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Preparation and long-term antibacterial activity of TiO_2 nanotubes loaded with Ag nanoparticles and Ag ions

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In this work anatase TiO_2 nanotubes were prepared by hydrothermally treating suspension of anatase TiO_2 particles in alkaline solutions without the following calcination process. Ag nanoparticles and Ag ions were both loaded on TiO_2 nanotubes by immersion in $AgNO_3$ solutions followed by ultraviolet light radiation. The chemical and morphological features of the products, and the Ag release property were investigated. The results demonstrated that the "open-ended" anatase TiO_2 nanotubes with diameter of about 10 nm and length of over 100 nm were successfully prepared; 15.3 wt% of $AgNO_3$ was loaded into the hollow tubular nanostructures and 9.2 wt% of Ag nanoparticles adhered uniformly to the wall of the nanotubes. The "open-ended" hollow tubular nanostructure of TiO_2 nanotubes could act as a controller for the Ag release, and this endowed Ag-TiO_2 nanotubes with an extended antibacterial period. The long-term antibacterial activities of the resultant Ag-TiO_2 nanotubes were examined against both gram-negative bacteria and gram-positive bacteria. It was confirmed that the "open-ended" hollow tubular nanostructure of TiO_2 nanotubes and the dual action of Ag nanoparticles and Ag ions made Ag-TiO_2 nanotubes attained a long-term antibacterial activity, which enhanced the antibacterial performance of Ag-based antibacterial agents.

1. Introduction

Biofouling caused by microorganisms attaching is an unavoidable, significant problem for the marine facilities, which largely shortens their service lifetime. Nowadays, antifouling surface coatings incorporated with antibacterial agents have attracted increasing interests in marine antifouling fields for their important applications in inhibiting microorganisms attachment on marine facilities. Among various antibacterial agents, silver-based antibacterial agents gain intense attention for their strong inhibitory and biocidal effects, commonly in the form of silver (Ag) ions and metallic silver (Ag). A broad spectrum of antibacterial activities at a low concentration of Ag ions has been confirmed for a long time.[1] Nowadays, Ag nanoparticles are more highly favorable owning to their excellent toxicity to a broad spectrum of microorganisms with low biotoxicity, and are widely being used in the research of food industry, water disinfection, and other applications related to disinfection.[2-4] In contrast to Ag ions, Ag nanoparticles are long-lasting and subject to controlled release. However, in some antibacterial researches, Ag ions showed more effective antibacterial property compared to Ag nanoparticle.[5,6] Recently, it has been found that the existing forms of Ag and the types of bacteria have an important influence on the antibacterial effects, respectively. Ag ions had a substantially higher antibacterial efficiency against gram-negative E.coli bacteria compared to Ag nanoparticles, while Ag nanoparticles were weakly more effective than Ag ions against gram-positive S.aureus.[7] Therefore, it is potentially important to broaden the antibacterial spectrum of silver-based antibacterial agents by utilize the synergistically antibacterial activities of Ag ions and Ag nanoparticles.

In view of the antibacterial mechanism of Ag nanoparticles, some studies confirmed that it was attributed to Ag nanoparticles dissolving into Ag ions and penetrating the membrane of bacteria to destruct the cells; while some studies concluded that the large ratio of surface to volume produced by the small size provided more efficient sites for antibacterial activity and Ag nanoparticles could easily react with the thiol groups present in bacteria, leading to the inactivation of the proteins.[8-10] According to these opinions, Ag nanoparticles must be dispersed uniformly to gain a more effective antibacterial property in the practical applications. However, the agglomeration tendency of nanoparicles makes it difficult to disperse Ag nanoparticles uniformly, thus decreasing their antibacterial efficiency. To overcome this shortcoming, some researchers loaded Ag nanoparicles onto other materials, such as clays, ceramics or polymers, for immobilization and dispersion.[11-13] Although efficiently antibacterial activities were realized, the release of Ag nanoparticles loaded onto the supports could not be controlled in most occasions, which caused a short-term and unstable antibacterial period. Hence, some other materials with special structures must be chosen as supporters of Ag nanoparticles to control the release of Ag nanoparticles.[14,15]

