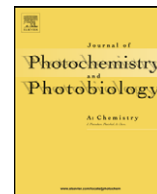




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# Journal of Photochemistry and Photobiology A: Chemistry

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## Antimicrobial activities of hydrophilic polyurethane/titanium dioxide complex film under visible light irradiation

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### ARTICLE INFO

#### Article history:

Received 7 August 2007  
 Received in revised form 20 April 2008  
 Accepted 1 May 2008  
 Available online 15 May 2008

#### Keywords:

Hydrophilic  
 Polyurethane  
 Nano-TiO<sub>2</sub>  
 Antimicrobial  
 Visible light

### ABSTRACT

Using the polyurethane (PU) resin modified by anion surfactant, the hydrophilic polyurethane/titanium dioxide (TiO<sub>2</sub>) complex film (HPTF) was prepared. The characteristics of the HPTF were described by Fourier-transform infrared spectrometry (FT-IR), ultraviolet–visible spectroscopy (UV–vis) and standard measurements of mechanical properties. Simultaneously, the antimicrobial activities of the HPTF were also studied. The results indicated that, after 8 h, nearly all of the *Escherichia coli* (*E. coli*) and *Candida albicans* (*C. albicans*) could be killed under visible light irradiation; the antimicrobial activity was evidently better than pristine polyurethane film. The antimicrobial ratio of the latter was less than 40% under the same conditions. The optimal TiO<sub>2</sub> amount in the HPTF preparation was 0.25 g (TiO<sub>2</sub>)/100 mL (emulsion). The antimicrobial activity of the HPTF under visible light was in accordance with the UV–vis absorption spectra, in which strong absorption extended over the visible light spectra region. The combination of the dodecyl sulfonate group and titanium dioxide with polyurethane was found via FT-IR.

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### 1. Introduction

The study on the photocatalytic properties of TiO<sub>2</sub> has received more attention since Fujishima and Honda [1] reported its characteristics in 1972. In 1985, Matsunaga et al. [2,3] reported that *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *Escherichia coli* could be killed by a TiO<sub>2</sub>–Pt catalyst under near-UV illumination. Since then, many studies on the antimicrobial characteristics of TiO<sub>2</sub> have been reported [4–11]. The majority of researches focused on the antimicrobial activities of TiO<sub>2</sub> film under ultraviolet radiation, however there are several different views about the antimicrobial activity of TiO<sub>2</sub> film under visible light. Scientists from Japan [12] reported that the antimicrobial activity of TiO<sub>2</sub> film was better under visible light within 12 h. Dye-sensitized semiconductor TiO<sub>2</sub> films prepared by Yu et al. [13] showed low antimicrobial activities of pure TiO<sub>2</sub> film under visible light in *E. coli* survival tests. In view of the limitation of photocatalytic properties under ultraviolet radiation, visible light-assisted antimicrobial activity of TiO<sub>2</sub> film would be more significant in daily life.

Organic–inorganic composites have also attracted much interest in recent years as they usually not only occupy the properties of organic polymers (e.g., flexibility, ductility and dielectric), but also show particular properties of inorganic materials such as photocatalysis [14]. Therefore these could be widely used in many fields. According to these advantages, several compound materials have been prepared by nano-TiO<sub>2</sub> and organic polymers recently. Chitosan–TiO<sub>2</sub> and Chitosan–SiO<sub>2</sub> complex films were reported due to their good surface properties and antimicrobial activities [15,16], but their mechanical intensities were low. Similarly, polyimide–TiO<sub>2</sub> film, polyethylene–TiO<sub>2</sub> film and other compound films have been reported [17,18], however the antimicrobial characteristics of these have not been reported. In this study, polyurethane (PU) was used due to its excellent mechanical properties and the presence of antimicrobial activity. Additionally, it is a well-known polymer used for various medical and coating applications.

Based on the above-mentioned properties, a hydrophilic polyurethane/titanium dioxide (TiO<sub>2</sub>) complex film (HPTF) was prepared in this study. The characteristics of HPTF was described by Fourier-transform infrared spectrometry (FTIR) and UV–vis spectrophotometry. Mechanical properties including acid–base resistance and antiwear performance were also measured. The antimicrobial activities of the samples were evaluated by the inactivation ability of three strains, *E. coli*, *Candida albicans* (*C. albicans*) and *Aspergillus niger* (*A. niger*). The results showed that the antimicrobial activity was related to the amount of TiO<sub>2</sub>, illumination

