



# Synthesis of antibacterial film CTS/PVP/TiO<sub>2</sub>/Ag for drinking water system

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## ABSTRACT

A CTS/PVP/TiO<sub>2</sub>/Ag functional film was prepared as an antibacterial composite used in storing drinking water. The orthogonal experiment showed that the optimal conditions for preparing membranes with best antibacterial activity and tensile strength are  $c(\text{AgNO}_3) = 0.08\%$ ,  $c(\text{TiO}_2) = 0.20\%$ ,  $c(\text{CTS}) = 2.25\%$ , and  $c(\text{PVP}) = 3.00\%$ . The FT-IR spectrum implies that hydrogen bonds are formed between acetyl in PVP and hydroxyl in CTS molecule, and  $-\text{NH}$  and  $-\text{OH}$  of CTS have some interactions with silver nano-particles (nano-Ags) which were reduced in situ. The SEM images show that the TiO<sub>2</sub> particles are displayed on the surface and embedded in the film. And nano-Ags are further proved through XRD and SEM images. The DSC curves show that the film has a favorable compatibility and heat stability. In application study, it is proved that this film has sustainable antibacterial activity and is safe in use.

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## 1. Introduction

Storing drinking water becomes increasingly common in some areas of China because of the shortage of fresh water and inadequate supply of drinking water. Secondary water supply has been used in many high buildings and large mansions by storage pools. Storage pools or tanks are largely used not only by rural residents to store drinking water for daily life, but also by urban residents who need the facility of secondary water supply (Luby, Syed, Atiullah, Faizan, & Fisher-Hoch, 2000; Momba & Kaleni, 2002). Unfortunately, most people do not pay attention to the sanitation of the drinking water storage, which results in the overabundance of harmful microbe in terminal drinking water system. Some bacteria can cause short-term effects like diarrhea, nausea, cramps, headaches, or other symptoms (Lukasik, Cheng, Lu, Tamplin, & Farrah, 1999). Given that the sanitation of drinking water is highly related to human health, extra attention must be paid to the disinfection of the drinking water storage.

To date, disinfection of drinking water is mainly carried out in the waterworks, and has not been used in drinking water storage. Chemical materials, such as chlorine dioxide, chlorine (as gas or hypochlorite), chloramines and ozone are commonly used in disinfection process of waterworks. These methods are not suitable for the disinfection of terminal drinking water in small pools or tanks

(Gunten, 2003; Nikolaou, Lekkas, Golfopoulos, & Kostopoulou, 2002). Although UV irradiation can effectively solve the disinfection problem of terminal drinking water, it is costly for the drinking water storage. Thus, developing a material which can provides effective and long-lasting antimicrobial effects, and safe to human health, is extremely urgent and beneficial, especially for those who rely heavily on small pools or tanks to store their daily drinking water.

Antibacterial materials are mainly divided into inorganic, organic, and natural materials (Dastjerdi & Montazer, 2010; Liu, Li, & Bai, 2010; Mahendra, Alka, & Aniket, 2009). Even though the organic materials sterilize water effectively, their use in drinking water is limited due to the poor heat-resistance and doubtful safety. And the natural materials have limited usage because of their narrow application scope (Liu et al., 2010). Compared with the above two materials, inorganic disinfectant (Dastjerdi & Montazer, 2010; Mahendra et al., 2009), especially heavy metal ion, has good chemical and thermal stability and does not result in drug-resistance of bacteria. However, these materials have not been developed for sterilization in terminal drinking water owing to the toxicity of heavy metal ions. To the best of our knowledge, there have been few studies about disinfectant in the drinking water storage so far. The materials used in terminal drinking water should have good antibacterial ability, and are non-toxic, economical, and easy to separate and recycle. Therefore, the inorganic antibacterial materials which can release some metal ions to eliminate bacteria cannot be considered as a good disinfectant used in drinking water.

Based on the above considerations, we choose nano-Ags, TiO<sub>2</sub>, and CTS in our research. Nano-Ags (Liu, Wang, Yang, & Yang, 2008; Mahendra et al., 2009; Nui et al., 2009; Pallab, Murugadoss, Durga,