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TiO_2 nanotubes have attracted much attention due to their unique hollow tubular structures. Many reports have investigated the incorporation of Ag nanoparticles into TiO_2 nanotube arrays prepared by anodization on Ti foils, and confirmed the efficiently antibacterial property.[16-18] However, the preparation process of TiO_2 nanotube arrays is complicated and low-yielding. And hydrothermal preparation of TiO_2 nanotubes has been getting more and more prominent due to the easy preparation and high yield. Ag-TiO_2 nanotubes prepared by hydrothermal method have been widely researched in the field of microelectronics, photocatalysis, and photoelectric conversions, but little work has been conducted on the exploration of their behavior of drug controlled release and antibacterial activity. Theoretically, the hollow tubular nanostructure of TiO_2 nanotubes can serve as nanocontainers to store antibacterial agents such as Ag, and its "open-ended" nanostructure and large length-diameter ratio make it feasible for controlling the release of these antibacterial agents, thus producing sustained antibacterial effects for antifouling surface coatings. Therefore, in the present work, we prepared anatase TiO_2 nanotubes loaded with both Ag nanoparticles and Ag ions with hydrothermal method. Both the gram-positive bacteria (S. aureus) and the gram-negative bacteria (E. coli, V. anguillarum) were used to test the synergistically antibacterial activities of Ag ions and Ag nanoparticles, also the long-term antibacterial activity of the products was investigated.

2. Experimental

2.1. Preparation of anatase TiO_2 nanotubes

Anatase TiO_2 nanoparticles (65 cm^2/g) were firstly prepared as precursors of TiO_2 nanotubes by a sol-gel method. In a typical process, anatase TiO_2 nanoparticles were dispersed in 10 mol/l NaOH aqueous solutions. Then the suspensions were transferred to Teflon-lined autoclaves, followed by a hydrothermal treatment at 150 °C for 24 h. After hydrothermal reaction, the autoclaves were cooled to room temperature naturally, and white plate-like precipitates were collected. The obtained samples were centrifuged with 0.1 mol/l HCl and distilled water until the pH value of the washing solutions was approximately 7. In the next, the powders were re-dispersed in 0.1 mol/l HCl solutions and acid-treated for 24 h, then washed continually by centrifugation with distilled water to pH 7. Finally, the white precipitants were dried at 80 °C.

2.2. Preparation of Ag-TiO_2 nanotubes

Loading of Ag nanoparticles and Ag ions on TiO_2 nanotubes was conducted as the follows process. TiO_2 nanotubes were soaked in 0.1 mol/l $AgNO_3$ solutions with magnetic stirring at 40 °C for 4 h at vacuum conditions. The suspensions were then centrifuged and some white precipitants were collected. These wet $AgNO_3$-loaded TiO_2 nanotubes were irradiated by 300 W ultraviolet light for 0.5 h. After that, the above process was carried out for twice to obtain more loading amount of Ag. Finally, the products were dried at 80 °C in a vacuum oven and some dark powders were obtained.

2.3 Characterization

To determine chemical states of elements in Ag-TiO_2 nanotubes, XRD patterns were measured on a X-ray diffractometer (D8, Bruker) with Cu Kα radiation (λ = 0.15405 nm) over the 2θ range of 5°-80° with a step size of 0.02°. The morphology and nanostructures were characterized with transmission electron microscope (JEM-2100F, JEOL). The concentration of $AgNO_3$ solutions was analyzed by inductively coupled plasma mass spectrometry (ICP-Q, Thermo Fisher), and the loading amount of $AgNO_3$ was calculated by equation (1).

$$AgNO_3\,(wt\%) = \frac{(C_1 - C_2) \times V \times M_{AgNO3}}{(C_1 - C_2) \times V \times M_{AgNO3} + m_{TiO_2}} \times 100\% \quad (1)$$

where V was the volume of $AgNO_3$ solution; C_1 and C_2 were the concentration of $AgNO_3$ solutions before and after immersion of TiO_2 nanotubes, respectively.

