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# I-$TiO_2$/PVC film with highly photocatalytic antibacterial activity under visible light

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ABSTRACT

Iodine-modified $TiO_2$(I-$TiO_2$) film were coated on medical-grade PVC material by impregnation-deposition method and subsequently characterized by XRD, SEM, TEM, AFM, DRS and XPS. The photocatalytic anti-bacterial activity of I-$TiO_2$/PVC was investigated both by in vitro anti-bacterial experiments and by clinical study. The results revealed that I-$TiO_2$/PVC exhibit excellent photocatalytic antibacterial activity, which can destroy the propagation of the *Escherichia coli* and cause the deactivation and death of most *E. coli* bacteria within 30 min visible light illumination. Clinical study on animals showed that I-$TiO_2$ coated on PVC decrease the formation of biofilm on PVC surface in the mechanical ventilation. Furthermore, I-$TiO_2$/PVC can effectively reduce inflammation of tracheal tissue of bam suckling pig and prevents the occurrence of VAP.



## 1. Introduction

The wide use of polymer materials such as polyethylene, polyurethanes, and poly (vinyl chloride) (PVC) in the hospital care have led to a concomitant increase in the incidence of biomaterial-related infections (BRI) [1–3]. Adhesion of bacteria to biomaterials' surface lead to the formation of "biofilms", a complex, adhering bacteria community that may cause pathogenic infection by protecting the bacteria from the host defense mechanisms and external agents as the drug treatments [4]. Biofilm formed in PVC endotracheal tubes has been reported to cause ventilator-associated pneumonia (VAP) of ventilated patients [5], which on one hand makes the cure of the bacterial infection quite difficult and on the other hand increase both the dose of the current antibiotic medicine and the cost for the exploitation of new and more effective antibiotics [6]. Undoubtedly, if the formation of biofilm can be effectively reduced, it can be envisioned that the biomaterial-related infections (BRI) resulted by adhering of bacteria community would has great chance to be avoided. A number of technologies have been explored for the protection of the biomaterials against biofilm formation. Some technologies such as modifying the physicochemical properties of biomaterial surface, like coating with silver and impregnating antibiotic into the polymer matrix, have been examined in recent years [5,7–10].

Recently, coating semiconductor photocatalysts on the surface of PVC endotracheal tubes to endow the tubes with improved antibacterial activity have attracted great interest due to the following advantages when compared with other methods: (i) Excellent photocatalytic and antimicrobial activity. (ii) Nontoxicity and biocompatibility, (iii) strong physicochemical stability and durable antibacterial property [11,12]. Among various oxides semiconductor photocatalyst (such as $TiO_2$, ZnO, $WO_3$, $SnO_2$), $TiO_2$ are generally considered to be the most suitable for antibacterial agents [11,13]. However, $TiO_2$ and some $TiO_2$-based photocatalysts can only be excited by UV light [11], which greatly limits their biomedical application under visible-light or normal room light illumination. Investigation for highly efficient antibacterial and visible-light responsive material is indisputably to be with great importance for the achievement of good antibacterial PVC endotracheal tubes. Iodine-modified $TiO_2$ have been reported with enhanced visible-light photocatalytic activities for the degradation of organic pollutant [14–18]. In our previous work, we also tested the antibacterial activity of powder photocatalyst of Iodine-modified $TiO_2$, which exhibits excellent disinfection effect on *Escherichia coli* [19].

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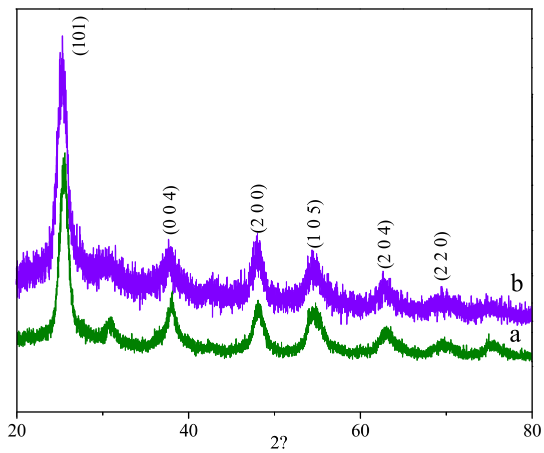


**Fig. 1.** XRD patterns of (a) $TiO_2$/PVC, (b) I-$TiO_2$/PVC.

In this letter, Iodine-modified $TiO_2$(I-$TiO_2$) film was coated on the surface of PVC endotracheal tubes in the form of film by facile dip-coating technique, in which method the PVC tubes were immersed in the I-$TiO_2$ sol for fixed time. The antibacterial activity of I-$TiO_2$/PVC film under visible light illumination was investigated. In addition, the ant-ibiofilm effect of I-$TiO_2$/PVC film was also tested on clinical animals experiments. To evaluate the antibacterial activity of I-$TiO_2$/PVC, the performance of I-$TiO_2$/PVC was compared with neat PVC and $TiO_2$/PVC under similar operating conditions. The results revealed that I-$TiO_2$/PVC exhibit excellent visible light photocatalytic antibacterial activity. It is believed that our work may provide a feasible and effective method to modify the surface of PVC endotracheal tubes and other similar biomaterials, extending the application of photocatalysts in the biomedical materials.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Materials and reagents