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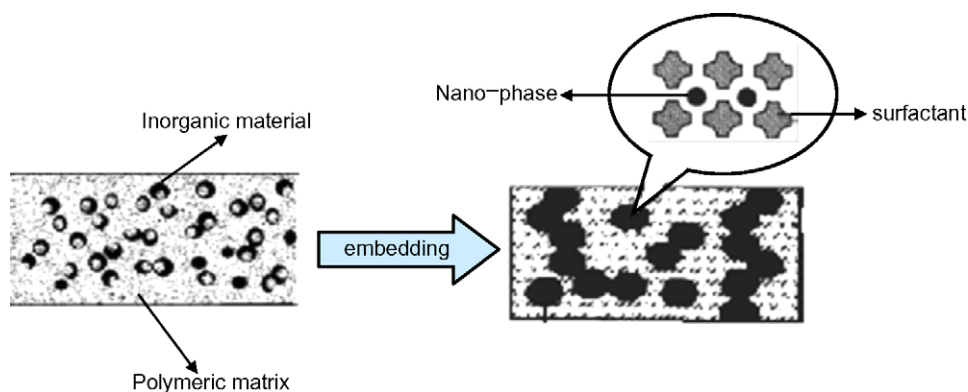


Fig. 1. The sketch map of the preparation process of HPTF.

time, the hydrophilicity of the film surface and the microorganism in question. Interestingly, the storing time of the film under visible light improved the antimicrobial activity of the complex films. A possible mechanism is proposed.

## 2. Experimental

### 2.1. Materials

Aqueous PU was supplied by Jinhuli (China), titanium dioxide (P25, 80% anatase, 20% rutile, 50 m<sup>2</sup>/g, primary particle size ~25–30 nm) was obtained from Degussa (Germany), and sodium dodecyl sulfonate (SDS) from Sigma (USA). Deionized water was used in all experiments.

### 2.2. Preparation of hydrophilic PU–TiO<sub>2</sub> complex film (HPTF)

Fifty milliliters of aqueous polyurethane emulsion was first diluted with deionized water to 100 mL. SDS was dissolved in this emulsion with stirring for 10 min at room temperature, after which 0.25 g TiO<sub>2</sub> was added under stirring for 2 h. TiO<sub>2</sub> powder was homogeneously dispersed by ultrasonic vibration for 15–20 min. The compound slide glass (1 in. × 3 in.) was used as the substrate for coating the hydrophilic PU–TiO<sub>2</sub> complex film using the streaming-coating method, after which the coated glass was dried at room temperature. As shown in Fig. 1, TiO<sub>2</sub> particles were embedded in the surfactant particles which were first used to modify polyurethane. The aggregation among TiO<sub>2</sub> particles was decreased, which favoured the dispersion of TiO<sub>2</sub> powder. Simultaneously, after being modified by the surfactant, the hydrophilicity of the film was improved, which could accelerate the photocatalysis and self-cleaning of the complex film.

**Table 1**  
Mechanical properties and adhesive force of HPTF

Test items	Results	Evaluation
State in container	Equality and no agglomeration	Eligible
Surface drying time	3 h at room temperature	Eligible
Dryness crack resistance	No cracking (room temperature)	Eligible
Acid–base resistance	No froth dipped in 1 M HCl or 1 M NaOH for 48 h	Eligible
Organic solvent resistance	No froth dipped in toluene and ligarine for 48 h	Eligible
Cold/heat resistance	No desquamation and froth under 100 °C/–20 °C for 15 cycles	Eligible
Adhesive force	2 grade	Eligible
Washability	No attenuation, cracking and desquamation	Eligible
Antiwear Performance	100 cycles	Eligible

Mechanical properties were according to the standard GB/T9756-2001 of China. The adhesive force was according to the standard ISO2409-1972 (E).

### 2.3. Culture of strain and experimental procedures

*E. coli*, *C. albicans* and *A. niger* were cultivated in respective medium. Then cells were collected by centrifugation and diluted using 0.9% saline until the cell count reached 2.0 × 10<sup>6</sup> cells/mL. 200 μL strain suspension was dropped onto the films to measure the antimicrobial effect. After irradiation for 2, 4, 6, 8 and 24 h, the strain suspension was washed from the surface of the sample using saline and then diluted to obtain 10 mL diluted solution. The diluted solution was shaken for 5 min (250 r/min), and then 300 μL of the solution was plated on agar plates. The plates were incubated at 37 °C (*E. coli*, *C. albicans*) and 28 °C (*A. niger*) for 48 h, after which the number of colonies on the plates were counted. All materials were autoclaved at 121 °C for 20 min to ensure sterility. The antimicrobial ratio was calculated as follows:

$$\text{Antimicrobial ratio (\%)} = \frac{N_0 - N}{N_0} \times 100 \quad (1)$$

where  $N_0$  is the number of colonies of the initial strain suspension and  $N$  is the number of colonies of the strain suspension at irradiation time  $t$  (h), respectively.