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Ghosh, & Arun, 2008; Ren, Wang, Sun, Zhang, & Chang, 2009; Wei, Sun, Qian, Ye, & Ma, 2009; Zhang et al., 2003) with special antibacterial properties have been verified, and are a non-toxic and non-tolerant disinfectant. In addition, using nano-Ags leads to increasing the number of particles per unit area and, thus, antibacterial effects can be maximized (Dastjerdi, Montazer, & Shahsavan, 2009).  $\text{TiO}_2$  as a photocatalysis has recently not only emerged as an alternative chemical for bacteria inactivation (Guin, Manorama and Latha, 2007; Ibanez, Litter, & Pizarro, 2003; Shah, Nag, Kalagara, Singh, & Manorama, 2008; Su, Wei, Hu, & Tang, 2009; Wu, Imlay, & Shang, 2010; Zhang & Yu, 2005), but also reduced the metal ions by the excited electron under UV irradiation. Furthermore, it is benefit for the disinfection of storing drinking water that the adhesion of these nano-Ags to  $\text{TiO}_2$  is strong enough to resist continuous water rinsing for a long time (Lim, Lee, Hwang, & Kim, 2006). Macromolecule material, such as CTS has attracted considerable interest due to its properties of film-forming, good adsorption and antimicrobial activity (Abdelrazek, Elashmawi, & Labeeb, 2010; Ignatova, Manolova, & Rashkov, 2007; Nui et al., 2009; Zhou et al., 2007). CTS has also function as stabilizing agent with strong affinity towards metal ions because of the presence of numerous amine and hydroxyl groups. Therefore, nano-Ags become attached to the polymer. In addition, CTS can reduce  $\text{Ag}^+$  to Ag in alkaline condition (Pallab et al., 2008).

In this study, after considering the characteristics of terminal drinking water, we have prepared a new composite functional film (CTS/PVP/ $\text{TiO}_2$ /Ag). In this composite material, the reusable polymer film acts as a supporting material for handling. In this composite film loaded with Ag and  $\text{TiO}_2$  nanoparticles, CTS is the primary component, and polyvinylpyrrolidone (PVP) (Ibanez et al., 2003; Sionkowska, Wisniewski, Skopinska, Vicini, & Marsano, 2005; Wu et al., 2010) is an additive. It is proved that PVP is used as the protective agent to prevent from agglomeration of Ag particles (Carotenuto, Pepe, & Nicolais, 2000; Dastjerdi and Babaahmadi, 2011). And different characterization methods were used to analyze the properties of the functional film, such as the diameter of the inhibition ring, tensile strength, endurable and recycle application. The results have proved that CTS/PVP/ $\text{TiO}_2$ /Ag film has a good property of tensile strength, antibacterial activity and sustainable activity in drinking water.

## 2. Experimental

### 2.1. Chemicals and materials

All reagents used in the study are of analytical grade. Chitosan-acetate solution was prepared by dissolving chitosan (CTS, 90.0% deacetylation degree, Sinopharm group Chemical Reagent Co., Ltd. China) in acetate solution (2% volume fraction). Polyvinylpyrrolidone (PVP, molecular weight 10,000–70,000) was purchased from Zhengzhou Chemical Industry Co. Ltd. Silver nitrate ( $\text{AgNO}_3$ , Shanghai Shenbo Chemical Industry Co., Ltd. China), and nanotitanium dioxide (nano- $\text{TiO}_2$ , 99.8% pure, 5–10 nm, Shanghai Jingchun reagent Co., Ltd. China) were used as main disinfectant. *Escherichia coli* were used as a model microorganism for bacteria inactivation study.

### 2.2. Analytical techniques

IR Prestige-21/FT-IR-8400S Fourier transform infrared spectrometer (FT-IR, Shimadzu Co., Japan) was used to characterize and analyze the complex mechanism of the composite membrane. Differential scanning calorimeter (910S DSC, TA instruments, USA) was used to detect the compatibility and heat resistance of the composite membrane. The concentration of  $\text{Ag}^+$  in water was detected

by Graphite Furnace Atomic Absorption Spectrophotometer (M/S GFAAS, USA). The surface morphology of film was examined using Quanta Scanning Electron Microscope fitted with Energy dispersive X-ray Spectrometer (SEM-EDS, Vega ps5136sm, Pescam, CZ). X-ray diffraction (XRD) analysis of CTS/PVP/Ag/ $\text{TiO}_2$  was carried out by a PerkinElmer PHI-5400 diffract meter, employing  $\text{Cu-K}\alpha$  radiation of wavelength 1.54. The data were taken in the range of 3–90° ( $2\theta$ ), with a step size of 0.02°. Tubular Double - Ended UV Lamp (ZW15819W(Y)-Z437) was used at wave number 253.7 nm from Cnligh Co., Ltd in china.

### 2.3. Preparation of CTS-PVP- $\text{Ag}^+$ membrane

CTS-acetate solution was prepared by dissolving 0.22 g CTS in 8.4 mL of acetate solution, and then 0.3 g PVP were added and stirred for about 30 min till the solution became homogeneous. After 1.6 mL of  $\text{AgNO}_3$  solution (5.0 mg/mL) was gradually dropped into the above solution, the mixture was stirred for about 60 min without light. After deaeration, the casting solution was coated on the glass at 0.25 mm, dried, and then placed in a hot blast drying oven at 50 °C isolated from air for heat treatment. CTS-PVP- $\text{Ag}^+$  film was then obtained by being peeled in 2% NaOH solution, washed with deionized water, and then dried at room temperature.

