Preparation of visible-light-responsive TiO$_2$ coatings using molten KNO$_3$ treatment and their photocatalytic activity

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**Abstract**

In this work, the process of mechanical coating followed by molten KNO$_3$ treatment is given to prepare visible-light-responsive K$^+$-doped TiO$_2$. X-ray diffraction (XRD), scanning electron spectroscopy (SEM), Energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS) were conducted to characterize these TiO$_2$ coatings. The results showed that K$^+$-doped anatase TiO$_2$/Ti composite coatings formed after molten KNO$_3$ treatment at elevated temperatures. Meanwhile, their photocatalytic degradation of methylene blue (MB) and the antibacterial activity against Escherichia coli (E. coli) was also studied. The visible-light-responsive photocatalytic activity of the coatings in MB degradation increased with increase of K$^+$ ions when holding temperature was raised from 673 to 773 K. An excellent antibacterial activity of the K$^+$-doped TiO$_2$/Ti coatings against E. coli was also obtained even in absence of light. The antibacterial activity in dark should attribute to the release of K$^+$ ions from the coatings. The photocatalytic activity under visible-light irradiation should result from the absorption spectrum extension due to the doping of K$^+$ ions into the lattice of TiO$_2$.

**1. Introduction**

Element doping has become one of the most frequently used methods to enhance visible-light-responsive photocatalytic activity since Asahi et al. [1] reported their achievement in the visible-light-responsive photocatalytic activity of nitrogen-doped TiO$_2$ in 2001. Doping elements can fall into nonmetallic elements and metallic ones. Carbon [2,3], nitrogen [1,3–5], sulfur [3], boron [6,7], fluorine [8,9] have been used as doping nonmetallic elements. On the other hand, a great number of transition metallic elements including iron [10], molybdenum [11], vanadium [12], chromium [13], nickel [14], copper [15], etc. have been used to extend the absorption edge of photocatalysts with large band gap. As far as I know, works on TiO$_2$ photocatalysts doped with other metallic elements especially with alkaline metals are relatively less. Shin et al. prepared K-doped TiO$_2$ nanostructures by wet corrosion reaction of Ti nanoparticles in an alkaline solution [16], Tolosa et al. [17] prepared K-doped TiO$_2$ photocatalyst by sol-gel method. However, the methods to prepare K-doped TiO$_2$ are scarce and the effect of K-doping is still not completely understood.

The great progress in visible-light-responsive photocatalyst in recent years makes it possible to remove bacterial contamination including E. coli, Staphylococcus aureus and Candida albicans in households and hospitals [18]. Few researchers also studied their bacterial mechanism. Chang et al. [19] considered that hydroxyl radicals play an important role in E. coli inactivation. Cao et al. [20] believed that reactive species such as hydroxyl radicals and superoxide radicals are responsible to kill the bacteria. Maness et al. [21] proposed that the damaged reaction occurred on the cell wall. After the damage of cell wall, the oxidative damage took place on the underlying cytoplasmic membrane. The intracellular contents were subsequently allowed to free outflow and eventually led to cell death. However, the antibacterial activity of K-doped TiO$_2$ is still not studied to the best of my knowledge.

In this work, we have tried to prepare visible-light-responsive K$^+$-doped TiO$_2$ photocatalyst coatings using a novel method named...
2. Experimental

2.1. Preparation of K⁺-doped TiO₂ coatings

First of all, we prepared Ti coatings on the matrix of Al₂O₃ balls by mechanical coating technique [22,23] using a planetary ball mill (Fritsch P6, Germany) as follows. 40.0 g Ti powder with an average diameter of 30 μm (purity: 99%) and 60.0 g Al₂O₃ balls with an average diameter of 1 mm (purity: 93.0%) were charged into a bowl made of Al₂O₃ with the volume of 250 ml. The bowl was fixed in the planetary ball mill, on which mechanical coating process was then performed. The revolution speed and the duration were 480 rpm and 10 h, respectively. After numerous impact and friction between Ti powder and Al₂O₃ balls, we obtained Ti coatings on Al₂O₃ balls. Secondly, an appropriate amount of KNO₃ powder (purity: 99.0%) was heated and then melted in an evaporating dish made of alumina using a muffle furnace. Subsequently, The Al₂O₃ balls coated with Ti coatings were immersed in the molten KNO₃ and then the samples were further heated in the muffle furnace at 673, 723 and 773 K holding for 20 h, respectively. The as-prepared samples were accordingly nominated as KN-673, KN-723, and KN-773, respectively. To clarify the influence of molten KNO₃, we also heated the Al₂O₃ balls coated with Ti coatings at 673, 723 and 773 K holding for 20 h, respectively. These samples were accordingly labeled with H-673, H-723, and H-773, respectively.