### 2.4. Irradiation

UV irradiation was applied by a UV lamp (20 W, 0.5-m long) placed 10 cm from the film, giving approximately 325 μW/cm<sup>2</sup> on the film surface, with maximum irradiation at 297 nm. Visible light was either natural indoor light during the day, or common household lights (100 W) overnight.

### 2.5. Characterization

Mechanical properties of the films were investigated according to the Chinese standard GB/T9756-2001. Adhesive force was tested according to the standard ISO2409-1972 (E).

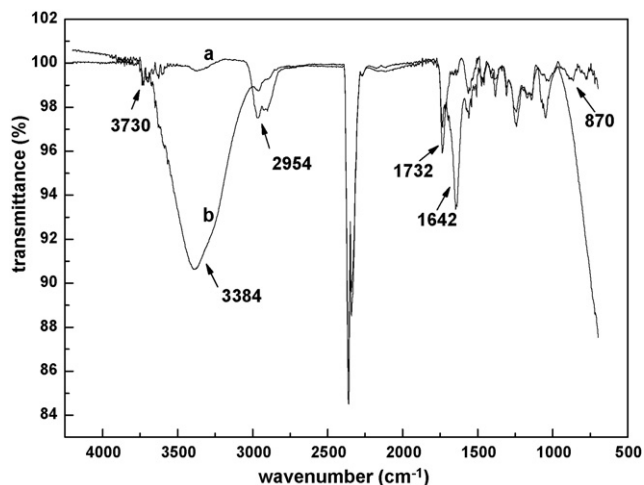


Fig. 2. FT-IR spectra of the films in the range 500–4000  $\text{cm}^{-1}$ : (a) HPTF and (b) PU film.

IR spectra of the PU film, the modified PU film and the HPTF were recorded with a VARIAN-3100 FTIR spectrometer in the range of 4000–500  $\text{cm}^{-1}$ .

A UV–vis spectrophotometer (Hitachi U-3010) was used to measure the absorbance and transmittance spectra of the films in the wavelength range of 200–800 nm.

### 3. Results and discussion

#### 3.1. Characterization of HPTF

The mechanical properties of HPTF are listed in Table 1.

As could be seen from Table 1, the HPTF with hydrophilic modification showed better mechanical properties than some other complex films under a hydrophilic state [15,16], and the mechanical properties reached the level of  $\text{TiO}_2$  film that obtained with calcinations at high temperature.

Fig. 2 shows the infrared spectra of the HPTF and PU film on KBr discs in the zone 500–4000  $\text{cm}^{-1}$ . The bands at 1642 and 3384  $\text{cm}^{-1}$  are attributed to C=O and N–H stretching vibration, respectively, in polyurethane [19], which disappeared due to the combination with the O=S–O groups in SDS, and the hydroxyl groups on  $\text{TiO}_2$ . Compared with the PU film, the HPTF showed the appearance of these bands at 2954 and 870  $\text{cm}^{-1}$ , which can be attributed to C–H stretching vibration and the O–Ti–O group. The above results imply that sodium dodecyl sulfonate and  $\text{TiO}_2$  particles were combined to polyurethane through hydrogen bonding.

Fig. 3 shows the UV–vis absorption spectra of the  $\text{TiO}_2$  powder, PU film and the HPTF. For the  $\text{TiO}_2$  powder (curve a), the strongest absorption was at 272 nm. The strong absorption range was about 200–400 nm, which was in the UV spectra region. The absorption values were close to zero over the visible light spectra, which accorded with the obvious photocatalysis of  $\text{TiO}_2$  powder only in UV light. As can also be seen for the PU film (curve b), almost zero absorption occurred from 250 to 800 nm. For the hydrophilic PU– $\text{TiO}_2$  complex film (curve c), absorption values gradually decreased at longer wavelengths until 300–350 nm, at which point was a wide and strong absorption band.