2.4 Silver release

To investigate the 50-day Ag release profile of Ag-TiO_2 nanotubes, 0.5 g of newly prepared Ag-TiO_2 nanotubes was dispersed in 25.0 ml phosphate buffered saline (PBS) solutions (pH = 8) by ultrasonication, and then the mixture solutions were kept in a digital shaking air bath at 37 °C. Samples were taken out at predetermined time interval, and then were dialyzed with a dialysis bag. The concentration of Ag in dialysate was detected by inductively coupled plasma mass spectrometry, and the precipitates were collected to determine the antibacterial activity of Ag-TiO_2 nanotubes in which Ag had been released. Each sample was performed in triplicate and the results were expressed as the mean.

2.5 Antibacterial assay

The antibacterial activity of the samples was studied by combining diffusion inhibition zone method with plate colony-counting method against E. coli, V. anguillarum and S. aureus under fluorescent light. E. coli and S. aureus were cultured with LB broth, while vibrio anguillarum was cultured with Zobell-2216E broth. The activated bacteria were diluted with fresh broth to a concentration of 1.0×10^5 cfu/ml. For diffusion inhibition zone tests, 0.5 ml suspensions of activated bacteria were spread onto agar plates, and several circular filter papers soaked in antibacterial agents suspensions (200 mg/l) were lightly placed on top of the inoculated agar plates and incubated at 37 °C for a period of time (3 days and 15 days), to evaluate the persistent antibacterial period of Ag-TiO_2 nanotubes. Plate colony-counting method was used to determine the MICs of Ag-TiO_2 nanotubes and the antibacterial activity of Ag-TiO_2 nanotubes that were immersed in PBS for different time. These antibacterial agents were dispersed in the liquid broth inoculated the activated bacteria and incubated at 37 °C for 24 h in a shaking incubator. After that, the bacteria suspensions were treated with ten-fold dilution method and pipetted onto agar plates respectively. The number of surviving bacteria was counted after 24 h of

incubation at 37 °C. The antibacterial rates were calculated by equation (2).

$$C(\%)=\left(\frac{A-B}{A}\right)\times 100\% \qquad (2)$$

where C represented antibacterial rates; A was the average number of colonies formed units in blank control group (no antibacterial agents added); and B was the average number of colonies formed units in experimental group.

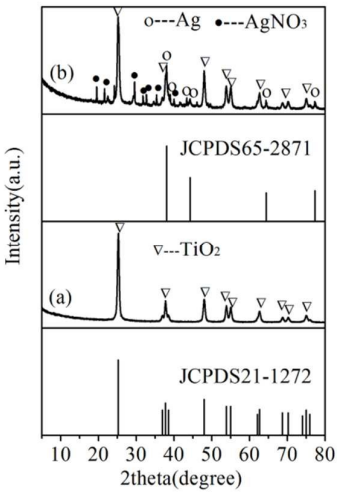

Fig. 1 XRD patterns of (a) TiO_2 nanotubes and (b) Ag-TiO_2 nanotubes

3. Results and discussion

3.1 XRD analysis

Fig. 1 showed the XRD patterns of TiO_2 nanotubes and Ag-TiO_2 nanotubes, curves a and b, respectively. All diffraction peaks in Fig. 1 (a) were indexed to the anatase TiO_2 (JCPDS21-1272), which had a favorable structure for Ag ions being photo-reduced to Ag nanoparticles. This result indicated that the crystalline phase of anatase TiO_2 was retained even after hydrothermal treatment, and this was different from those hydrothermal researches in which only by calcinations at 400 °C could anatase TiO_2 nanotubes be obtained.[19-21] After the loading of both Ag nanoparticles and Ag ions, all diffraction peaks of TiO_2 nanotubes, shown in Fig. 1 (b), were quite similar to those in Fig. 1 (a), indicating that the nanostructure of TiO_2 nanotubes was unaffected. More importantly, the diffraction peaks of $AgNO_3$ (JCPDS43-0649) and the face-centered cubic Ag crystals (JCPDS65-2871) were both expectedly observed in Fig. 1 (b), and this was related to the fact that a part of Ag ions were reduced to metallic Ag nanoparticles during the process of ultraviolet light radiation. According to the results of quantitative analysis using Rietveld whole pattern fitting method, the molar ratio of Ag ions to Ag nanoparticles was about 1:1 in Ag-TiO_2 nanotubes, and the composites were composed of 9.2 wt% of Ag nanoparticles, 15.3 wt% of $AgNO_3$ and 75.5 wt% of TiO_2.