2.2. Characterization of these coatings

Before the characterization, all the samples have to be cleaned in distilled water using an ultrasonic cleaner. An X-ray diffractometer (JDX-3530, JEOl) with Cu-Kα irradiation in the condition of 30 kV and 20 mA was used to characterize their chemical composition and crystal types. We also observed the surface morphology of these coatings using a scanning electron microscope (JSM-6500A, JEOL). Meanwhile, the quantitative analysis for elements was also conducted by energy dispersive spectrometer (EDS) equipped on SEM. Surface element valence state and doping of K⁺ ions were analyzed by X-ray photoelectron spectroscopy (Escalab 250Xi, Thermo Scientific, US). The UV–vis spectra were recorded by UV–vis spectrophotometer (V-670DS, Jasco Corporation).

2.3. Evaluation of visible-light-responsive photocatalytic activity

In this work, we referred to JIS R 1703-2 to evaluate the visible-light-responsive photocatalytic activity of these coatings. Specifically, methylene blue (MB) was used as the target pollutant. Before the photocatalytic activity evaluation, all the samples were cleaned in acetone for 30 min. After that, these samples were dried at room temperature for 24 h. Subsequently; an ultraviolet lamp with an intensity of 1 mW/cm² irradiated these samples for 24 h to degrade the remaining organic pollutants on their surface. We also performed the pre-adsorption procedure of MB in consideration of the adsorption effect of MB on the surface of these coatings. A fluorescent lamp (Panasonic FL20SS-ECW) with an illuminance of 5000 lx was used as the visible-light irradiation source. An optical filter, through which light with the wavelength more than 400 nm can pass, was fixed between the lamp and the MB aqueous solution to eliminate the effect of UV light. A colorimeter (miniphone 10, Sanshin) with a wavelength of 660 nm was used to record the light transmittance of MB aqueous solution and then the data was trans-

Fig. 1. Appearance of the as-prepared TiO₂ coatings prepared by (a) molten KNO₃ treatment and (b) heat oxidation in air. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

formed into their corresponding concentration. The concentration ratio C₀/Cₐ was used to evaluate their photocatalytic activity.

2.4. Evaluation of antibacterial activity under visible-light irradiation

We carried out the antibacterial test referred to JIS R1702: 2012. The target bacterium was Escherichia coli (E. coli). The light source and the corresponding illuminance were identical to those in photocatalytic activity. As for the samples to be tested, we chose KN-723 and the Ti coatings (labeled as M10-Ti), which was used as the control group. Meanwhile, the antibacterial activity tests in dark place for these samples were also conducted to clarify whether these samples themselves have an antibacterial activity or not.

3. Results and discussion

3.1. Appearance of the as-prepared TiO₂ coatings

Fig. 1 shows the appearance of the as-prepared TiO₂ coatings by molten KNO₃ treatment and by heat oxidation in air. The sample prepared by mechanical coating procedure (M10-Ti) shows silvery white color corresponding to metal titanium. After molten salt treatment at 673 K, 723 K and 773 K holding for 20 h, they show light brown, lilac and light gray, respectively (Fig. 1a). On the other hand, the samples show brown, blue and silvery white, respectively after oxidized in air at 673 K, 723 K and 773 K holding for 20 h. Their colors should relate to their surface resultant and elemental valence states.