### 2.4. Preparation of CTS-PVP- $\text{TiO}_2$ film

The homogeneous CTS-PVP- $\text{TiO}_2$  emulsion was prepared by dropping 1.0 mL of 2% nano- $\text{TiO}_2$ / $\text{C}_2\text{H}_5\text{OH}$  suspensions into CTS-PVP mixture (prepared as described in Section 2.3), and the mixture was stirred for about 60 min until the color of solution turned to ivory-white. After deaeration, the casting solution was coated on the glass at 0.25 mm, dried, and placed in a hot blast drying oven at 50 °C for heat treatment. The CTS-PVP- $\text{TiO}_2$  film was obtained by being peeled into 2% NaOH solution, washed with the deionized water, and dried at room temperature.

### 2.5. Preparation of CTS-PVP- $\text{TiO}_2$ -Ag film

A 8.4 mL of homogeneous CTS-PVP- $\text{TiO}_2$  emulsion was prepared as mentioned before. A 1.6 mL solution of  $\text{AgNO}_3$  (5.0 mg/mL) was gradually dropped into the emulsion, and then the emulsion was stirred without light for about 60 min. After deaeration, the casting solution coated on the glass at 0.25 mm was placed under the UV radiation for 60 min until its color turned to dark brown. After being dried, the film was placed in a hot blast drying oven at 50 °C for heat treatment isolated with air. The CTS-PVP-  $\text{TiO}_2$ - Ag film was obtained by being peeled into 2% NaOH solution, washed with deionized water, and then dried at room temperature.

### 2.6. Tensile strength of film

Mechanical properties of film are very important if they were applied in drinking water storage. The film should have good tensile strength for convenient operation, especially for being separated from water system easily and for recycling. Therefore, tensile strength was supposed as an important character for evaluation.

The composite film was cut into the size of  $20 \times 40 \text{ mm}^2$  to test the tensile strength. The film was clamped at both sides and hanged up with the top fixed. The weight was added to the bottom clamps until the film breaks, at which point the film reaches its extreme in tensile strength. The tensile strength of film can be calculated by Eq. (1).

$$\sigma = \frac{m \cdot g}{10^6 A} \quad (1)$$

where  $\sigma$  is the tensile strength of film (MPa);  $m$  is the total quality of system including clamps, cord, the weight (kg);  $g$  is acceleration of gravity ( $\text{N kg}^{-1}$ );  $A$  is the areage of cross section of film ( $\text{m}^2$ ).

### 2.7. Antibacterial study

Before the test, all the glassware should be autoclaved at  $121^\circ\text{C}$  for 20 min. The third generation of cultivated *E. coli* was used as model bacteria in this test.

A suspension of 1.0 mL initial bacteria was taken into tube (I), and then was diluted to 10 mL with normal saline. And the dilution factor is  $10^{-1}$ . Then 1.0 mL solution in tube (I) was transplanted to tube (II), according to the same dilution process, and the dilution factor is  $10^{-2}$ . Similarly, the dilution factors of tube (III) and tube (IV) were  $10^{-3}$  and  $10^{-4}$ , respectively.

5.0 mL warm liquid culture medium (Nutrient agar) was put into a Petri dish. 0.2 mL bacteria dilution from tube (IV) was added onto the surface of the solid culture medium after which was cooled to ambient temperature, and then uniformly daubed with coating stick. The circular film ( $\varnothing 16\text{ mm}$ ) was attached onto the center of the solid culture medium, and then the plates were incubated for 24 h at  $37^\circ\text{C}$ . Finally, the diameter of inhibition ring of film was measured, and the longer the diameter of inhibition ring of film is, the better the effects of antibacterial.

### 2.8. Sustainable activity of antibacterial film in drinking water

In practical application, sustainable activity of antibacterial is also very important. If sustainable activity of antibacterial is good, the material will have very good prospects.

The sustainability on anti-microbe of film in water was measured by the following method: Dip the circular film above into tap water for about 5 days, 10 days, 15 days, 20 days, 25 days and 30 days respectively. Then the films were taken out to for the antibacterial testing mentioned and the concentration of releasing  $\text{Ag}^+$  in these solution were detected by GFAAS.

## 3. Results and discussion

### 3.1. Optimization of preparation conditions for film

#### 3.1.1. Optimal conditions obtained by tensile strength of film

The composite film used in drinking water system must have not only good antibacterial activity but also good mechanical strength for being easily separated from water, and for recycle. And the tensile strength is determined by the content of CTS,  $\text{Ag(I)}$ ,  $\text{TiO}_2$ , and PVP.