The absorption spectrum of HPTF red shifted to visible light relative to the naked particles, and strong absorption was observed. Photocatalysis of HPTF under visible light in the experiments showed that the apparent optical bandgap ( $E_g$ ) of HPTF shifted to a lower value compared with that of bulk  $\text{TiO}_2$ . The  $E_g$  could be cal-

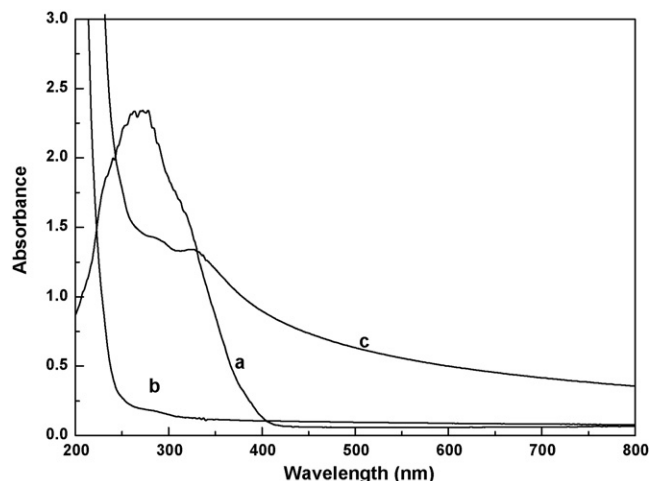
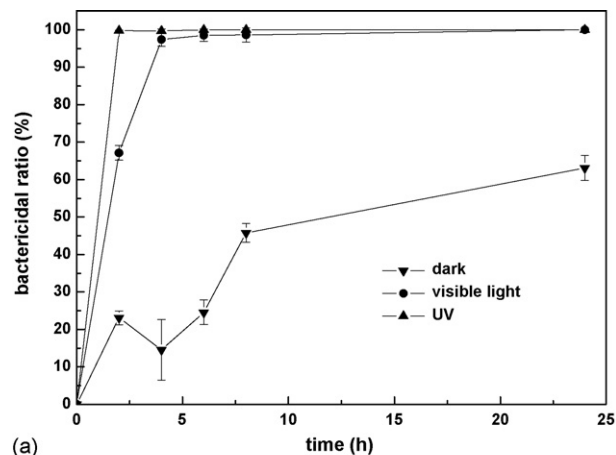


Fig. 3. UV–vis spectra of  $\text{TiO}_2$  powder (a), pristine PU film (b) and HPTF (c).

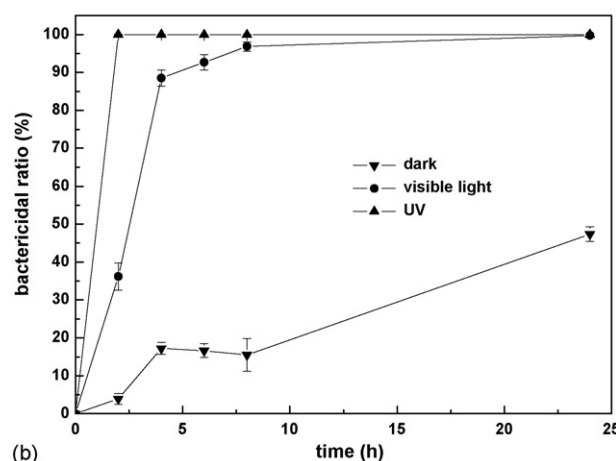
culated according to the absorption coefficient, and can be written as [25]:

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (2)$$

where  $\alpha$ ,  $h\nu$  and  $E_g$  are absorption coefficient, photon energy, and apparent optical bandgap, respectively.  $A$  is a constant characteristic of the amorphous semiconductor.



(a)



(b)

Fig. 4. Bactericidal effect of HPTF on (a) *E. coli* and (b) *C. albicans* under different light sources.

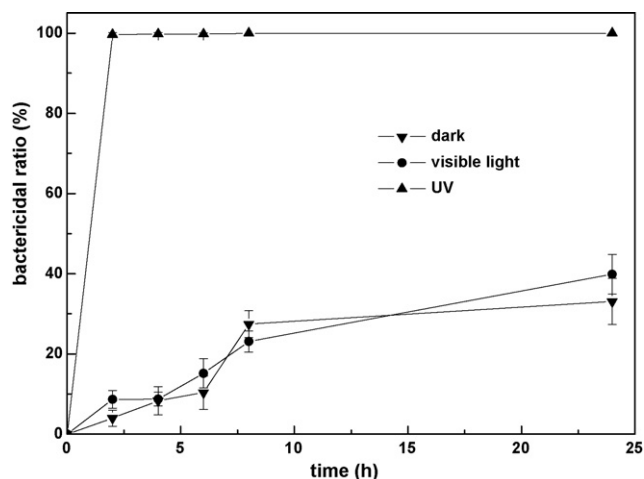


Fig. 5. Bactericidal effect of pristine PU film on *E. coli* under different light sources.

