



Induced antibacterial capability of TiO₂ coatings in visible light via nitrogen ion implantation

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Abstract: In order to enhance the antibacterial ability of titanium components, an antibacterial coating was fabricated on Ti surface by micro-arc oxidation (MAO) and further nitrogen plasma immersion ion implantation (N-PIII). The XPS spectra demonstrated that nitrogen was incorporated into TiO₂ coatings by N-PIII and the nitrogen content on the surface of TiO₂ coatings increased as the N-PIII time increased. Nitrogen-incorporated samples exhibited remarkably increased absorbance in the visible region and the light absorption edge of nitrogen-incorporated samples showed a redshift compared to MAO samples. *Escherichia coli* and *Staphylococcus aureus* were seeded on the samples to assess their antibacterial ability. The bacterial experiment demonstrated that nitrogen-incorporated TiO₂ could effectively reduce the bacterial viability in visible light. Thus, the antibacterial TiO₂ coatings fabricated by MAO and further N-PIII might have large potential in the medical and marine fields.

Key words: TiO₂; micro-arc oxidation; nitrogen ion implantation; antibacterial capability

1 Introduction

Titanium and its alloys are widely used in medical instruments and marine components because of their low density, high specific strength and excellent processability [1]. As a relatively simple and reliable technique, micro-arc oxidation (MAO) has been widely used to improve wear resistance and corrosion resistance of these titanium instruments and components [2,3]. However, conventional MAO medical instruments and marine components are lack of antibacterial ability. The bacteria on medical instruments will induce bacterial infection, ultimately leading to surgical

failure. The overgrowth of bacteria will accelerate the corrosion damage of marine components, resulting in shorter service life [4]. Therefore, it is essential to enhance the antibacterial ability of medical instruments and marine components.

Many research efforts have been devoted to endowing MAO coatings with antibacterial ability, and the following two techniques are the most investigated: (1) loading antibiotics [5,6], and (2) doping antibacterial elements such as copper, silver, and zinc [7–9]. The release of oxides of antibiotics and antibacterial elements can effectively kill most bacteria [10,11]. However, the toxicity of these biocidal coatings is under scrutiny, and the antibacterial efficiency cannot maintain

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over a more extended period. Therefore, it remains a challenge to design an antibacterial surface to fulfill various requirements of titanium instruments and components.

Photoactivated self-cleaning coatings have become a significant focus in recent years as environmentally friendly materials. The most commonly known photoactive material is TiO_2 . Under ultraviolet irradiation, TiO_2 can generate electron-hole pairs and exhibits strong oxidizing abilities, which is expected to kill organisms on the surface of materials [12]. However, pure TiO_2 can only undergo photocatalysis under ultraviolet light, limiting its antibacterial effect under the sunlight. Doping TiO_2 with foreign atoms, such as C [13], N [14,15], and S [16], can effectively regulate the band structure of TiO_2 and give TiO_2 photocatalytic properties in visible light. Taking into account environmental and safety requirements, we selected nitrogen, a significant element in the atmosphere, as the doping element, looking forward to acquiring an active antibacterial surface.

Herein, we fabricated environmentally friendly antibacterial TiO_2 coatings on Ti by MAO and further N-PIII without destroying the integrity of the coatings. Moreover, the effects of N-PIII on the surface composition, contact angle, gap band and antibacterial properties of TiO_2 were systematically characterized. The method in this study might provide new insights into the antimicrobial surface design of medical instruments and marine components.

2 Experimental

2.1 Sample preparation

Commercial pure Ti plates ($10\text{ mm} \times 10\text{ mm} \times 1.0\text{ mm}$) were used in the experiments. Firstly, these plates were ultrasonically pretreated in a mixed acid solution ($V(\text{HF}):V(\text{HNO}_3):V(\text{H}_2\text{O})=1:5:4$) twice, 10 min totally. Then, the samples were ultrasonically cleaned with deionized water several times and micro-arc oxidized in 0.2 mol/L sulfuric acid solution to fabricate TiO_2 coatings. The MAO process was conducted with a constant current of 1.8 A, a frequency of 800 Hz and a duty cycle of 10% and ended at 270 V. The micro-arc oxidized samples were designated as MAO.

Afterward, these MAO samples were exposed to N-PIII treatment for 30, 60 and 90 min,

respectively. And the obtained samples were denoted as N-30, N-60 and, N-90, accordingly. Other important processing parameters were listed in Table 1.

