnO/PVC was composed by irregularity cross-linked ZnO sheets. This result indicated that pretreated PVC by THF-PVC solution improves the adherent amount of ZnO on PVC surface. The Optical absorption property of PVC, ZnO/PVC and THF-ZnO/PVC were examined with UV-Vis reflectance spectra (DRS), as shown in **Figure 4**. The DRS spectra show that ZnO/PVC and THF-ZnO/PVC exhibit significant enhancement of light absorption in the UV region than nude PVC, which is attributed to band-gap excitation of ZnO. Another difference in the DRS spectra is that the absorption baseline of the resulting samples in visible light region is decrease in the order of PVC > ZnO/PVC > THF-ZnO/PVC. This is originated from the transparent nature of the samples. ZnO deposited on PVC reduces transparency of PVC, which causes more of incident light reflect and consequently enhances the baseline absorption in visible light region. The more amount of ZnO coated on PVC, the lower baseline absorption of the sample.

3.2. Photocatalytic Activity

Figure 5 shows the change in photocatalytic conversions

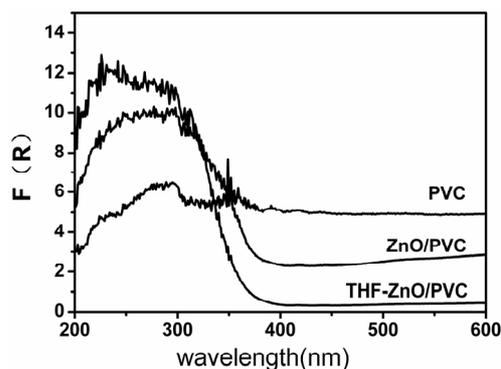


Figure 4. UV-vis diffuse reflectance spectra of PVC, ZnO/PVC and THF-ZnO/PVC.

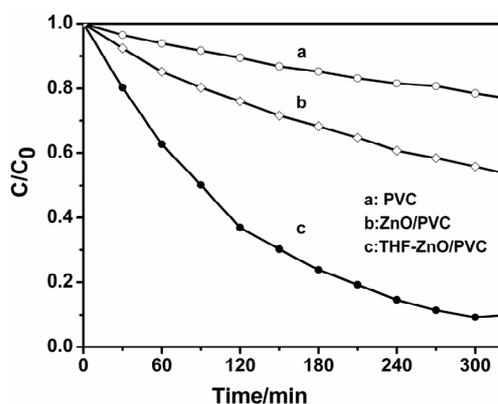


Figure 5. Photocatalytic degradation conversion of RhB on PVC, ZnO/PVC and THF-ZnO/PVC.

of RhB with reaction time on the nude PVC, ZnO/PVC and THF-ZnO/PVC. As can be seen from these spectra, the nude PVC sheet exhibits no photocatalytic activity. Only about 25% of RhB are photodecomposed following about 300 min of illumination. The photocatalytic activity of ZnO/PVC samples exhibit a little better than that of neat PVC, with the conversion rate of RhB increases to about 50% of RhB upon about 300 min of illumination. The pretreatment of THF-PVC solution for PVC has much great effect on the photocatalytic activity of the resulting sample. As can be seen from spectra c in **Figure 5**, the degraded rate of RhB on THF-ZnO/PVC is greatly increased and about 90% of RhB are degraded upon about 300 min of illumination. The result shows that pretreatment of THF-PVC for PVC is beneficial for the coating of ZnO on PVC surface.

3.3. Bacterial Adhesion and Sterilization Behavior

Figure 6 shows the adherent number of *E. coli* to the surface of nude PVC, ZnO/PVC and THF-ZnO/PVC under dark condition. After culture bacteria on the sample surface in dark for 18h, the number of *E. coli* adhered on nude PVC is similar to initial number of *E. coli* (**Figure 6(d)**), showing that the nude PVC material is inertial to prevent adhesion of bacterial. The adherent number of *E. coli* on ZnO/PVC decreases a little when compared with that of nude PVC as shown in **Figures 6(a)** and **(b)**, suggesting that coating ZnO on PVC helps to enhance antibacterial activity of PVC. Especially, when the PVC was pretreated with mix solution of THF-PVC and subsequently coated with ZnO, the antibacterial activity of THF-ZnO/PVC increases greatly with the adherent number of *E. coli* is almost zero (**Figure 6(c)**). The result suggests that THF-ZnO/PVC can effective prevent the adhesion and growth of bacterial on PVC surface.

Figure 7 shows the kill percentage of *E. coli* on PVC, ZnO/PVC and THF-ZnO/PVC under UV irradiation for 150 min. PVC exhibits no antibacterial activity under UV light. And ZnO/PVC shows a little antibacterial activity with the survival ratio of *E. coli* on ZnO/PVC is 46.8% after irradiation for 150 min. However, the THF-ZnO/PVC exhibits stronger antibacterial property. More than 99% of the bacteria were killed under UV irradiation for 150 min.

