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RESEARCH ARTICLE

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# Application of beam irradiation in preparation of visible light responsive $TiO_2$ Films



**Abstract** $TiO_2$ films were prepared by sol-gel method. In order to improve the utilization of light, the technologies of implantation of transition metal ions ($V^+$ and $Cr^+$) and electron beam irradiation to deposit noble metal particles (Ag and Pt) were used. A red shift was found in the spectrum of modified $TiO_2$ films. The photocatalytic experiments showed that the photocatalytic ability under visible light irradiation could be improved dramatically by both the implantation of transition metal and the electron beam irradiation.

**Keywords** electron beam, ion implantation, beam irradiation modification, $TiO_2$, visible light degradation

## 1 Introduction

$TiO_2$ has been studied widely for decades [1,2]. A great deal of noxious industrial waste water and gas can be decomposed by this material. Nevertheless, the application of $TiO_2$ in industry is still limited by the shortcoming of using only ultraviolet (UV) light as a excitation source. One of the main goals of $TiO_2$ research is to broaden its absorbance spectrum to visible light area and enhance its photocatalytic efficiency. The utilization of metal ions is a common and effective method. Traditional ways to utilize metal ions are doping transition metal ions by chemical technique and loading noble metal ion on the surface of $TiO_2$ by photodeposition method [3−5]. However, the identical purpose can also be achieved via beam irradiation technique [6−9].

Up to now, there is lack of references about modification of $TiO_2$ by beam irradiation. In this study, the results of implantation of transition metal ions into $TiO_2$ films via an ion implanter and deposition of noble metal on the surface of $TiO_2$ by electron beam irradiation were reported. Scanning electron microscopy (SEM), transmission electron microscopy/e (TEM), X-ray diffraction (XRD), ultraviolet-visible (UV-Vis), energy dispersive X-ray analysis (EDX) and photooxidation of methyl orange (MO) were used to characterize and evaluate the photocatalytic activity of improved $TiO_2$ films.

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## 2 Experimental

### 2.1 Preparation and modification of $TiO_2$ photocatalytic films

The photocatalytic $TiO_2$ films were prepared by dip-coating and sol-gel method [6], and the $TiO_2$ films for UV-Vis spectra were spin-coated on a quartz glass (2.5 mm × 7 mm) by a spin-coater at 4,000 r/min.

A metal vapor vacuum arc ion implanter (MEVVA-10 [10]) was used to perform the implantation of $V^+$ and $Cr^+$ at 40 kV and average current of 1 mA. The fluences of implanted ions were chosen as $6 \times 10^{15}$, $1 \times 10^{16}$, $3 \times 10^{16}$ and $6 \times 10^{16}$ ions/cm$^2$. After the implantation, $TiO_2$ films were annealed at 450°C for 240 min to study the influence of annealing process on the photocatalytic ability under visible light irradiation.

Electron beam irradiation was performed on a Linac with energy of 5 Mev and average current of 200 μA for 30 min at room temperature in ambient atmosphere. In order to deposit noble metal particles, the irradiated $TiO_2$ films were impregnated into $H_2PtCl_6$ or $AgNO_3$ solutions with concentrations of $10^{-5}$, $10^{-4}$, $10^{-3}$, $10^{-2}$ and $10^{-1}$ M, respectively. After irradiation, the films were washed thoroughly by de-ionized water and dried at 60°C.

### 2.2 Characterization of $TiO_2$ films

An X-ray diffractometry (XRD, PAN analytical) was used to observe the crystalline states of the films. The surface structure was studied by a field emission scanning electron microscope (FESEM, Hitachi S4800) and a transmission

electron microscope (TEM, Tecnai F20) with an energy dispersive X-ray analysis (EDX, EDAX). The optical transmittance spectra were measured by a UV-Visible spectrometer (UV-160, Shimadzu).

### 2.3 Measurement of photocatalytic activity

Aqueous solution (60 mL) of MO with concentration of $3.5 \times 10^{-5}$ mol/L was placed on the catalytic films in a shallow round glass vessel and was irradiated under a continuous stirring. A glass cover with an open slit was placed on the top of the vessel to limit the illumination area, and the cover was also filled with cooling water to control the temperature of photocatalytic reaction. A 150 W high-pressure sodium lamp with an emission peak above 420 nm was used and 72,000 LUX was obtained at the $TiO_2$ films position (measured by an illumination photometer ST-85, BNU). The amount of photodegradation of MO under visible light irradiation was determined by the optical density at 465 nm measured by a UV-visible spectrometer (UV-160, Shimadzu).