From formula (2), it can be seen that  $(\alpha h\omega)^{1/2}$  has a linear relation with  $h\omega$ . The slope of the straight line gives  $E_g$  of the material.

The red shift of apparent optical band-edge of the prepared sample can be explained by two factors. Firstly, the sizes of  $\text{TiO}_2$  particles were limited by the chains of polyurethane around them, which controls the size of the  $\text{TiO}_2$  particles. Secondly, the dielectric

confinement effect and dipole effect play a critical role. Takagkhara [26] illuminated the energy of the nanometer-system in different mediums as

$$E_g = \frac{(E_{g'} + \pi^2)/(\rho^2 - 3.572)}{(\rho - 0.248\varepsilon_1)/\varepsilon_2} + \Delta E \quad (3)$$

where  $\rho = R/aB$ ,  $R$  is the radii of  $\text{TiO}_2$ ,  $aB$  is the exciton Bohr radius of bulk  $\text{TiO}_2$ ,  $E_{g'}$  is the bandgap of bulk  $\text{TiO}_2$ ,  $\varepsilon_1$ ,  $\varepsilon_2$  are the dielectric constants of  $\text{TiO}_2$  and the medium (sodium dodecyl sulfonate). The second item in formula (3) results in blue shift, the third and fourth items result in a red shift. When  $\text{TiO}_2$  was chemically modified on surface with an anion surfactant, the evident dielectric confinement effect appeared because the value of  $\varepsilon_1/\varepsilon_2$  ( $\varepsilon_1$  was about 60,  $\varepsilon_2$  was about 2) was large. The stronger the dielectric confinement effect is, the stronger the red shift. At the same time, as the size of the sample is larger than the exciton Bohr radius of bulk  $\text{TiO}_2$ , the sample has a weak quantum confinement and the blue shift of absorption band-gap due to the quantum size effect is very small. Thirdly, the interactions between interfacial  $\text{TiO}_2$  particles and capped surfactants will lead to the formation of trapped states, which form a series of metastable energy levels within the band-gap, resulting in the red shift of the apparent optical band-gap. That is the strong absorption edge extends over the visible light spectra region which enables photocatalysis of HPTF under visible light.

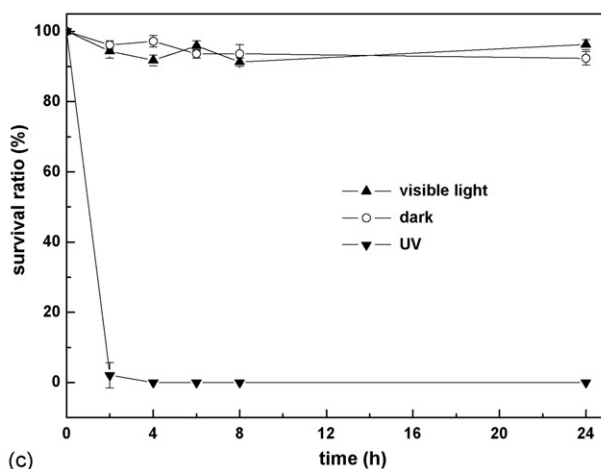
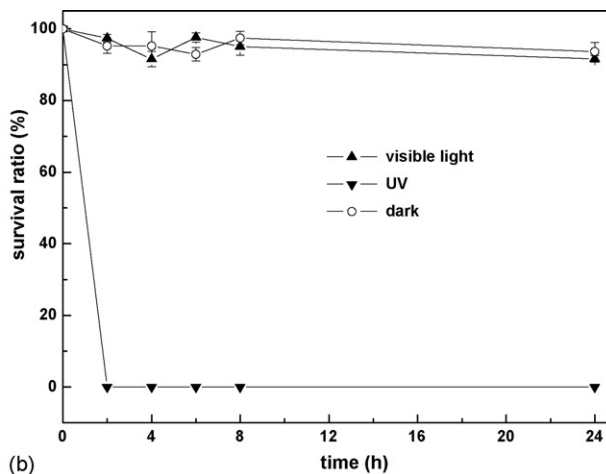
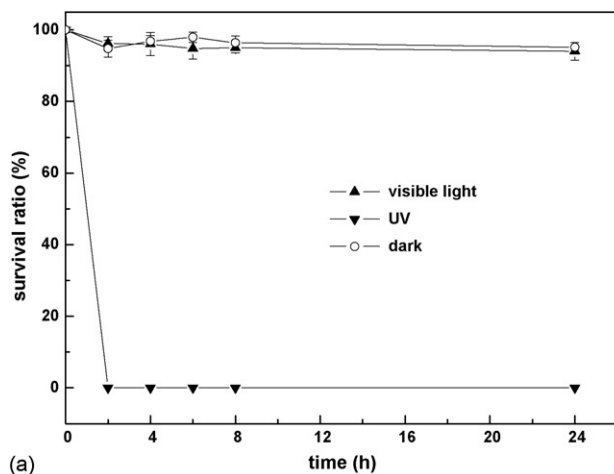