In Fig. 1, it shows that the effect of  $\text{Ag}^+$  concentration on the tensile strength of film. The tensile strength was improved due to the increasing concentration of  $\text{Ag}^+$ . However, when the concentration of  $\text{Ag}^+ > 0.12\%$ , the tensile strength displayed a downward trend. When the  $\text{Ag}^+$  concentration was lower, the silver ions were distributed uniformly. After they were deoxidized in situ to nano-Ags under UV irradiation, nano-Ags were stuffed at the coalescent point of macromolecules to increase the tensile strength of film. The subsequent FT-IR spectrum also showed that Ag is affected by  $-\text{NH}$  and  $-\text{OH}$ . However, too much nano-Ags in situ reunited again so that the regularity of molecular chains would be broke, which results in the decline of the tensile strength.

Our study also shows that with the increasing of CTS, the tensile strength display an increasing trend. When the content of CTS is over 3.0%, the film is difficult to be obtained by coating casting solution, which is caused by high viscosity. Similar results are obtained after changing the contents of  $\text{TiO}_2$ . At the beginning, the tensile strength is improved due to the increasing contents of  $\text{TiO}_2$ .

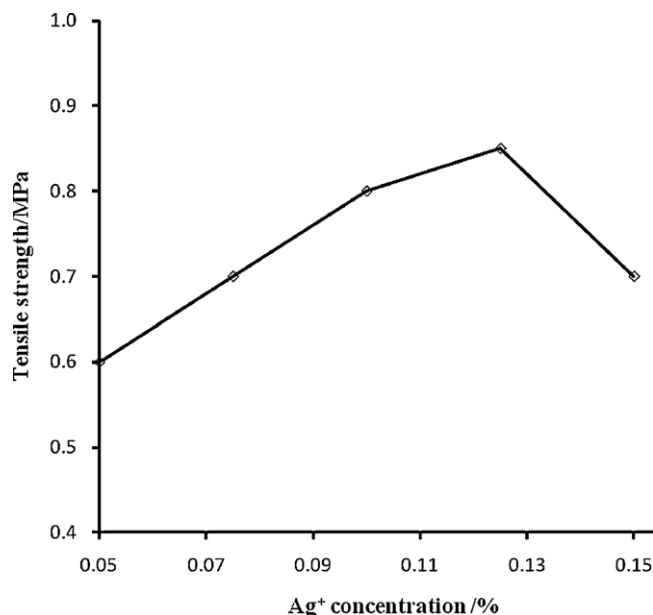


Fig. 1. Effect of  $\text{Ag(I)}$  concentration on the tensile strength of film.

After the contents of  $\text{TiO}_2$  are over 0.3%, the tensile strength cannot be detected because the film become fragile and some visible accumulation of  $\text{TiO}_2$  particles are found.

The two curves in Fig. 2 represent anti-bacteria activity and tensile strength of the same membrane, respectively. The results indicate that the tensile strength of film increased with the increasing content of PVP. It is found that the cast solution could not be obtained when the PVP content of this film is more than 3.0%. In addition, the experimental results also suggest that the content change of PVP has no effect on the antimicrobial ability of the membrane. Therefore, 3.0% PVP is used in the subsequent experiments.

#### 3.1.2. Optimal conditions obtained from anti-bacterial activity

CTS,  $\text{Ag(I)}$  and  $\text{TiO}_2$  are three main chemicals having anti-bacteria activity. The content of CTS,  $\text{Ag(I)}$  and  $\text{TiO}_2$  in the casting solution were further investigated by orthogonal experiments in the range determined above. Orthogonal design ( $L_9(3^4)$ ) and the results of experiments are showed in Table 1.

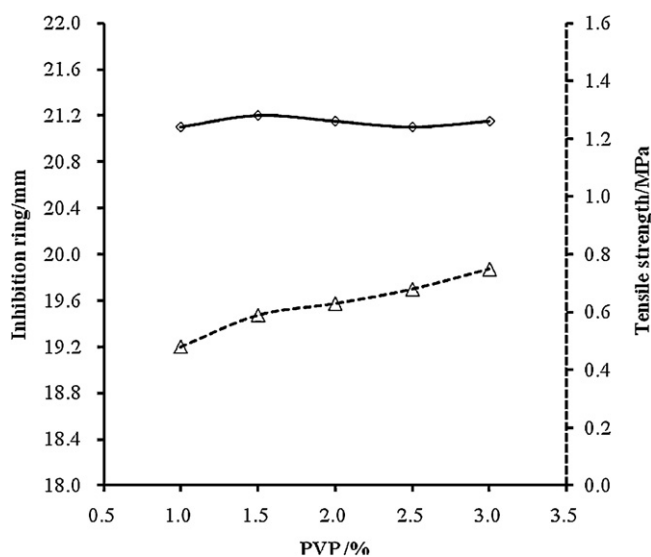


Fig. 2. Effect of PVP concentration on antibacterial ring and the tensile strength of film.