3.2 TEM analysis

The typical TEM image TiO_2 nanotubes and Ag-TiO_2 nanotubes were shown in Fig. 2, respectively. According to Fig. 2 (a), TiO_2 nanotubes were successfully prepared after the alkaline-hydrothermal treatment of TiO_2 nanopaticles. The nanotubes exhibited uniformly straight hollow tubular nanostructure with diameter of about 10 nm and length of over 100 nm, which was similar to the previous reports.[19-23] Furthermore, the nanotubes possessed open-ended structures that were extremely beneficial for the loading of Ag ions. According to the calculation result of equation (1), 30.9 wt% of $AgNO_3$ was loaded on TiO_2 nanotubes (molar ratio of Ag/Ti was 1:5), and it was very close to the quantitative analysis of XRD patterns using Rietveld whole pattern fitting method (molar ratio ofAg/Ti was 1:5.5). After the ultraviolet light radiation, Ag ions derived from $AgNO_3$ were photo-reduced to Ag nanoparticles. Fig. 2 (b) depicts the spherical morphology and distribution of Ag nanoparticles loaded on TiO_2 nanotubes. The majority of Ag nanoparticles with the size of 5-10 nm distributed uniformly on the outer wall of TiO_2 nanotubes, while minority of Ag nanoparticles with the shorter size absorbed on the inner wall of TiO_2 nanotubes, seen in Fig. 2 (b)-A. Moreover, it was found that the size and the shape of the TiO_2 nanotubes remained unchanged with Ag nanoparticles attached to the wall of tubular nanostructure, which was consistent with the XRD analysis of Ag-TiO_2 nanotubes.

3.3 Ag release test

The concentration of the Ag released into the PBS solution was illustrated in Fig. 3. The Ag release rates from Ag-TiO_2 nanotubes rose faster with time in the first several days. After 14 days, the release rates reached a near steady-state. When the immersion time was 14 days or longer, the total Ag delivery from Ag-TiO_2 nanotubes was about 0.27 wt%, which was much lower than 9.2 wt% of Ag nanoparticles and 15.3 wt% of $AgNO_3$. From the aforementioned analysis, it was concluded that Ag-TiO_2 nanotubes underwent a long-term sustainable Ag release process. In other words, TiO_2 nanotubes acted as nanocontainers for Ag storage and the “open-ended” hollow tubular nanostructure could control the Ag release rates due to diffusion and osmosis effects,[24,25] and this endowed Ag-TiO_2 nanotubes with an extended antibacterial period, which would be further confirmed in antibacterial tests.

3.4 Antibacterial test

The antibacterial activities of the newly prepared Ag-TiO_2 nanotubes against different types of bacteria were conducted by using the diffusion inhibition zone method under fluorescent light. To monitor the sustained antibacterial effects, the bacteria incubation time was extended to 15 days. Fig. 4 showed the results of diffusion inhibition zone incubated for different time. As control groups, the diffusion inhibition zones of TiO_2 nanotubes were not apparent, which was attributed the shortage of the photogenerated carriers under