Fig. 6. The survival ratios of (a) *E. coli*, (b) *A. albicans* and (c) *A. niger* on the bare glass under different light sources.

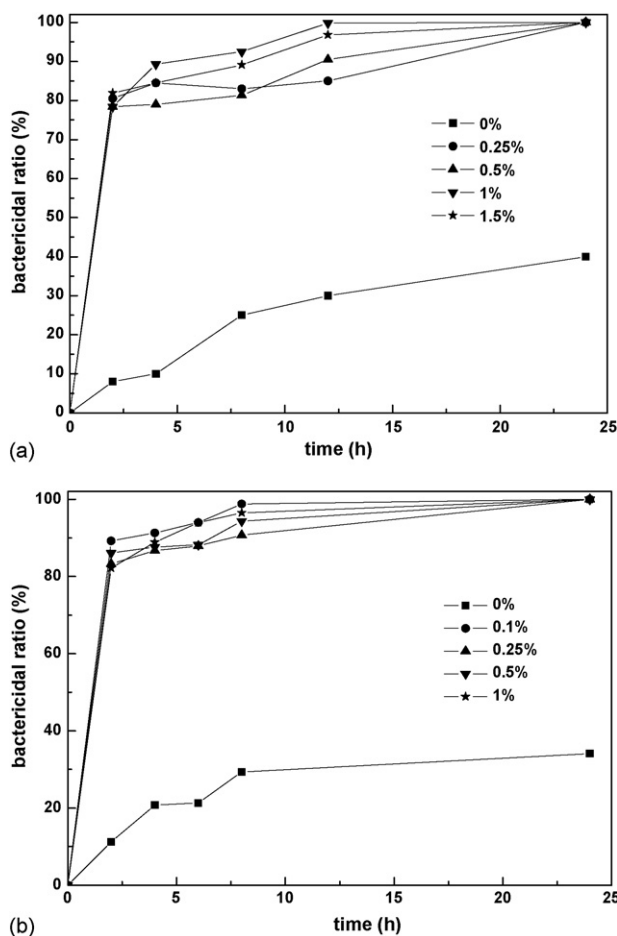


Fig. 7. The bactericidal activity of HPTF containing different amount of TiO<sub>2</sub>: (a) *E. coli*; (b) *C. albicans*.

### 3.2. Antimicrobial activity

The results of several antimicrobial tests are shown in Figs. 4–9. Each experiment contained triplicate samples, with error bars representing standard deviations.

#### 3.2.1. Visible light-assisted antimicrobial activity of HPTF

The antimicrobial activity of TiO<sub>2</sub> films under UV irradiation have been previously reported [13,20,21]. In this work, the antimicrobial activities under different light sources were determined for HPTF (Fig. 4). The antimicrobial ratio for *E. coli* and *C. albicans* of HPTF in the dark had also a rather better level, reaching about 60% within 24 h. The effect was remarkably higher under visible light, reaching over 95% sterilization of *E. coli*, and 90% of *C. albicans* within 4 h, with 100% sterilization being reached within 24 h. The effect was enhanced under UV light, as the antimicrobial ratio of HPTF achieved 100% within 2 h. It is well known that photons are absorbed by TiO<sub>2</sub> and then excited the generation of holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) [13]. The hydrophilicity on the surface of HPTF caused the retention of H<sub>2</sub>O. In the reactive process of h<sup>+</sup> and H<sub>2</sub>O, hydroxyl radicals were generated, which damaged the bacterial cells [13]. The absorption strength of photons in UV light was stronger than in visible light, therefore the antimicrobial ratio soon reached 100% on HPTF within 2 h exposure to UV light. In addition, the antimicrobial activity on *E. coli* of the pristine PU film without TiO<sub>2</sub> was also studied. The results indicated that the antimicrobial ratios were approximately 30% in both dark and visible light