Medical-grade PVC endotracheal tubes were purchased from Tyco Healthcare International Trading (Shanghai) Co., Ltd., The bacterial cells were cultured in nutrient broth (BioLife, Milano, Italy) solution at 37 °C for 18 h and immediately diluted. The concentration of cell density is $10^7$ cfu (colony forming unit)/ml. $TiO_2$ sol (Research Institute of Photocatalysis, State Key Laboratory Breeding Base, Fuzhou University, Fuzhou, China) was used as the Ti source. Hydroiodic acid (HI, ≥45%, Sinopharm Chemical Reagent Co., Ltd., Shanghai) was used as the iodine source. Deionized water was used throughout the study. All glass apparatuses used were washed with deionized water, and then autoclaved at 121 °C for 15 min. Other reagents were of analytical grade and used as received.

#### 2.1.2. Synthesis of iodine-modified $TiO_2$ sol (I-$TiO_2$)

200 ml $TiO_2$ sol and 5 ml HI were mixed and stirred at room temperature for 4 h. Then the mix sol was transferred to a Teflon-lined autoclave and reacted at 160 °C for 12 h, after that time a yellow solution was formed, which denote as I-$TiO_2$.

#### 2.1.3. Coating I-$TiO_2$ on PVC (I-$TiO_2$/PVC)

The PVC material were fastened and pressed flat into 3 × 5 cm pieces, and cleaned it in ultrasonic acetone bath and deionized water to remove impurities. 10 g of polyvinyl alcohol (PVA) was first dissolved into 200 ml boiling deionized water, and then cool to room temperature. The PVC pieces were completely submerged into the PVA solution and pull out immediately. I-$TiO_2$/PVC was achieved by dipping the above PVC pieces into I-$TiO_2$ sol and then keeping for different time (5 days, 7 days, 9 days and so on). $TiO_2$/PVC was achieved by a similar procedure only without adding HI. For ease of presentation, the corresponding samples

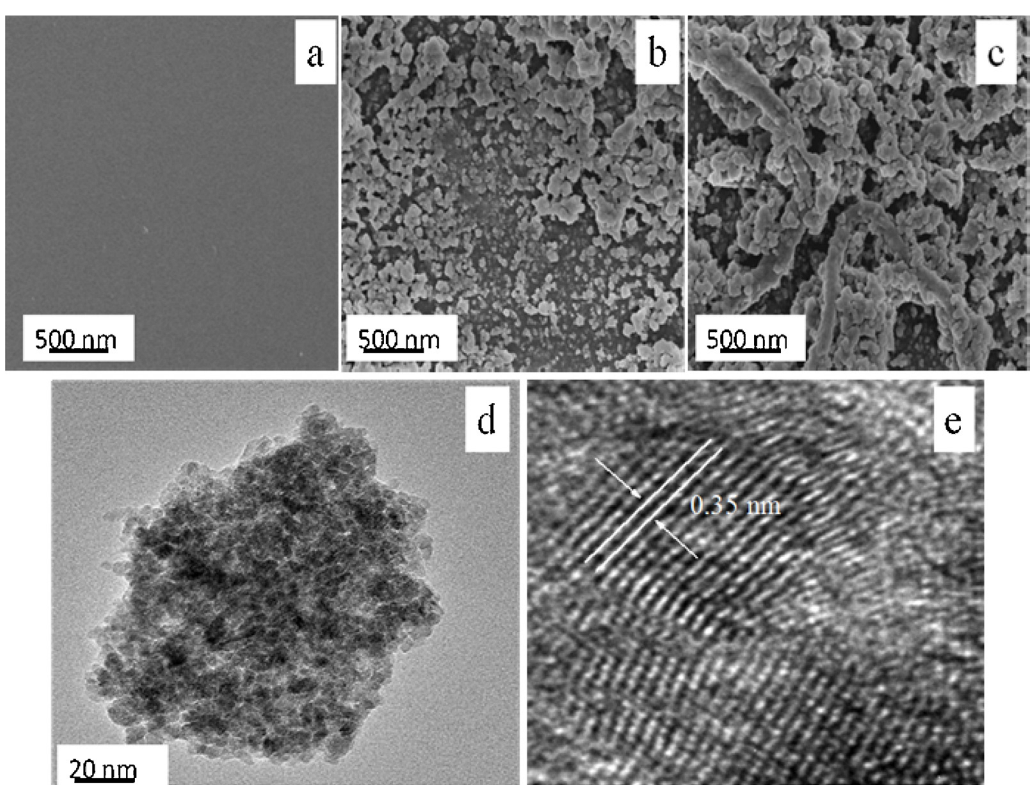


**Fig. 2.** SEM images of (a) PVC, (b) $TiO_2$/PVC, (c) I-$TiO_2$/PVC, (d) TEM image of I-$TiO_2$/PVC, (e) HRTEM image of I-$TiO_2$/PVC.