## 3 Results and discussion

### 3.1 Characterization of $TiO_2$ films

#### 3.1.1 XRD

Figure 1 shows the XRD patterns of $TiO_2$ films after beam irradiating. It can be seen from Fig. 1 that all $TiO_2$ films are of anatase phase, and no rutile phase is observed in all samples, which suggests that the phase change does not occur under the condition of both 450°C annealing and beam irradiation with high-energy and high-dose. The strongest peak at $2\theta = 25.3°$ corresponds to (101) anatase phase of $TiO_2$ crystal, the most stable crystal phase of anatase in thermodynamics. All XRD patterns from (1) to (5) in Fig. 1 are similar, which indicates the similar grain size of $TiO_2$ crystals. It implies that beam irradiation has no obvious impact on the grain size of $TiO_2$ in this experiment. The grain size of $TiO_2$ can be estimated as 30 nm by the Scherrer formula.

In Fig. 1(5), a weak peak of Pt is found, which implies the presence of crystal state of $Pt^0$ when the concentration of impregnating solution is high ($1 \times 10^{-1}$ mol/L). However, no Ag peak can be found in Fig. 1(4), which indicates the absence of crystallized Ag after electron beam irradiation even when the concentration of impregnating solution is high ($1 \times 10^{-1}$ mol/L). In the case of transition metal ion implantation, the obvious change of field emision scanning electron microscopy (FESEM) was not found in Fig. 1(2) and (3) after implantation and annealing process, which proved that the grain size of $TiO_2$ did not grow remarkably.

#### 3.1.2 FESEM

The FESEM photographs of Pt/$TiO_2$ films prepared by beam irradiation are shown in Fig. 2. It clearly shows the porous $TiO_2$ surface with particles around 30 nm in diameter, and the thickness of $TiO_2$ films is about 1.5 μm. It is obvious from Fig. 2(a) and (b) that Ag and Pt were reduced, deposited and agglomerated on the surface of $TiO_2$ films under electron beam irradiation. The Ag particles with a well uniform distribution are close to 30−70 nm in diameter. It has been proved in the previous work that the amount and size of Ag particles deposited on the surface of $TiO_2$ films increased with the increase in the concentration of $AgNO_3$ impregnating solution. Except for a few large particles, most Pt particles are smaller than Ag in size and some of Pt particles even smaller than $TiO_2$ particles. The amount and size of Pt particles deposited on the surface of $TiO_2$ films also increased with the increase in the concentration of impregnating solution. Figure 2(c) shows FESEM picture of transverse section of $TiO_2$ film after implanting $Cr^+$, it is noticeable that the implantation had no influence on the morphology of $TiO_2$ film. Figure 2 clearly demonstrates that high-energy beam irradiation did not destroy the surface structure.

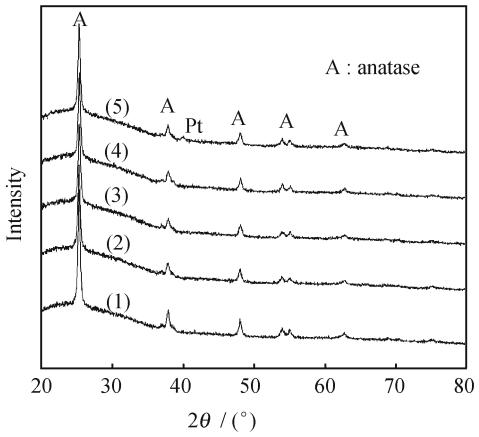


**Fig. 1** XRD pattern of $TiO_2$ films prepared by beam irradiation (1) $TiO_2$; (2) Cr/$TiO_2$ ($6 \times 10^{16}$ $cm^{-2}$, annealed at 450°C for 240 min); (3) V/$TiO_2$ ($6 \times 10^{16}$ $cm^{-2}$, annealed at 450°C for 240 min); (4) Ag/$TiO_2$ ($1 \times 10^{-1}$ mol/L) and (5) Pt/$TiO_2$ ($1 \times 10^{-1}$ mol/L)

#### 3.1.3 TEM

The TEM and EDX pictures of Ag/$TiO_2$ film are shown in Fig. 3. It clearly explores that the $TiO_2$ surface area is covered by tiny particles of Ag except for the lager particles observed in Fig. 2(a). Most Ag particles have sizes less than 2 nm. Meanwhile, very weak signals shown in EDX pattern (Fig. 3(b)) prove the presence of Ag.