**Table 1**  
Orthogonal design experiment of antibacterial membrane.

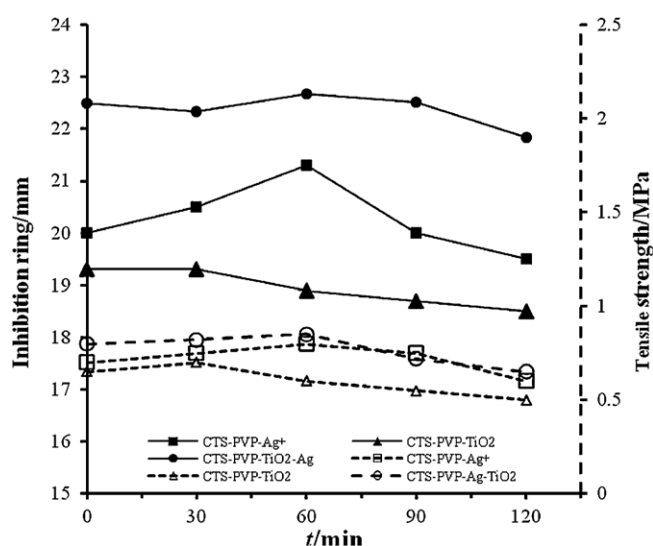
	$\varphi(\text{Ag}^+) (\%)$ A	$\varphi(\text{TiO}_2) (\%)$ B	Mutual interaction $C(A \times B)$	$\varphi(\text{CTS}) (\%)$ D	Inhibition ring $\varnothing$ (mm)
1	1(0.12)	1(0.15)	1	1(2.25)	21.7
2	1(0.12)	2(0.25)	2	2(2.50)	21.6
3	1(0.12)	3(0.20)	3	3(2.75)	21.6
4	2(0.10)	1(0.15)	2	3(2.75)	22.2
5	2(0.10)	2(0.25)	3	1(2.25)	22.4
6	2(0.10)	3(0.20)	1	2(2.50)	22.3
7	3(0.08)	1(0.15)	3	2(2.50)	22.8
8	3(0.08)	2(0.25)	1	3(2.75)	22.8
9	3(0.08)	3(0.20)	2	1(2.25)	23.1
$K_1$	64.95	66.6	66.86	67.11	
$K_2$	66.9	66.87	66.85	66.73	
$K_3$	68.63	67.01	66.77	66.64	
$k_1$	21.65	22.2	22.29	22.37	
$k_2$	22.3	22.29	22.28	22.24	
$k_3$	22.88	22.34	22.26	22.21	
R	1.23	0.14	0.03	0.16	
Influenced factor			$A > D > B > C$		
Optimal scheme			$A_3B_3D_1$		

The results show that  $A_3B_3D_1$  is the best program by evaluating the  $K(k)$  values of each factor in Table 1, and the optimization conditions are  $C(\text{AgNO}_3) = 0.08\%$ ,  $C(\text{TiO}_2) = 0.20\%$ ,  $C(\text{CTS}) = 2.25\%$ . To verify the result with the best activity of antibacterial in Table 1, we get  $23.0 \pm 0.3$  mm of inhibition ring for three repeated times. It is in agreement with the results from orthogonal experiment. The results in Table 1 also show that the order of impact on antibacterial activity is  $\text{Ag(I)} > \text{CTS} > \text{TiO}_2$ . Nevertheless, the mutual interaction between  $\text{Ag(I)}$  and  $\text{TiO}_2$  could be ignored since its impact on antibacterial activity is quite subtle from the  $R$  value.

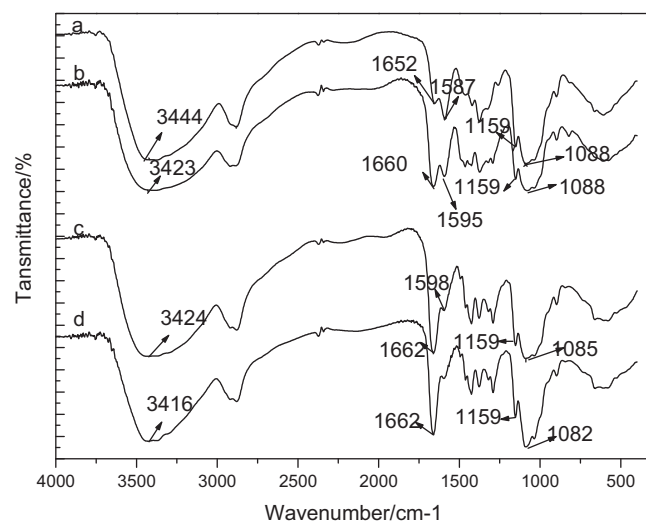
### 3.2. Effect of UV irradiation time on antibacterial activity of film

It is well known that  $\text{TiO}_2$  in the anatase form shows enhanced photocatalytic and antimicrobial activity only under UV illumination (Nikolaou et al., 2002; Zhang & Yu, 2005). In the study, the aim using UV illumination was to reduce  $\text{Ag}^+$  to nano-Ags in situ, and then nano-Ags as main bactericide are utilized to effectively disinfect water. As shown in Fig. 3, the disinfection effect of CTS-PVP- $\text{TiO}_2$ -Ag film slightly decreased at the beginning of