Table 1 Parameters of nitrogen plasma immersion ion implantation for different samples

Parameter	N-30	N-60	N-90
Voltage/kV	30	30	30
Pulse/ μs	30	30	30
Frequency/Hz	100	100	100
N_2 flow rate/($\text{cm}^3 \cdot \text{min}^{-1}$)	15	15	15
Time/min	30	60	90
RF power/W	200	200	200

2.2 Characterization of MAO and N-PIII samples

The surface morphologies of samples were observed by scanning electron microscope (SEM; S-4800, Hitachi, Japan). The crystalline phases of samples were analyzed by X-ray diffraction (XRD; D/max 2500PC, Rigaku, Japan). Elemental compositions and elemental chemical states were determined by X-ray photoelectron spectroscopy (XPS; RBD upgraded PHI-5000C ESCA system, USA). UV-visible absorption spectra of samples were recorded by ultraviolet and visible spectrophotometer (UV-vis; Lambda 750, PerkinElmer, USA). The water contact angles of samples were measured by the contact angle instrument (SL20 0B, Solon, China).

2.3 Antibacterial tests

Escherichia coli (*E. coli*, ATCC 25922) and *Staphylococcus aureus* (*S. aureus*, ATCC 25923) were used to assess the antibacterial ability of the samples. A 60 μL suspension of the bacteria was dropped onto each sample, and the bacterial density was 5×10^6 CFU/mL. After incubated at 37 °C for 12 h in the dark and visible light, respectively, the samples attached with bacteria were stained for fluorescent observation. The LIVE/DEAD BacLight Kit (L13152, Molecular Probes, USA) was used to stain the bacteria in the dark according to the manufacturer's instruction. Then, the samples with the bacteria were observed by the confocal laser scanning microscope (CLSM, Leica SP8, Germany).

For the SEM observation, additional samples

with bacteria were cultured at 37 °C for 12 h. Then, the samples were rinsed with phosphate buffered saline (PBS) twice, and fixed with 2.5% glutaraldehyde (Sigma-Aldrich, USA) at 4 °C for 6 h. The samples were dehydrated with a series of ethanol solutions, and the bacterial morphologies were observed by SEM.

After being cultured at 37 °C for 12 h, samples attached with bacteria were put into the sterilized centrifugal tube, which contained 4 mL of physiological saline. The tube was agitated vigorously for 30 s by a vortex mixer to separate bacteria from the surface of samples. After being diluted 10, 100, and 1000 times by sterile physiological saline, 100 μ L of the diluted suspension was dropped on the standard Luria-Bertani (LB, Sigma, USA) or Nutrient Broth (NB, Oxoid, UK) agars. All plates were incubated at 37 °C for another 18 h and the colonies were counted according to the National Standard of China (GB/T 4789.2 protocol).

2.4 Statistical analysis

All data were presented as the mean $\pm$ standard deviation. Statistically significant differences (*P*) between different groups were assessed via one-way analysis of variance and Turkey's multiple comparison tests.

3 Results and discussion

3.1 Material characterization

The surface morphologies of MAO samples before and after N-PIII were shown in Fig. 1. The microporous structures were formed on the surface of MAO samples by micro-arc oxidation treatment. After nitrogen ion implantation treatment for 30, 60 and 90 min, respectively, the original surface topographies of MAO samples have not been altered, indicating that the incorporation of nitrogen by N-PIII had no influence on the structure of TiO₂ coatings.

The XRD patterns of MAO and N-PIII samples are shown in Fig. 2(a). From the XRD spectra of MAO samples, strong diffraction peaks at 2θ values of 25.2° and 48.0° corresponded to (101) and (200) crystal planes of anatase TiO₂ (JCPDS No.21–1272), respectively. And diffraction peaks at 2θ values of 27.4°, 36.0°, 41.2° and 54.3° corresponded to (110), (101), (111) and (211) crystal planes of rutile TiO₂ (JCPDS No.21–1276), respectively. After N-PIII, the diffraction peaks of crystalline anatase and rutile could also be observed at the same position, indicating that N-PIII did not induce the formation of new crystal phases on the surface of MAO samples.