3.2. XRD analysis

Fig. 2 show the XRD patterns of these coatings prepared by mechanical coating followed by molten KNO₃ treatment or heat oxidation in air. After molten KNO₃ treatment (Fig. 2a), the diffraction peaks of anatase TiO₂ besides those of titanium were observed, which means that anatase TiO₂ formed. Moreover, the diffraction peaks of anatase TiO₂ became stronger as holding temperature was elevated from 673 K to 773 K. It suggests that the amount of anatase TiO₂ increased as holding temperature increased. A similar evolution tendency was observed for the samples prepared by heat oxidation in air (Fig. 2b). We can safely conclude that all the samples mainly consist of anatase TiO₂ and Ti although they show different colors. The color difference may relate to surface elemental valence states and element doping of TiO₂. However, the surface elemental doping and valence state change were not observed as the doping amount and the valence state change were rather tiny.

3.3. SEM and EDS analysis

The SEM images for the surface morphologies of the as-prepared samples by molten KNO₃ treatment and heat oxidation in the air
are shown in Fig. 3. After the molten KNO3 treatment, nano-sized resultants are observed to form and they grew up in size as holding temperature was elevated (Fig. 3a–d). Combined with the results from XRD patterns in Fig. 2, we can judge that the nano-sized resultants should be anatase TiO2. On the other hand, no obvious change in morphology is observed for the samples after and before heat treatment in air although anatase TiO2 was also formed (Fig. 3e–f). From the above results, it is evident that molten KNO3 treatment altered the surface morphology of anatase TiO2 that was formed at elevated temperature. Concretely speaking, the molten salt treatment may benefit to the formation of nanosized anatase TiO2. The nanosized structure has a larger specific surface area, which favors the adsorption of organic molecular or bacteria and therefore improves photocatalytic activity or antibacterial activity. The average thickness of Ti coatings and TiO2 coatings were 50 and 100 μm, respectively. The cross-sectional SEM images are not represented in this work since molten KNO3 treatment did not change the thickness and the cross-sectional microstructure of TiO2 coatings. The information on the cross-sectional SEM images can be seen in our published work [24].

Element analysis for selected areas on the surface of these samples was also conducted with the results shown in Table 1. After molten KNO3 treatment, the relative ratio of element O versus Ti became greater as holding temperature was elevated from 673 K to 773 K. It suggests that the degree of oxidation got higher.

The amount of element K was simultaneously increased from 0 to 2.6 wt%. It confirms the doping of element K. On the other hand, during heat oxidation in air, the degree of oxidation shows a similar tendency as that during the molten KNO3 treatment. Compared molten KNO3 treatment with heat oxidation in air, the former restrained the oxidation of metallic Ti in a greater degree.

### 3.4. XPS analysis

Fig. 4a shows the XPS spectra of K+ doping in TiO2 coatings. Three dashed lines correspond to K_{2p1/2}, K_{2p3/2} and K_{3p3/2}, respectively. No peaks at the above three positions for sample H-673 and H-723 are observed, which means that there is no K+ doping. On the other hand, we can see that peaks of K+ doping and the peaks became greater as temperature was elevated. We can infer that K+ ions doped into anatase TiO2 and the doping amount was increased as temperature was raised. The quantitative analysis of element potassium shows a doping amount of 2.6, 6.7 and 10.6 at% at 673, 723 and 773 K, respectively. Fig. 4b gives us the XPS spectrum of Ti for the as-prepared samples. Three dashed lines represent Ti^{4+}, Ti^{3+} and Ti^{4+} from left to right, respectively. The peaks for the samples except KN-773 are located between the two dashed lines corre-
3.5. UV-vis spectra analysis

Fig. 5 shows the UV-vis absorption spectra of the as-prepared samples. We can see that all the samples intensively absorb UV light and visible light. For the samples after oxidation in air, there is obvious absorption edge. On the other hand, the absorption edge is about 395 nm for the samples after the molten KNO3 treatment. Correspondingly, their band gap is calculated to be 3.14 eV, which is close to 3.2 eV of pure anatase TiO2. We have to note that an intensive absorption of UV and visible light doesn’t always result in excellent photocatalytic activity.