UV irradiation, whereas disinfection effect of the film obviously became better with the increasing UV irradiation time which is over 60 min. After that, the antibacterial ability becomes weaker with the time increasing. The color of film changed from ivory-white to dark brown while UV irradiation time increased. The reason might be that antibacterial particles changed from  $\text{Ag}^+$  to partial  $\text{Ag}^+$  and nano-Ags (Awazu et al., 2008; Dastjerdi, Montazer, & Shahsavan, 2010; Lim et al., 2006), which resulted in the decreasing of disinfection effect at the beginning. While  $\text{Ag}^+$  on the surface is reduced to nano-Ags with the irradiation time increasing, antibacterial ability obviously became better. After that, the antibacterial ability becomes weaker with time increasing, which might because the inner  $\text{Ag}^+$  is reduced to Ag, and Ag begins aggregating due to the deterioration of tensile strength under UV irradiation. The tensile strength of films is deteriorated with the increasing UV irradiation time, which is in agreement with the results of CTS/PVP blends obtained by Sionkowska et al. (2005). Other films have analogous change tendency comparing with CTS-PVP- $\text{TiO}_2$ -Ag film, but they are less than CTS-PVP- $\text{TiO}_2$ -Ag film in the antibacterial ability.



**Fig. 3.** Effect of Ultraviolet radiation time on antibacterial activity and tensile strength of film.



**Fig. 4.** FTIR spectra of CTS (a), CTS-PVP (b), CTS-PVP- $\text{TiO}_2$  (c) and CTS-PVP- $\text{TiO}_2$ -Ag (d).



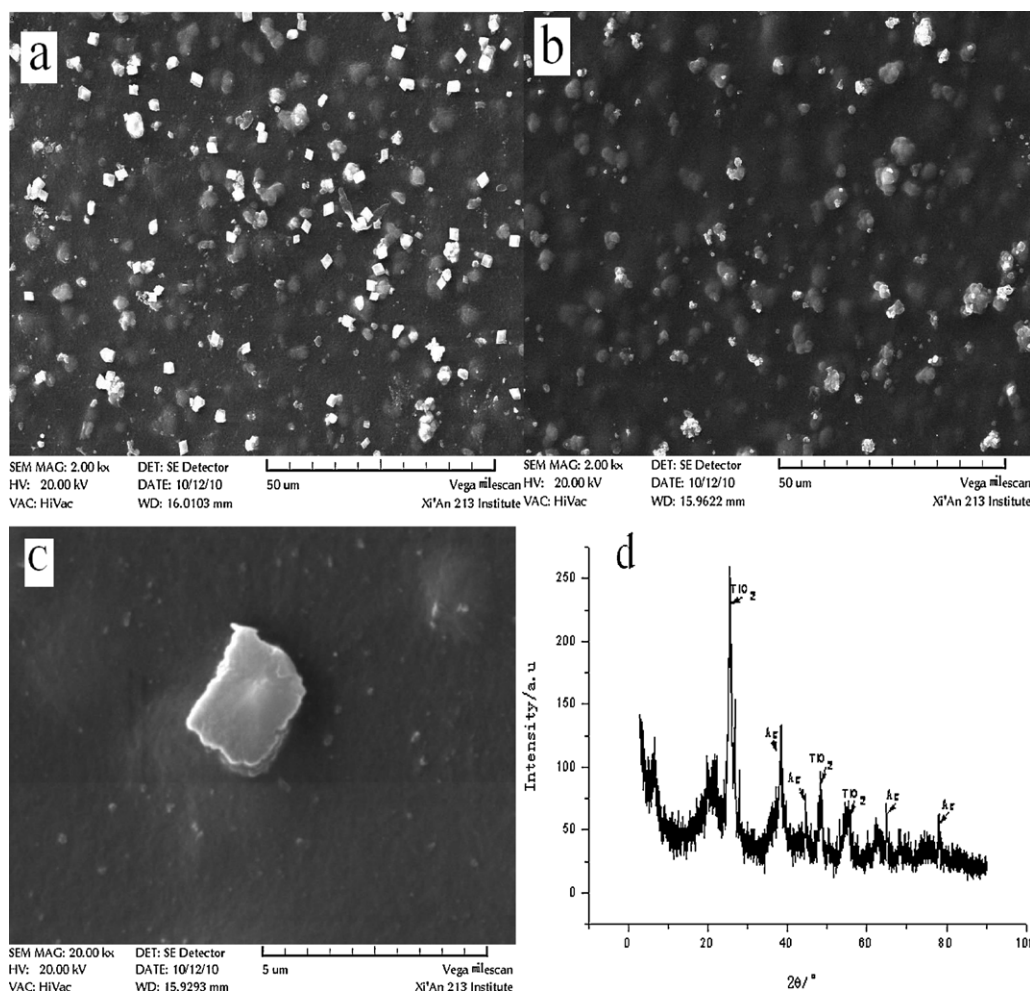


Fig. 5. SEM image of CTS/PVP/TiO<sub>2</sub> (a, 2000×) and CTS/PVP/TiO<sub>2</sub>/Ag (b, 2000×, c, 20,000×) and X-ray diffraction pattern of CTS/PVP/TiO<sub>2</sub>/Ag composite film (d).