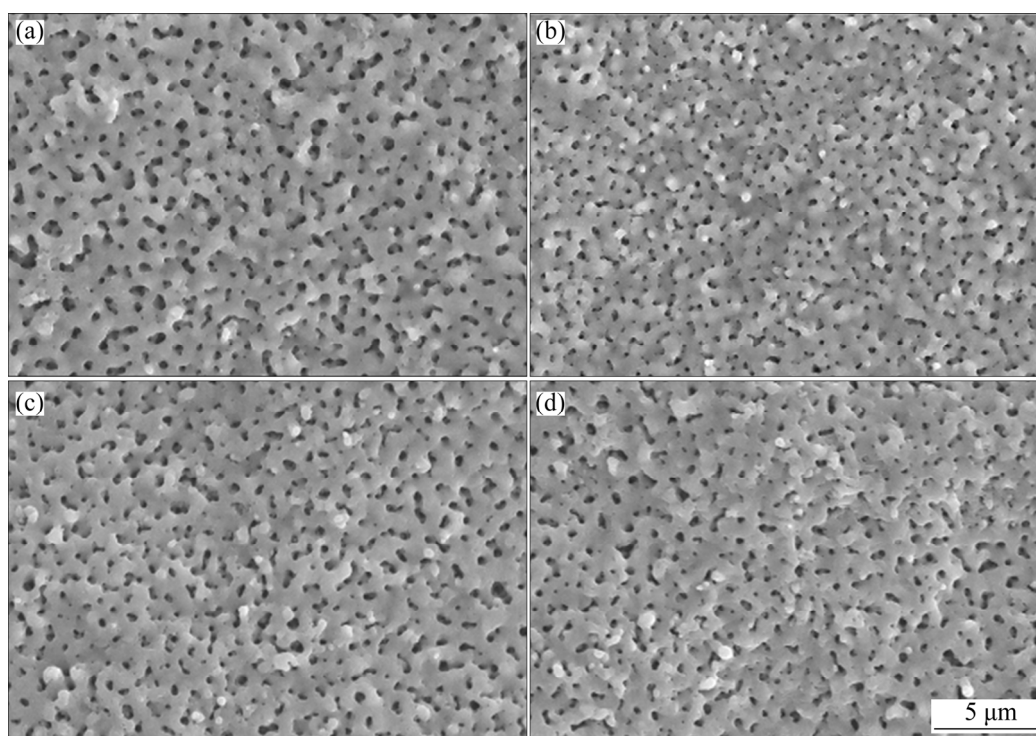


Fig. 1 SEM images of MAO (a), N-30 (b), N-60 (c) and N-90 (d) samples

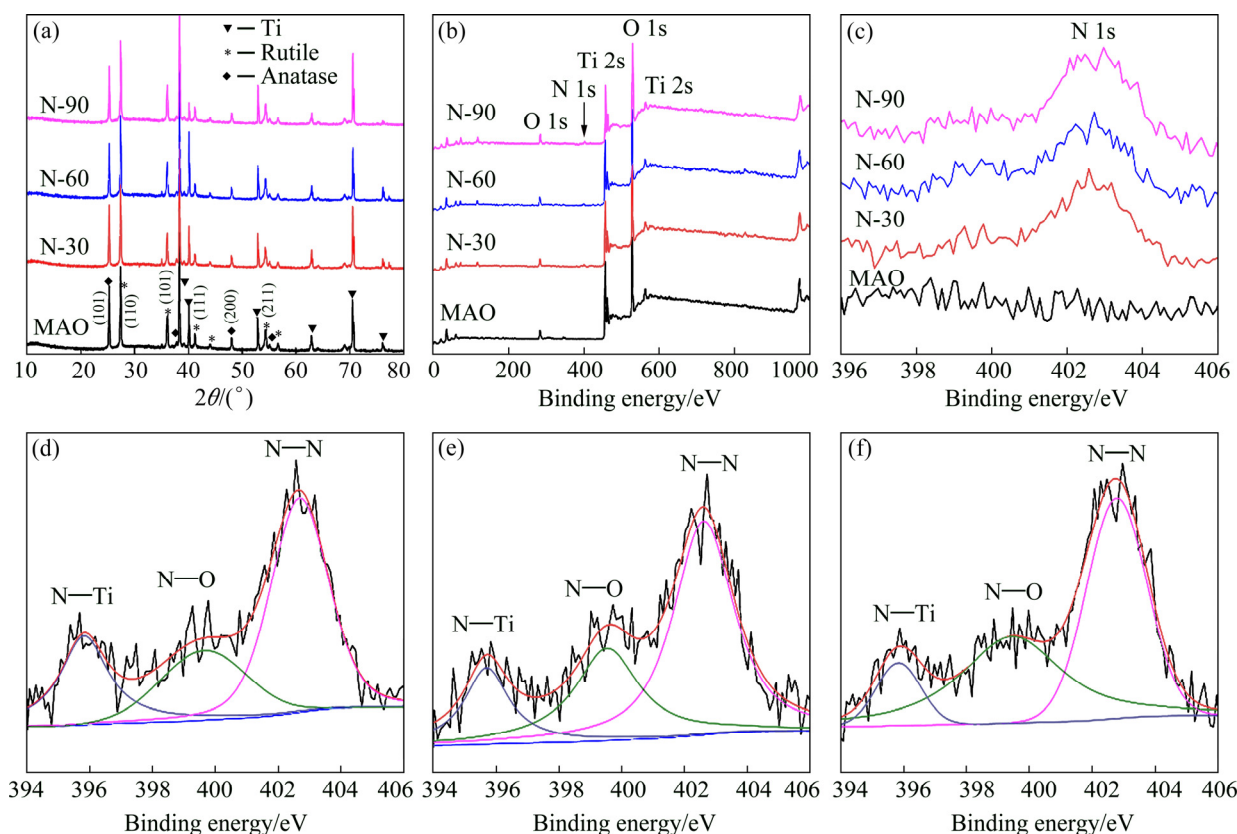


Fig. 2 XRD patterns (a), XPS spectra (b) and XPS N 1s spectra (c) of MAO, N-30, N-60, and N-90, and XPS spectra of N in N-30 (d), N-60 (e) and N-90 (f) samples

The elemental compositions and elemental chemical states on the surface of all samples were determined by XPS. As shown in Figs. 2(b) and (c), the presence of nitrogen on the surface of N-30, N-60 and N-90 samples was confirmed, while there was no nitrogen on the surface of MAO samples. From the surface elemental compositions (Table 2) detected by XPS, it is known that the nitrogen content on the surface of N-PIII samples increased as the nitrogen ion implantation time increased, which meant that incorporated nitrogen content could be controlled by nitrogen ion implantation time.

The chemical states of nitrogen on the surface of N-PIII samples were further analyzed by the

XPS N 1s spectra (Figs. 2(d–f)). The N 1s spectra of N-PIII samples exhibited several broad peaks ranging from 395 to 405 eV, indicating that nitrogen had multiple bonding states in TiO_2 . Moreover, the N 1s curves could be divided into three peaks centered at ~395.6, 399.5 and 402.7 eV, correlated to the chemical bonding of N—Ti, N—O and N—N, respectively [17]. Among these chemical bonds, N—Ti was thought to be mainly responsible for the enhanced visible light absorption of TiO_2 [18].

The ultraviolet and visible spectrophotometer was used to study the optical properties of MAO samples and N-PIII samples (Fig. 3(a)). The light absorption edge of MAO sample was situated at ~440 nm, which was in accordance with the band gap of a mixture of anatase and rutile TiO_2 (2.8 eV). A broader absorption ranging from 400 to 550 nm occurred in N-30, N-60 and N-90 samples, revealing a wider distribution of local energy levels in the band gap. More importantly, N-PIII samples showed significantly increased absorbance in the visible region compared to MAO samples. From the relationship between the Kubelka–Munk function and the absorbed light energy [19] (as shown in

Table 2 Surface elemental compositions of different samples acquired by XPS (at.%)

Element	MAO	N-30	N-60	N-90
C	20.4	17.5	17.2	18.9
O	59.8	61.5	61.9	62.8
N	0	1.6	2.2	2.6
Ti	19.8	19.4	18.7	15.7