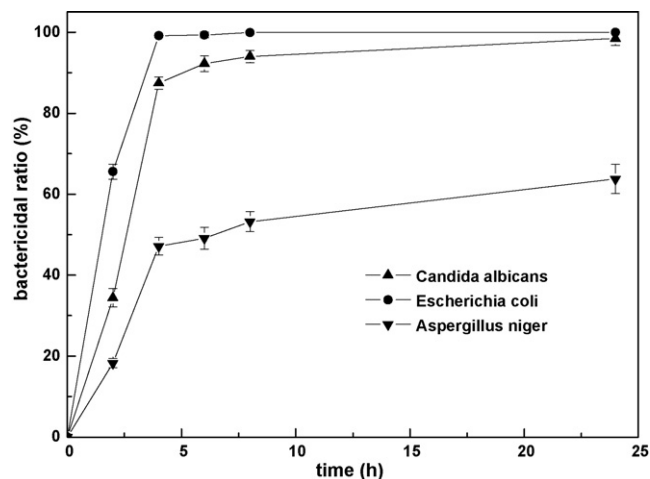


Fig. 8. Bactericidal effect of HPTF on *A. niger* compared with *E. coli* and *C. albicans* under visible light.

after 24 h, and was 100% in UV light after 2 h (Fig. 5). Furthermore, Fig. 6 shows the survival ratios of *E. coli*, *C. albicans* and *A. niger* on bare glass. After 24 h, the survival ratios of the three species were all above 92% in both dark and visible light, and were zero in UV light. Our results show only neglectable antimicrobial activity of the bare glass. Thus the antimicrobial effect of the pristine PU film (30% antimicrobial ratio within 24 h in the dark) can be attributed to the antibacterial activity of PU [27]. The antimicrobial ratio of HPTF in the dark increased to 60% in the presence of TiO<sub>2</sub>.

#### 3.2.2. The antimicrobial activity of HPTF containing different amounts of TiO2

The concentration of TiO<sub>2</sub> in the complex film directly affects the application, economical efficiency and photocatalytic effect of the subsequent film. The effect of the amount of TiO<sub>2</sub> in HPTF on antimicrobial activity under visible light irradiation is shown in Fig. 7. It can be seen that the antimicrobial activity was low in the absence of TiO<sub>2</sub>, however the antimicrobial ratios increased with increasing concentrations of TiO<sub>2</sub> up to 0.25%. The antimicrobial ratios reached almost 100% after 24 h in the presence of 0.25% TiO<sub>2</sub>. However with concentrations exceeding 0.25%, the antimicrobial ratios decreased. One possible explanation is that the increase in TiO<sub>2</sub> promoted the recombination of TiO<sub>2</sub> particles in the emulsion.

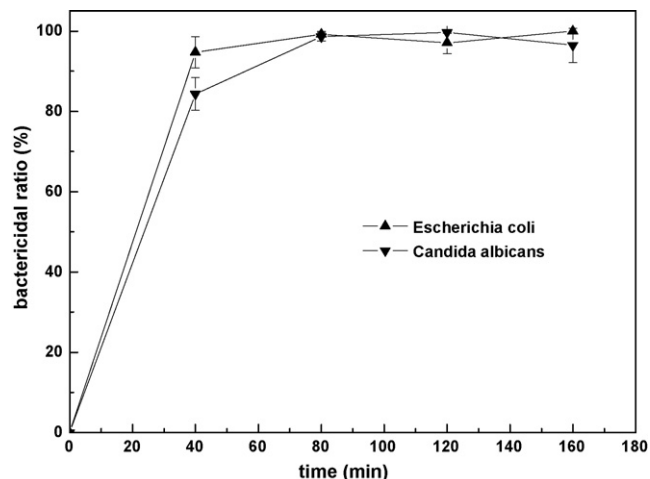


Fig. 9. Effect of storing time on bactericidal activity after 3 months (HPTF).

**Table 2**  
Effect of the storing time on bactericidal effect (bactericidal time was 2 h)

Bacteria	Storing time			
	Intraday (%)	2 weeks later (%)	1 month later (%)	2 months later (%)
<i>Escherichia coli</i>	67.5	92.4	99.6	99.9
<i>Candida albicans</i>	36.5	58.3	98.7	99.5

Generally, photons are the source of the generated oxidative free radicals which destroy the bacterial cell under light irradiation [22,23]. Therefore the partial recombination of TiO<sub>2</sub> decreased the surface area to accept photons, which affected the antimicrobial ratios. Therefore the 0.25 g (TiO<sub>2</sub>)/100 mL (emulsion) was selected as the optimum in this experiment.