### 3.3. FT-IR analysis

To ascertain the complex mechanism of film formation, FT-IR spectrum is used to characterize the membranes of CTS, CTS-PVP, CTS-PVP-TiO<sub>2</sub> and CTS-PVP-TiO<sub>2</sub>-Ag. The shapes and positions of most peaks in Fig. 4 are exhibited similarly. In curve a, the peak at 3444 cm<sup>-1</sup> responds to N-H and O-H stretching vibration of CTS, and the peaks at 1652 cm<sup>-1</sup> and 1587 cm<sup>-1</sup> are acetyl stretching vibration (CTS, 90.0% deacetylation degree) and N-H deformation vibration of CTS, respectively. Compared with the peak at 3444 cm<sup>-1</sup> in curve a, the peak of curve b moves to 3423 cm<sup>-1</sup>, and the peaks at 1652 cm<sup>-1</sup> and 1587 cm<sup>-1</sup> move to 1660 cm<sup>-1</sup> and 1595 cm<sup>-1</sup> respectively (Smitha, Sridhar, & Khan, 2006). The peak at 1652 cm<sup>-1</sup> moves to 1660 cm<sup>-1</sup> and becomes much stronger, but the peak of N-H deformation vibration becomes weaker, which indicates the existence of amide carbonyl of PVP in film. As a result, the CTS/PVP blends show a increasing carbonyl band at 1660 cm<sup>-1</sup>, which indicates that hydrogen bonds have been formed between CTS and PVP (Smitha et al., 2006). The FT-IR spectra of composite CTS/PVP/TiO<sub>2</sub> shows more peaks than that of CTS and CTS/PVP, but TiO<sub>2</sub> in the film has no obvious effect on the peak of N-H and O-H. The curve d shows that the peaks at 3424 cm<sup>-1</sup> and 1085 cm<sup>-1</sup> for CTS/PVP/TiO<sub>2</sub> move to 3416 cm<sup>-1</sup> and 1082 cm<sup>-1</sup> respectively, which show that Ag obtained by reducing Ag<sup>+</sup> is affected by -NH and -OH (Wei et al., 2009). It is also indicated that Ag obtained by

reducing Ag<sup>+</sup> in situ has more durative antibacterial activity than adsorption.

### 3.4. Morphological and XRD analysis

It has been proved that Ag could be obtained by TiO<sub>2</sub> photoreduction at UV irradiation (Guin et al., 2007; Zhang et al., 2003). The films (CTS-PVP-TiO<sub>2</sub>-Ag) show dark brown under UV irradiation in our study, which is attributed to the surface plasmon resonance of nano-Ags synthesized on TiO<sub>2</sub> nanoparticles. (Awazu et al., 2008; Lim et al., 2006; Dastjerdi et al., 2009, 2010). The morphology of composite films was further analyzed by scanning electron microscopy (SEM). In Fig. 5, it is showed that some particles were dispersed on the surface of the film, and others were embedded in the film. Obviously, these big particles (>500 nm) are aggregates of nano-TiO<sub>2</sub>, and others (<500 nm) are well distributed in the film. X-ray diffraction (XRD) in Fig. 5d studies further indicates that the film is containing anatase TiO<sub>2</sub> and Ag phase. The crystal structures of TiO<sub>2</sub> agree well with the corresponding reported JCPDS data (JCPDS powder diffraction data card no. 21-1272) (Guin et al., 2007). XRD patterns also proved the formation of silver crystal. The peaks assigned to Ag in the film at 2θ = 38.4° (1 1 1), 2θ = 44.5° (2 0 0), 2θ = 64.7° (2 2 0) and 2θ = 77.4° (3 1 1) (Amin, Pazouki, & Hosseinnia, 2009) suggest successful reduction of Ag metal. Line broadening of the diffraction peaks is an indication that crystallite sizes of Ag are