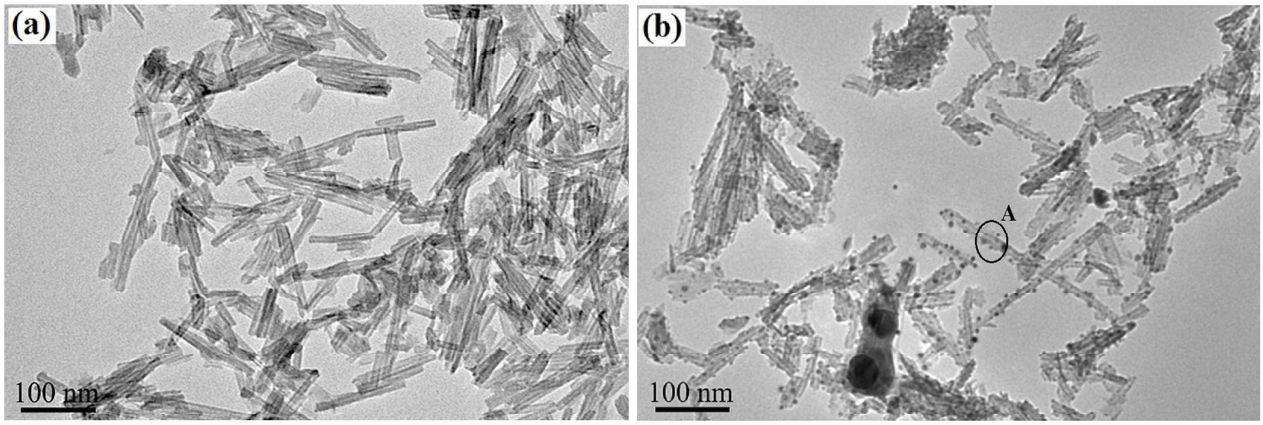

Fig. 2 TEM images of (a) TiO_2 nanotubes and (b) Ag-TiO_2 nanotubes

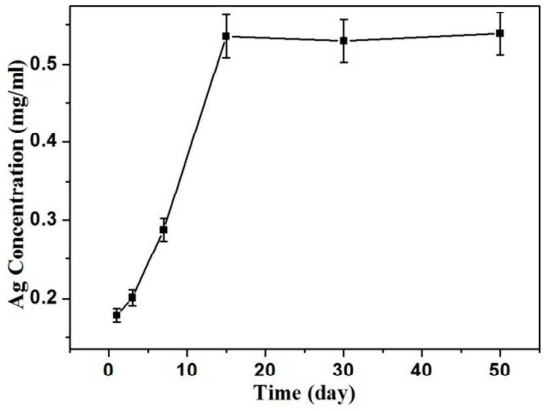

Fig. 3 Silver release profile of Ag-TiO_2 nanotubes in PBS during 50 days of immersion.

fluorescent light irradiation.[26] However, Ag-TiO_2 nanotubes showed prominent inhibition effect on the testing bacteria, which highlighted the importance of the loading of Ag nanoparticles and Ag ions on TiO_2 nanotubes. Interestingly, when the specimens were incubated for 3 days, shown in Fig. 4 (1)-(3), the extent of antibacterial activity against bacteria showed the order as S. aureus < E. coli < V. anguillarum, which indicated the better antibacterial activity against gram-negative bacteria than against gram-positive bacteria. However, with incubation time increasing, Ag-TiO_2 nanotubes displayed a slightly reduced diameters of inhibition zones against E. coli (E.C) and V. anguillarum (V.A), while the diameters of inhibition zones against S. aureus (S.A) increased slightly, comparing Fig. 4 (1) (3) with Fig. 4 (4) (6). That was to say, Ag-TiO_2 nanotubes exhibited better antibacterial activity against gram-positive bacteria than against gram-negative bacteria in the late stage of the experiments. This phenomenon could be explained that Ag ions with a quicker release rate played primarily roles in the early stage of the antibacterial experiment. With Ag ions content decreasing, Ag nanoparticles with long-lasting antibacterial activity dominated the antibacterial activity of Ag-TiO_2 nanotubes in the late stage of the antibacterial experiment. Furthermore, the thicker bacterial cell wall of S. aureus and harder time-dependent Ag penetrations also delayed the cell death, and this was confirmed by the results of the time-dependent Ag leaching study.[23]