### 3.2.3. Visible light-assisted antimicrobial effect of HPTF on *A. niger*

*A. niger* is ubiquitous in moist and unclean environments. *A. niger* is generally more resistant than *E. coli* and *C. albicans*. The antimicrobial effect of HPTF on *A. niger* is shown in Fig. 8. Compared with *E. coli* and *C. albicans*, the antimicrobial ratio on *A. niger* was approximately 65% after 24 h under visible light.

The results indicated that the antimicrobial ratio of HPTF on *A. niger* was lower than on *E. coli* and *C. albicans*. A likely explanation is the production of spores by *A. niger*. The spores have a very firm spore coat, containing multilayer proteins, which can strongly resist environmental stresses such as those imposed by chemicals, heat and pressure. On the other hand, as reproductive means, a spore is generated from *A. niger* cell which propagates many more cells again. The oxidative free radicals generated from HPTF were insufficient to kill all the spores. Further investigation is required to define the optimum conditions to achieve photo-inactivation of *A. niger* under visible irradiation.

### 3.2.4. Effect of the storing time of HPTF on antimicrobial ratio

The antimicrobial activities were also examined after the HPTF was placed for three months under visible light (Table 2, Fig. 9). As can be seen in Table 2, the antimicrobial rate increased compared to that of the HPTF used immediately after preparation. The antimicrobial time of the stored film decreased to 160 min with antimicrobial activity similar to that found after 24 h for the fresh film (Fig. 9). According to the generative mechanism of free rad-

icals (Fig. 10), a possible explanation was that the oxidative free radicals generated were more stable in hydrophilic circumstances. The super-hydrophilicity of surface prevented the reverse reaction of h<sup>+</sup> and e<sup>-</sup>. Ireland [24] proposed that 10<sup>-9</sup> mol/L OH<sup>•</sup> were generated and were stable when light struck the surface of TiO<sub>2</sub> film. Is this correct? The real mechanism of the improved antimicrobial activity is yet to be fully defined.

## 4. Conclusion

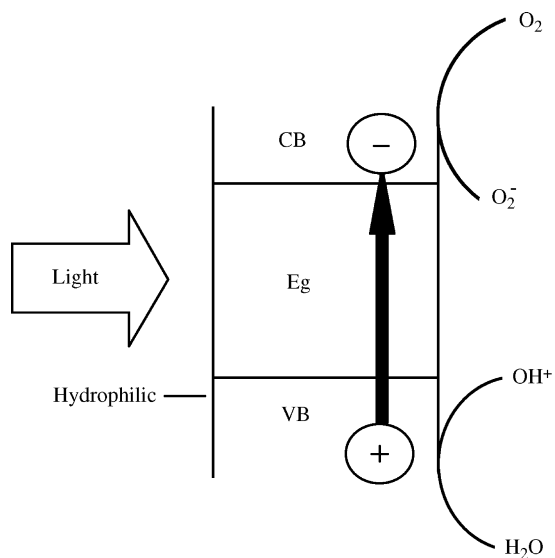
Using the polyurethane resin modified by anion surfactant, the HPTF was prepared, and the antimicrobial activities of HPTF were tested in this paper. The HPTF showed significant antimicrobial activities under visible light irradiation. *E. coli*, *C. albicans* and *A. niger* could be effectively killed by HPTF. When 0.25% TiO<sub>2</sub> and 0.5% SDS were incorporated into the film, over 95% sterilization of *E. coli* and 90% sterilization on *C. albicans* could be achieved within 4 h. The antimicrobial ratio reached 100% within 24 h under visible light irradiation. The antimicrobial effect of HPTF on *E. coli* and *C. albicans* were much better than that of *A. niger*. However, the antimicrobial ratio increased upon storage, as a result of the improved hydrophilicity of the film. The antimicrobial activity of HPTF under visible light was in accordance with the UV-vis absorption spectra, in which strong absorption extended over the visible light spectra region. Introducing nano-TiO<sub>2</sub> into polyurethane resins improved the mechanical properties of the system, and the antimicrobial activity of HPTF under visible light was also as good as TiO<sub>2</sub> films in UV irradiation.

## Acknowledgements

The authors want to express their thanks for the supports from Natural Science Foundation of China (20636010, 50373003), the (863) High Technology Project (2006AA020101) and the National Basic Research Program (973 Program) of China (2007CB714305).

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**Fig. 10.** The generative process of free radicals on hydrophilic surface.

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