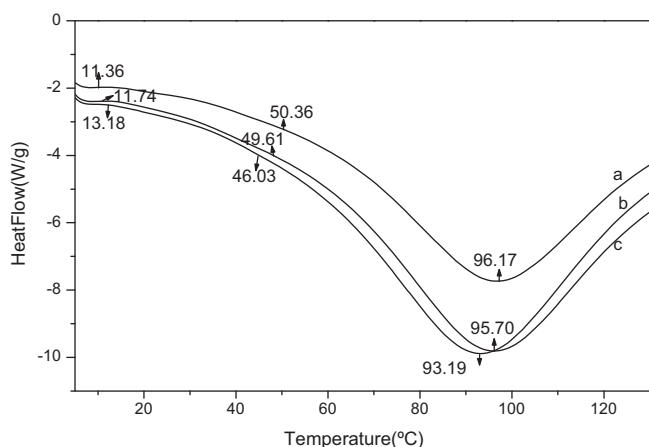


Fig. 6. DSC curves of CTS/PVP/TiO<sub>2</sub>/Ag (a), CTS/PVP (b) and CTS/PVP/TiO<sub>2</sub> (c).

in nanometer range. The crystallite sizes are calculated from Scherrer formula (Amin et al., 2009) applied to the major intense peaks and are found to be about 20 nm.

### 3.5. DSC curves analysis

It can be seen in Fig. 6 that there is only one  $T_g$  peak in each film, which indicates that the three blend films have good compatibility. The existence of TiO<sub>2</sub> ascends  $T_g$  (from 46.03 to 49.61 °C), which indicates that the composite film of CTS/PVP/TiO<sub>2</sub> has a better molecule force so that it improves the rigidity of polymers. The film of CTS/PVP/TiO<sub>2</sub>/Ag has the highest  $T_g$  (50.36 °C). The thermal stability of this film become more well than that of the other two membranes, which may because a number of nano-Ags make the rigidity and hardness of film increased.

### 3.6. Examination the ion release of Ag(I) film in water

When the antibacterial film is applied in drinking water, it is crucial to keep the water clean and would not cause new pollutions. So the possible release of Ag(I) from film should be measured. According to the Abnormal Limitation of Water Quality enacted in China, Ag(I) concentration in water must not exceed 50.0  $\mu\text{g L}^{-1}$  (People's Medical Publishing House, 2006). In this study, the composite films were placed into the deionized water for several days, and Ag(I) concentration in drinking water was tested with GFAAS. It has been proved that Ag(I) concentration in water is less than 7.0  $\mu\text{g L}^{-1}$ , which is much less than the standard value of 50.0  $\mu\text{g L}^{-1}$ , so the drinking water disinfected by this material is safe.

### 3.7. Effect of different pH on antibacterial activity of film

As we known, the pH of drinking water varies in the range from 6.5 to 8.5, so it is necessary to analyze the possible effect of water pH on antibacterial activity of membrane. The antibacterial membranes were placed into water with different pH for one week, and then the antibacterial study was carried out. The results show that antibacterial activity is independent when the pH of water varies from 5.4 to 9.6.

### 3.8. Sustainable antibacterial activity of film

In Fig. 7, it shows the sustainable antibacterial activity of film in different time. After dipping the composite film into water for 5 days, we found the sterilizing rate was slightly decreased. And it maintained more than 95% within one-week dipping. After a period of 30 days, relative sterilizing rate of film was yet over 75%.

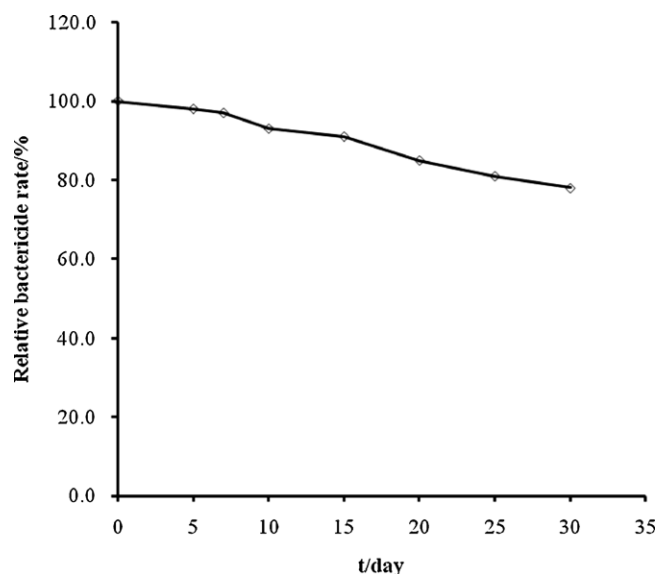


Fig. 7. Sustainable activity of antibacterial film in a period of time.

Those results indicate that this kind of film has good performance in sustainable antibacterial activity.

## 4. Conclusion

In this paper, the CTS/PVP/TiO<sub>2</sub>/Ag film was prepared as a new antibacterial film in the usage of drinking water storage. The optimized conditions of preparing CTS/PVP/TiO<sub>2</sub>/Ag film were obtained. The film has a good sustainable antibacterial activity in practical application. Moreover, the releasing of trace amount Ag(I) in water has no effect on safety of drinking water. This kind of film presented good tensile strength, which is suitable for disinfecting drinking water due to easy operation. Therefore, it could be applied as an effective disinfectant in the storage of drinking water.

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