3.6. Visible-light-responsive photocatalytic activity

Fig. 6 recorded the concentration change of MB aqueous solution under the irradiation of visible light. The MB concentration change with the samples prepared by heat oxidation in air under visible light irradiation was not illustrated in this chart since it was hardly decreased. It means that the samples prepared by heat oxidation in the air did not show visible-light-responsive photocatalytic activity. On the other hand, the samples prepared by molten KNO3 treatment show photocatalytic activity in MB degradation to varying degrees under the visible light irradiation. The degradation constant, k of KN-773, KN-723 and KN-773 calculated from Fig. 6 reached 4, 7 and 8 nmol L⁻¹ h⁻¹, respectively. In other words, the photocatalytic activity was enhanced with the increase in holding temperature from 673K to 773K. We also noted that the doping amount of element K increased as holding temperature was elevated. Therefore, we can say that the photocatalytic activity improvement is accompanied by the doping amount increase of element K.

Antibacterial activity of the samples was studied with the cell viability of E. coli given in Fig. 7 and the quantitative results in Table 2. In the Petri dish with Ti coatings (control group) in dark, the
average colony counts of E. coli increased from the initial $4.0 \times 10^5$ to $17.0 \times 10^5$ after 8 h. When the irradiation illumination changed from zero (dark) to 5000 lx, the average colony counts of E. coli increased to 20.0 after 8 h. It indicates that Ti coatings have no antibacterial activity against E. coli. Meanwhile, the irradiation of visible light accelerates the propagation of E. coli. As for the Petri dish with the samples prepared by the molten KNO₃ treatment, the average colony count decreased from $4.0 \times 10^5$ to $0.97 \times 10^5$ after 8 h even in dark. It means that not only did the sample inhibit the reproduction of E. coli but also kill part of them in darkness. It is well known that pure anatase TiO₂ has no antibacterial activity no matter with or without the irradiation of visible light [18,26–28]. Therefore, it is valid to believe that the doped K⁺ ions play a key role in antibacterial activity against E. coli although there is no direct evidence shown here. However, some published works have proved the key role of doped ions. The work of Wang et al. [18] considered that the co-doped TiO₂ with Zn and Y could release Zn and Y ions, which can kill C. Albicans and S. aureus. Hou et al. [26] have shown that the antibacterial activity of Ag₃-TiO₂ nanotubes against S. aureus increased with the implantation dose increase of Ag⁺ ions into TiO₂ nanotubes and proved that the released Ag⁺ ions were responsible for the antimicrobial activity. Hu et al. [29] also considered that the improved antibacterial activity should ascribe to constant and slow release of Zn²⁺ ions. Therefore, we infer that the doped K⁺ ions released from the surface of TiO₂ coatings. The released K⁺ ions play a key role in the antibacterial activity in absence of light.

We also noted that the average colony counts of E. coli with the sample KN-723 got smaller after 8 h irradiation of visible light compared with that without visible light irradiation. Therefore, we can safely say that the sample KN-723 has visible-light-responsive antibacterial activity just as shown in the photocatalytic degradation of MB. As for the antibacterial activity of photocatalysis has been intensively studied [18,19,30–32]. They believe that the doping of K⁺ ions extends the absorption spectrum of the TiO₂ coatings, thereby decreasing the band gap. It allows that the visible light can excite electrons to jump from valence band to conduction band. Finally, hydroxyl radicals and superoxide radicals are generated. These highly active radicals attack the bacteria, leading to phospholipid peroxidation and finally cell death.

4. Conclusions

In present work, K⁺-doped TiO₂ coatings were prepared using the process of mechanical coating followed by molten KNO₃ treatment. The characterization of the samples showed that only anatase TiO₂ were formed during no matter the molten salt treatment or heat oxidation in air. The visible-light-responsive photocatalytic activity of the K⁺-doped TiO₂ coatings in MB degradation was discovered. The samples also showed good antibacterial activity against E. coli under visible light irradiation even in absence of light. It is believed that the visible-light-responsive photocatalytic activity and antibacterial activity result from the absorption spectrum extension due to the doping of K⁺ ions into the lattice of TiO₂. The antibacterial activity in darkness should attribute to the release of K⁺ ions from the coatings.

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References