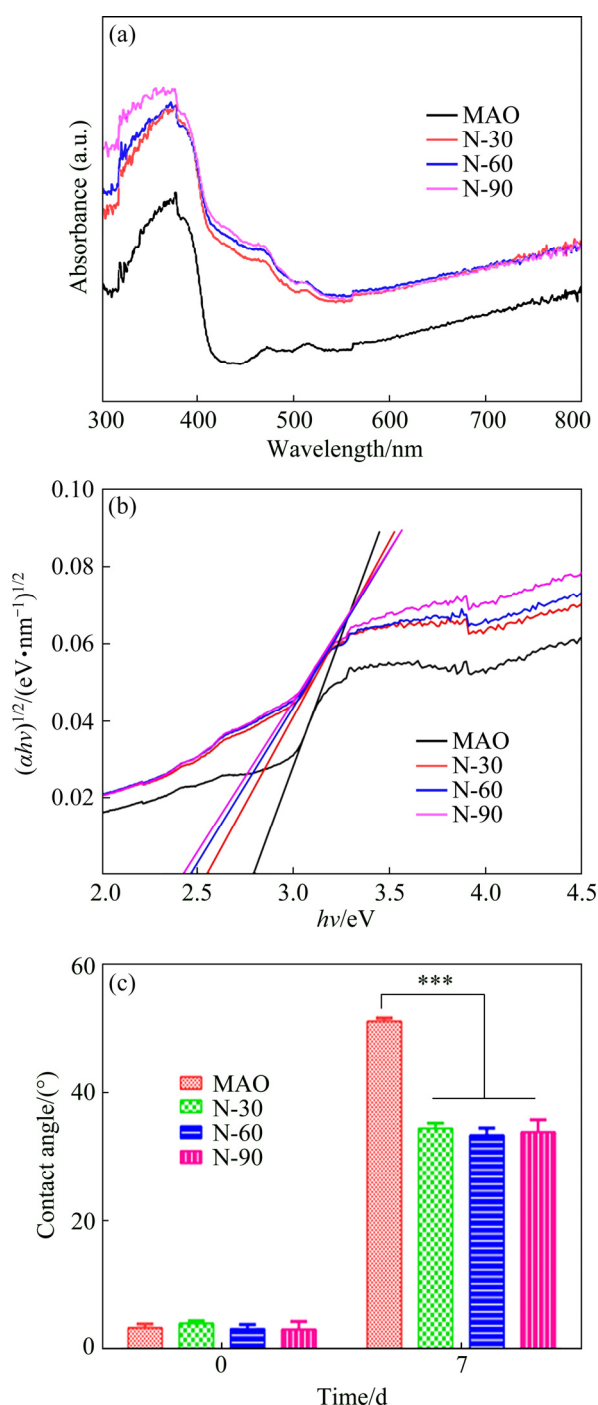


Fig. 3 UV-visible spectra (a), plot of transformed Kubelka–Munk function versus light energy (b) and contact angles (c) of MAO, N-30, N-60 and N-90 samples

Fig. 3(b)), the optical gaps of N-30, N-60 and N-90 samples were reduced to ~2.52, 2.45 and 2.39 eV, respectively, showing a redshift compared to MAO samples.

The reduction of the optical gaps of N-PIII samples might be due to the formation of the local intermediate band gap (N 2p) level above the O 2p

valence band of TiO_2 [18]. The intermediate band gap (N 2p) energy level was slightly higher than the top of the O 2p valence band and the visible light irradiation could stimulate electrons from the N 2p valence band to the conduction band, forming positive holes in the N 2p valence band [20]. Electrons in the conduction band and holes in the N 2p valence band exhibited high reducing and oxidizing power, respectively [21]. The electrons reacted with oxygen, leading to the formation of superoxide radicals (O_2^-) [21]. Meanwhile, the holes reacted with water, producing hydroxyl radicals ($\cdot\text{OH}$) [21]. Hydroxyl radicals and superoxide radicals could react with the organic compounds to form H_2O and CO_2 [22], which was beneficial to improving the hydrophilicity and antibacterial properties of the surface.

The water contact angles of all samples were shown in Fig. 3(c). The surfaces of fresh MAO samples and N-PIII samples were very hydrophilic. However, after 7 d of storage under the same conditions, the contact angles of all samples increased largely due to the unavoidable accumulation of hydrocarbons on the surfaces of these samples [23]. Hydroxyl radicals and superoxide radicals produced by N-PIII samples could reduce the C content on the surfaces (Table 2) and hydroxyl radicals could also increase the hydrophilicity of the surfaces. Thus, the contact angles of N-PIII samples were approximately 16° lower than that of MAO samples after 7 d of storage.

3.2 Antibacterial ability

S. aureus and *E. coli* were used to examine the antibacterial ability of the samples. The Live/Dead assay was performed on all samples, and the nucleic acid of both living and dead bacteria could be stained by SYTO 9 to produce green fluorescence while only the nucleic acid of dead bacteria could be stained by PI to produce red fluorescence [24]. The fluorescent images of *E. coli* and *S. aureus* were shown in Fig. 4. For *E. coli* cultured in the dark (Fig. 4(a)), there were no obvious reduction in green fluorescence among N-30, N-60 and N-90 samples relative to MAO samples and no obvious visible red fluorescence. It was suggested that N-PIII samples did not display significant antibacterial ability in the dark condition. Interestingly, in the light condition, a significant reduction of the