In the experiment of electron beam irradiation, the concentration of impregnating solution varied from $1 \times 10^{-5}$ to $1 \times 10^{-1}$ mol/L. In radiochemical experiment, the solution with concentration under $1 \times 10^{-3}$ mol/L is called thin solution, and the solution with concentration above $1 \times 10^{-1}$ mol/L is called dense solution. In thin solution, the metal ion is reduced mainly by hydro-electron produced during electron beam irradiation, and then metal atoms aggregate and deposit. On the other hand, there is another way to reduce metal ions on the surface of $TiO_2$ films. During electron beam

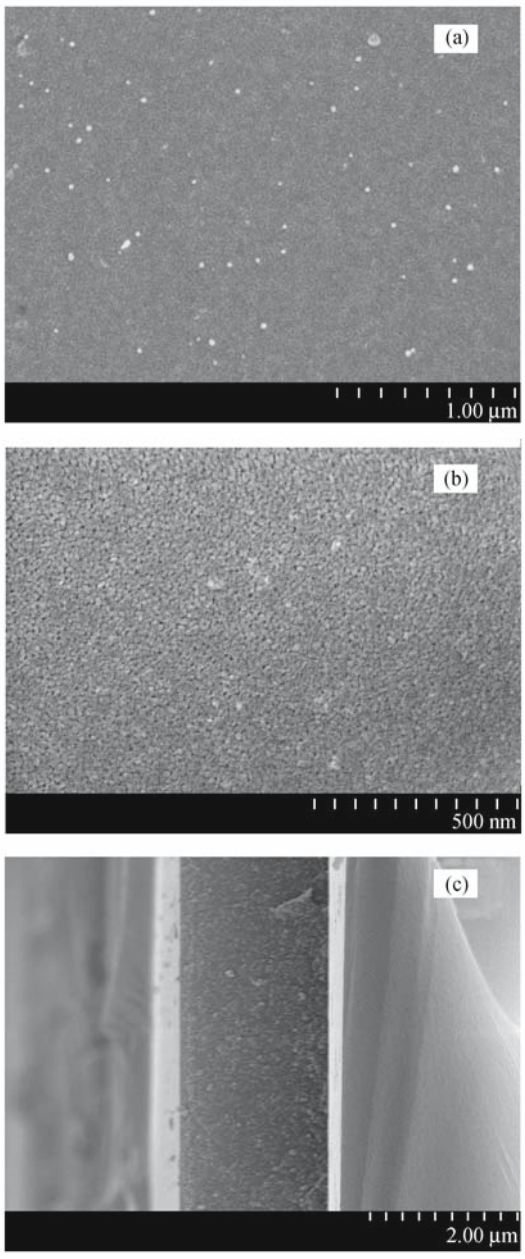


**Fig. 2** Field emission scanning electron microscopy photographs of $TiO_2$ films prepared by beam irradiation
(a) $Ag/TiO_2$ ($1 \times 10^{-1}$ mol/L), (b) $Pt/TiO_2$ ($1 \times 10^{-1}$ mol/L), (c) $Cr/TiO_2$ ($6 \times 10^{16}$ $cm^{-2}$)

irradiation, $Ti^{3+}$ is formed on the surface of $TiO_2$ due to the reduction of $Ti^{4+}$ by electron beam [11]. The $Ti^{3+}$ can therefore reduce metal ions absorbed on the surface of $TiO_2$ into atom [5,12]. In dense solution, apart from solvated electron, dry electron beam will play a major role in reducing noble metal ions in this experiment because of thin solution above $TiO_2$ films. A part of metal ions may be reduced by electron beam irradiation directly. Therefore, in Fig. 3, a lot of tiny Ag nano-particles were produced on the surface of $TiO_2$ film for the reason of short time and plentiful ways of reduction. The similar process occurred during the reduction of Pt by electron beam irradiation.

### 3.1.4 UV-Visible spectra

The optical transmittance spectra of the $TiO_2$ film prepared by beam irradiation are shown in Fig. 4. It exhibits clearly red shift for the $TiO_2$ films modified by beam irradiation. The $TiO_2$ films modified by implantation show a larger red shift than those films modified by electron beam, and exhibit further red shift after annealing. The red shit also varies with the modifying metal ions, and the order is $V > Cr > Pt > Ag$. Compared with the samples modified by electron beam irradiation, $TiO_2$ films modified by implantation can absorb more visible light.