The MICs of the newly prepared Ag-TiO_2 nanotubes against different bacteria were determined by plate colony-counting method. The typically inhibitory effect of Ag-TiO_2 nanotubes at three different concentrations was shown in Fig. 5. Ag-TiO_2 nanotubes showed the MIC values of 40 mg/l for V. anguillarum, 100 mg/l for E. coli, and 200 mg/l for S. aureus (Fig. 6). This result demonstrated that Ag-TiO_2 nanotubes showed relatively high short-term antibacterial activity against gram negative bacteria (E. coli and V. anguillarum) as compared to gram positive bacteria (S. aureus), which was consistent with the results of diffusion inhibition zone method.

According to the results of MICs of Ag-TiO_2 nanotubes against different bacteria, the antibacterial activity of the Ag-TiO_2 nanotubes that were immersed in PBS for different time was quantitatively investigated. From Fig. 7, it could be seen that Ag-TiO_2 nanotubes still exhibited antibacterial effects to E. coli and S. aureus, and they were more effective against E. coli than against S. aureus. However, the antibacterial activity of Ag-TiO_2 nanotubes against E. coli decreased quickly with immersion time increasing but that against S. aureus decreased slowly. Eventually, the difference of the antibacterial activity of Ag-TiO_2 nanotubes against E. coli and S. aureus became weak, which was consistent with the results of the diffusion inhibition zone method. That was to say, it was probably due to the quicker release rates of Ag ions that had higher antibacterial efficiency against E. coli than against S. aureus. With immersion time increasing, Ag ions loaded on TiO_2 nanotubes released quickly and the amount of Ag remaining on TiO_2 nanotubes diminished, so the antibacterial activity of Ag-TiO_2 nanotubes against E. coli decreased quickly. For Ag-TiO_2 nanotubes in the late stage of immersion, Ag nanoparticles with slower release rates dominated the

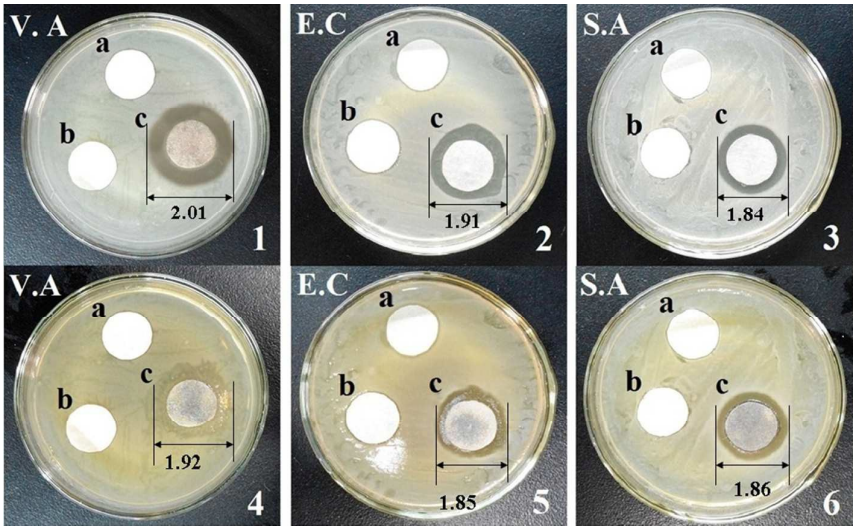

Fig. 4 Diffusion inhibition zone of the (a) blank, (b) TiO_2 nanotubes and (c) Ag-TiO_2 nanotubes against different bacteria under fluorescent light /cm: (1)-(3) incubated for 3 days; (4)-(6) incubated for 15 days.