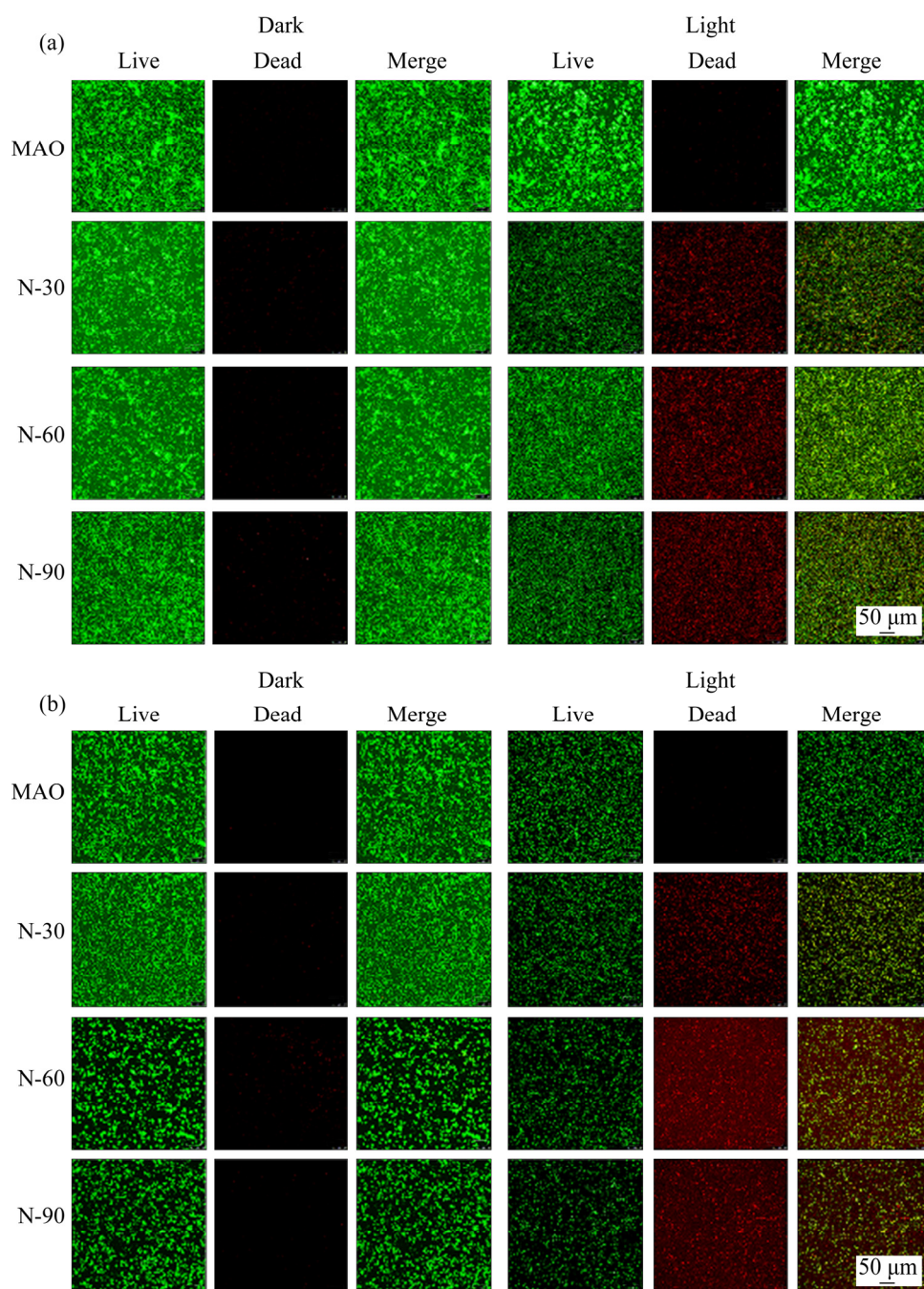


Fig. 4 Fluorescent images of *E. coli* (a) and *S. aureus* (b) on different samples in dark and light conditions (50 μm)

green fluorescence on N-PIII samples was found. Additionally, a significant increase of the red fluorescence was observed on N-PIII samples. These results indicated that N-PIII samples could effectively inhibit the adhesion of *E. coli* and destroy *E. coli* on the sample surfaces, and the antibacterial ability of N-PIII samples increased with the increase of nitrogen content in visible light. The similar trend was found in the *S. aureus* culture experiments as shown in Fig. 4(b).

The morphology and membrane integrity of *E. coli* and *S. aureus* were observed by SEM as shown in Fig. 5. Large amounts of *E. coli* were seen on all samples in the dark (Fig. 5(a)) and the cytoplasmic membranes of *E. coli* were intact and smooth, which indicated that *E. coli* could grow well on all samples and N-PIII samples had no significant negative effects on the growth of *E. coli* in the dark. After cultured for 12 h in visible light (Fig. 5(a)), there was less *E. coli* on the surface of

N-PIII samples compared with MAO samples. The bacteria on MAO samples could keep the typical rod-like shape while partial bacteria on N-30, N-60 and N-90 samples appeared to be disrupted in shape and lose the integrity of cell membrane, which suggested that N-PIII samples could inhibit the adhesion of *E. coli* and exhibit good antibacterial ability in visible light. *S. aureus* also grew well on all samples and had a spherical shape with a smooth

surface in the dark (Fig. 5(b)). After being cultured for 12 h in visible light (Fig. 5(b)), a decrease of the bacteria number on N-PIII samples could be observed while some *S. aureus* on N-PIII samples was distorted in shape.

To further investigate the antibacterial performance of N-PIII samples, the bacteria were detached from the samples and cultured on agar plates for 18 h, and the results were shown in Fig. 6.