## 3.2 Photocatalytic efficiency of $TiO_2$ films modified by beam irradiation

First, pure $TiO_2$ films were tested under visible light irradiation (Fig. 5). The pure $TiO_2$ films show a weak degradation of MO under visible light excitation due to the defects on the surface of $TiO_2$ films and impurities, such as V and Ca, diffused into $TiO_2$ films from substrate. In Fig. 5, the solid lines are exponentially fitted to the experimental data that give the pseudo-first-order rate constant $k$ (0.006 3 $h^{-1}$) of MO degradation. In the report of Yamashita et al. [8,9], implanted $TiO_2$ films showed better photocatalytic efficiency after 450°C annealing process. Therefore, the annealed sample was also tested and the result is listed in Fig. 5. The process of decomposing MO still accords with pseudo-first-order rule, but the photocatalytic efficiency of the film decreases dramatically ($k = 0.001\ 7\ h^{-1}$). The research of Beydoun and Amal [13] showed that the ability of absorbing –OH and water vapour can be decreased after the annealing process, and then the photocatalytic efficiency decreases.

The degradation of MO by modified $TiO_2$ films under visible light still obeys the rule of pseudo-first-order, so the photocatalytic efficiencies can be compared with each other using the rate constant $k$. The photocatalytic efficiencies of $TiO_2$ films modified by electron beam irradiation are listed in Table 1 in comparison with those of pure $TiO_2$ film. The photocatalytic efficiencies of $Ag/TiO_2$ and $Pt/TiO_2$ films

**Table 1** Photocatalytic efficiency of $TiO_2$ films prepared by electron beam irradiation under visible light irradiation

| Sample | Concentration of immerging solution (mol/L) | $k$ ($\times 10^{-3}$ $h^{-1}$) | Multiple |
|---|---|---|---|
| $Ag/TiO_2$ | $1 \times 10^{-5}$ | 6.9 | 1.1 |
| | $1 \times 10^{-4}$ | 9.5 | 1.5 |
| | $1 \times 10^{-3}$ | 13.2 | 2.1 |
| | $1 \times 10^{-2}$ | 15.1 | 2.4 |
| | $1 \times 10^{-1}$ | 9.5 | 1.5 |
| $Pt/TiO_2$ | $1 \times 10^{-5}$ | 14.5 | 2.3 |
| | $1 \times 10^{-4}$ | 22.1 | 3.5 |
| | $1 \times 10^{-3}$ | 22.7 | 3.6 |
| | $1 \times 10^{-2}$ | 23.9 | 3.8 |
| | $1 \times 10^{-1}$ | 18.9 | 3.0 |

Note: $k = 0.006\ 3\ h^{-1}$ for $TiO_2$.