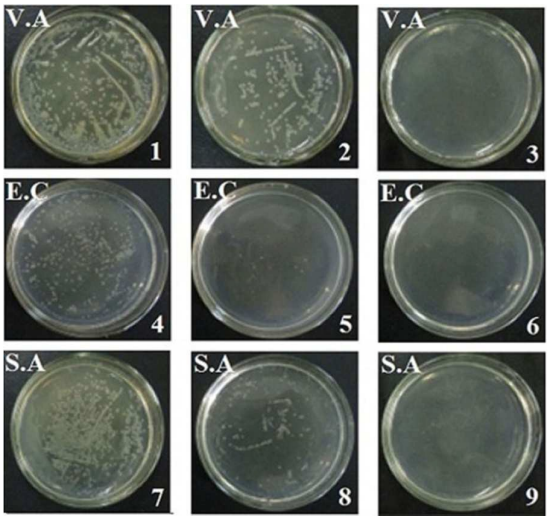

Fig. 5 The typically inhibitory effect of Ag-TiO_2 nanotubes at different concentrations /mg/l: (1)-(3) 0, 20, 40; (4)-(6) 0, 40, 100; (7)-(9) 0, 100, 200.

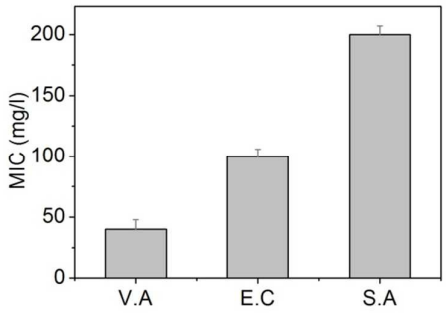

Fig. 6 MIC values of Ag-TiO_2 nanotubes against different bacteria.

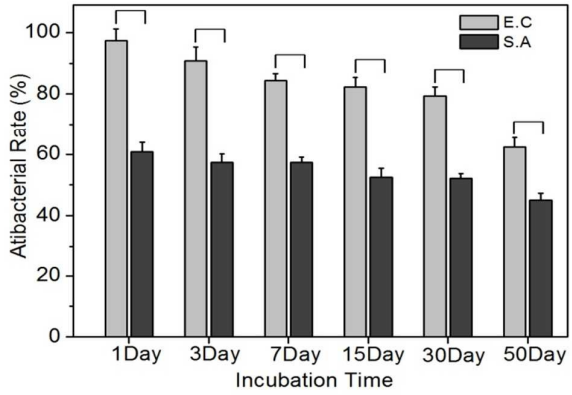

Fig. 7 Antibacterial effects of Ag-TiO_2 nanotubes that were immersed in PBS for different time.

antibacterial activity of Ag-TiO_2 nanotubes. Because Ag nanoparticles were more effective than Ag ions against S.aureus,[7] therefore, the antibacterial activity of Ag-TiO_2 nanotubes against S. aureus was constant relatively.

4. Conclusion

Anatase TiO_2 nanotubes were successfully prepared by a modified hydrothermal method. 15.3 wt% of $AgNO_3$ and 9.2 wt% of Ag nanoparticles were loaded into the hollow tubular nanostructures of TiO_2 nanotubes by combining immersion and photo-reduction. TiO_2 nanotubes helped to stabilize Ag ions and Ag nanoparticles and prevent Ag nanoparticles from agglomerating. Among the antibacterial tests, the prepared Ag-TiO_2 nanotubes showed better antibacterial activity against gram-negative bacteria than against gram-positive bacteria in the early stage of the experiments because of the mainly

antibacterial effect of Ag ions. However, in the late stage of the experiments, Ag-TiO_2 nanotubes showed better antibacterial activity against gram-positive bacteria than against gram-negative bacteria for the antibacterial effect of Ag nanoparticles. In general, Ag-TiO_2 nanotubes exhibited the synergetic antibacterial activity against gram-negative and gram-positive with the dual action of Ag nanoparticles and Ag ion, and this enlarged the antibacterial spectrum and attained a sustained antibacterial period. Finally, the present Ag-TiO_2 nanotubes enhanced the antibacterial activity of silver-based antibacterial agents so that they could be considered as some potent antibacterial agents in various industrial and medical applications.

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