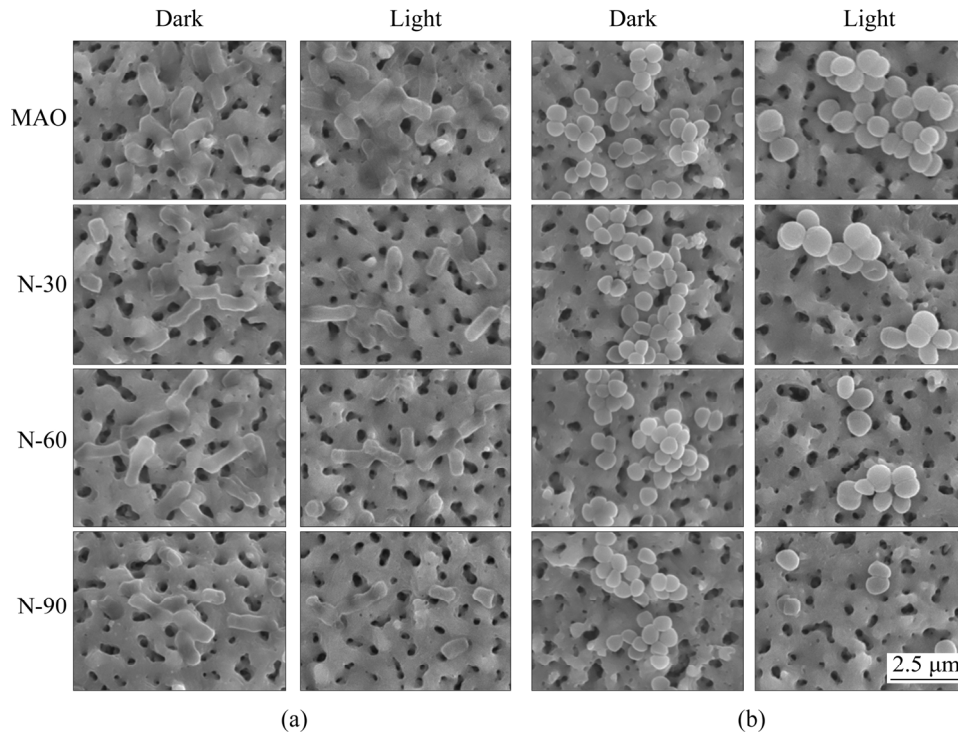


Fig. 5 SEM morphologies of *E. coli* (a) and *S. aureus* (b) on different samples in dark and light conditions

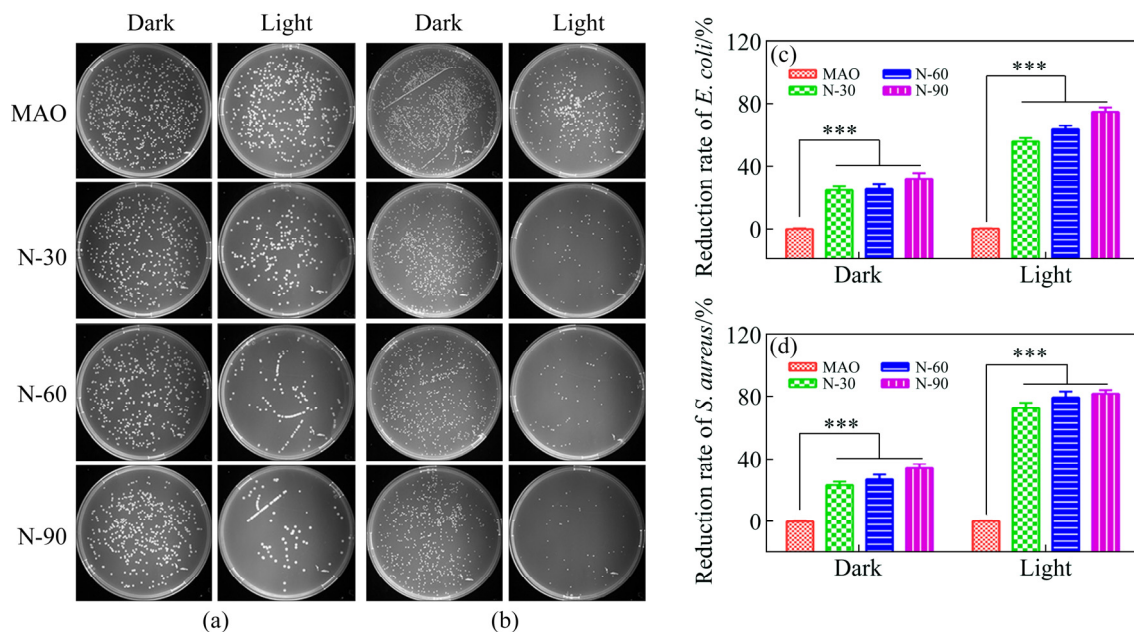


Fig. 6 Images of recultivated *E. coli* (a) and *S. aureus* (b) colonies on agar culture plates and reduction rates of *E. coli* (c) and *S. aureus* (d) colonies