It has been reported that it is the photocatalytic property of metal oxide that is responsible for the excellent sterilization properties [15,24]. In other words, the higher the photocatalytic property, the higher the sterilization activity, and vice versa. This proposition was identified by the photocatalytic property and sterilization activity of TiO₂ [15]. In the present work, the photocatalytic property and sterilization activity of THF-ZnO/PVC are much better than that of ZnO/PVC. The main reason is may be

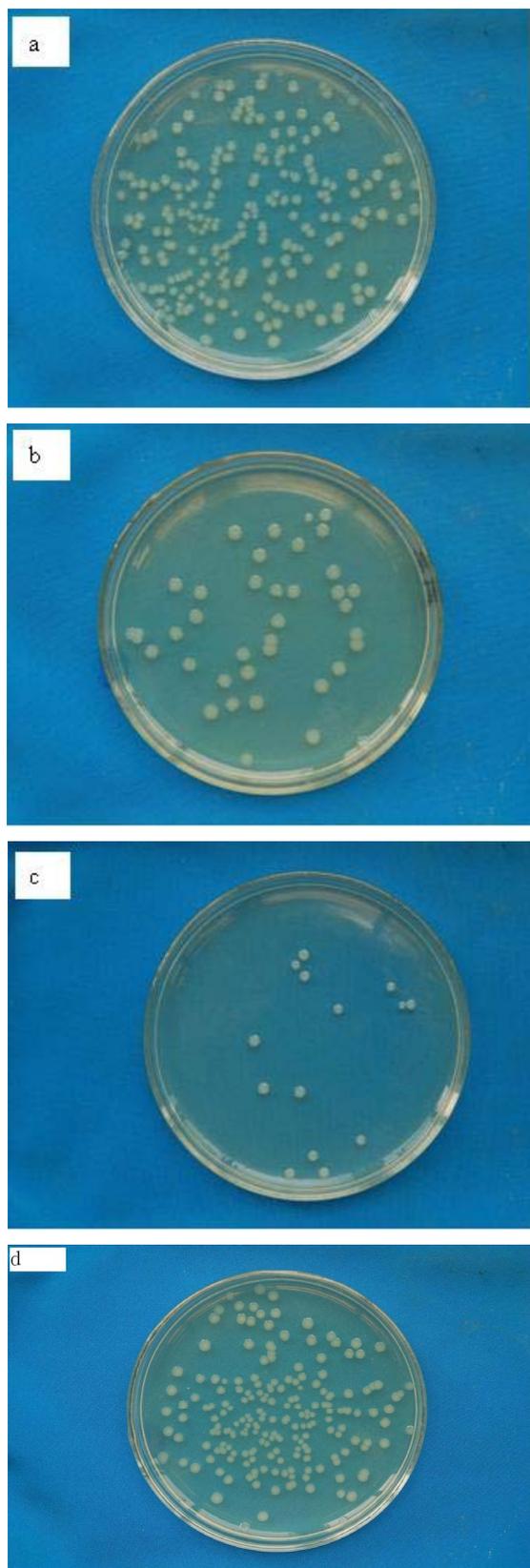


Figure 6. Bacteria adherent number on different PVC surface under dark condition. a) neat PVC; b) ZnO/PVC; THF-ZnO/PVC; d) initial number.

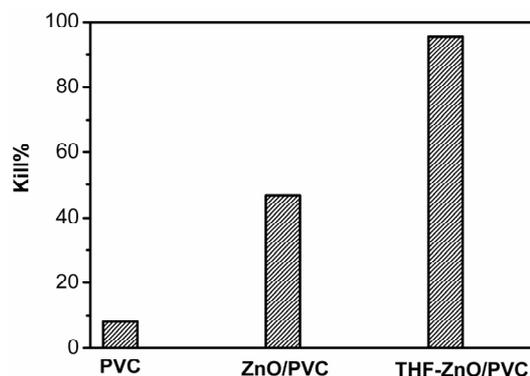


Figure 7. Kill percentage of bacteria on the samples under UV irradiation for 150 min.

that the amount of ZnO on THF-ZnO/PVC is larger than that on ZnO/PVC. Under UV irradiation, the amount of electron and hole produced on THF-ZnO/PVC were higher than that on ZnO/PVC that resulted in higher concentration of radicals ($O_2\cdot$ and $HO\cdot$) on THF-ZnO/PVC.

4. Conclusion

This work infers that the antibacterial properties of medical-grade PVC material can be enhanced by coating with ZnO. After pretreatment by THF-PVC solution and subsequently coated with ZnO, the PVC surface can not only inhibit the growth of bacteria on dark conditions effectively but also kill bacteria under UV irradiation. The result provides a convenient method that can enhance the adhesive strength and the amount of inorganic oxide film coated on organic materials. It is also easy to operate and can be applied in various substrates.

5. Acknowledgements

This work was financially supported by the NSFC (Grants Nos. 21003021, 21173044 and 21203029), the great Science and Technology Project of Fujian Province of P. R. China (2012Y4003), the National Science Foundation for Fostering Talents in Basic Research of China (No. J1103303), and National Basic Research Program of China (973 Program, No. 2012CB722607) and the Science and Technology project of Fuzhou University (2011-XQ-09).

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