For the dark group, there was no significant difference in the amounts of *E. coli* and *S. aureus* on all samples. However, for the lighting group, a dramatic decrease of the bacteria number was found on the plates corresponding to N-PIII samples compared with that of MAO samples. The bactericidal rates of N-30, N-60 and N-90 samples against *E. coli* were 56%, 66% and 75%, respectively. Meanwhile, the bactericidal rates of those samples against *S. aureus* were 73%, 78% and 81%, respectively, exhibiting a similar trend.

From these results of bacterial experiments, it could be concluded that the bacteria on N-PIII samples could grow well in the dark, while the viability of the bacteria on N-PIII samples was reduced in visible light. It was proposed that the antibacterial ability of N-PIII in visible light was due to the incorporation of nitrogen, which narrowed the optical gaps of N-PIII samples. Reactive oxygen species (ROS, including superoxide radicals and hydroxyl radicals) could be produced by photocatalysis of N-PIII samples with narrowed gaps in visible light [18], as shown in Fig. 7. Hydroxyl radicals were a strong and nonselective oxidant [20], which could virtually damage all types of organic biomolecules, including carbohydrates, nucleic acids, lipids, proteins, DNA, and amino acids [25]. Aqueous reactions of superoxide radicals could produce singlet oxygen ($^1\text{O}_2$) [20], which was the main mediator of phototoxicity and could irreversibly damage the treated tissues [26], causing biomembrane oxidation and degradation [25]. Critical bacteria functions could be damaged by ROS and the bacteria eventually died [27,28]. Thus, N-PIII samples exhibited good antibacterial properties in visible light.

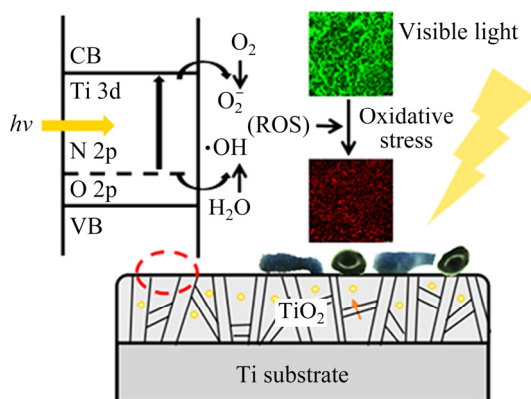


Fig. 7 Schematic illustration of antibacterial mechanism of N-PIII samples

4 Conclusions

(1) Nitrogen-incorporated TiO_2 coatings were produced by MAO and N-PIII. The SEM and XRD results demonstrated that nitrogen could be successfully incorporated into TiO_2 coatings by N-PIII without destroying the surface topographies and phase compositions of the coatings.

(2) Nitrogen-incorporated samples exhibited remarkably increased absorbance in the visible region and the light absorption edge of nitrogen-incorporated samples showed a redshift compared with MAO samples.

(3) The bacterial experiment demonstrated that nitrogen-incorporated TiO_2 coating did not exhibit significant antibacterial property in the dark, while it could effectively reduce the bacterial viability in visible light.

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氮离子注入诱导 TiO_2 涂层 在可见光下的抗菌能力

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摘 要: 为了提高钛组件的抗菌能力, 通过微弧氧化(MAO)处理和进一步的氮等离子体浸没离子注入(N-PIII)处理, 在钛表面制备抗菌涂层。XPS 光谱测试结果表明, 采用氮离子注入 N-PIII 法将氮掺入 TiO_2 涂层, 随着注入时间的增加, TiO_2 涂层表面氮含量增加。掺氮样品在可见光区域的吸光度显著增加, 并且氮注入样品的光吸收峰边缘与微弧氧化样品的光吸收峰相比向红外光区移动。将大肠杆菌和金黄色葡萄球菌接种在样品表面, 以评估样品的抗菌能力。细菌实验结果表明, 掺氮态 TiO_2 在可见光下可以有效降低细菌活力。由实验结果可见, 微弧氧化和氮离子注入复合工艺制备的抗菌 TiO_2 涂层在医学和海洋领域具有很大潜力。

关键词: TiO_2 ; 微弧氧化; 氮离子注入; 抗菌能力

(Edited by Wei-ping CHEN)