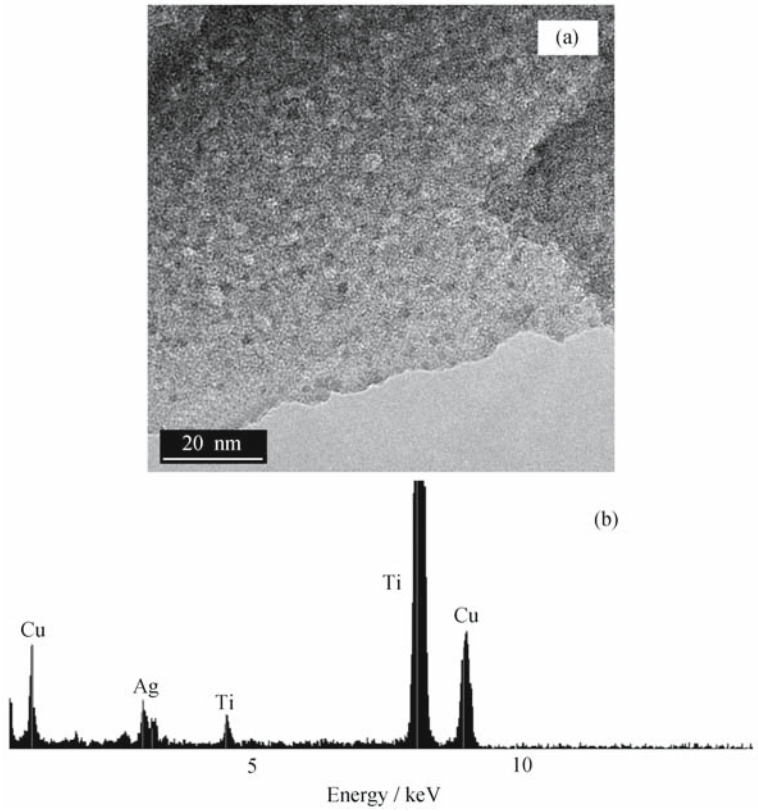


**Fig. 3** (a) TEM photograph and (b) EDX spectrum of $Ag/TiO_2$ film prepared by electron beam irradiation

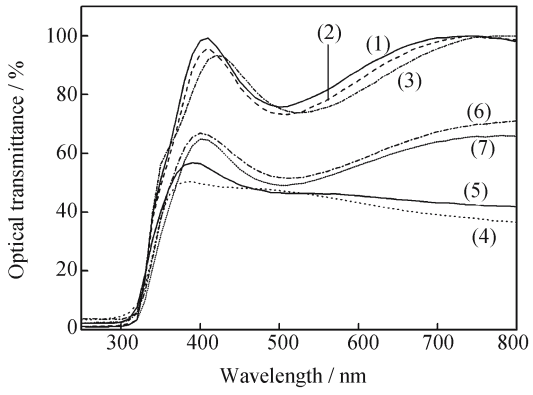


**Fig. 4** UV-Vis spectra of $TiO_2$ films prepared by beam irradiation (1) $TiO_2$; (2) $Ag/TiO_2$ ($1 \times 10^{-1}$ mol/L); (3) $Pt/TiO_2$ ($1 \times 10^{-1}$ mol/L); (4) $Cr/TiO_2$ ($6 \times 10^{16}$ $cm^{-2}$); (5) $V/TiO_2$ ($6 \times 10^{16}$ $cm^{-2}$); (6) $Cr/TiO_2$ ($6 \times 10^{16}$ $cm^{-2}$, annealed at 450°C for 240 min) and (7) $V/TiO_2$ ($6 \times 10^{16}$ $cm^{-2}$, annealed at 450°C for 240 min)

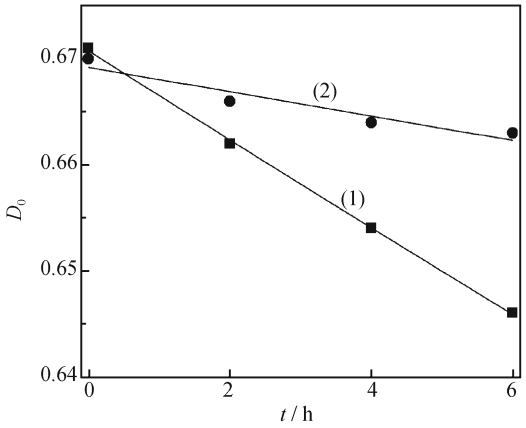


**Fig. 5** Photocatalytic activity of $TiO_2$ films under visible light irradiation (1) $TiO_2$; (2) $TiO_2$, annealed at 450°C for 240 min

increase with the increase in the concentration of impregnating solution. The $Ag/TiO_2$ and $Pt/TiO_2$ films impregnated in $1 \times 10^{-2}$ mol/L solution exhibit the best photocatalytic efficiency. The values of $k$ at this point are about 2.4 ($Ag/TiO_2$) and 3.8 ($Pt/TiO_2$) times of that pure $TiO_2$ film. With further increase in the concentration of impregnating solution, the photocatalytic efficiency decreases.

When noble metal contacts with $TiO_2$, Schottky barrier will be formed and electron will transfer from the $TiO_2$ film to noble metal [14,15], and then the opportunity of recombination of electron-hole pair decreases. The work function of Pt is higher than that of Ag, so $Pt/TiO_2$ shows better photocatalytic efficiency. The research of Liu et al. [16] shows that the work function of noble metal is influenced by the particle size. The particle size has an optimum value. If the size of noble metal particles is too large, the work function will be decreased, and then electron can not be transferred efficiently. With the increase in the concentration of impregnating solution, the size of the noble metal particles also increases. The photocatalytic efficiency of $TiO_2$ films

**Table 2** Enhanced multiple of photocatalytic efficiency of $TiO_2$ films implanted by ion beam under visible light irradiation

| Sample | Implantation dose ($10^{16}$ cm$^{-2}$) | Without annealing | | Annealed at 450°C for 240 min | |
|---|---|---|---|---|---|
| | | $k$ ($\times 10^{-3}$ h$^{-1}$) | Multiple | $k$ ($\times 10^{-3}$ h$^{-1}$) | Multiple |
| $V/TiO_2$ | 0.6 | 17 | 2.7 | 4.8 | 2.7 |
| | 1 | 18.3 | 2.9 | 6.8 | 4.0 |
| | 3 | 12.6 | 2.0 | 4.3 | 2.5 |
| | 6 | 8.2 | 1.3 | 3.2 | 1.9 |
| $Cr/TiO_2$ | 0.6 | 12.6 | 2.0 | 4.9 | 2.9 |
| | 1 | 15.8 | 2.5 | 6.1 | 3.6 |
| | 3 | 14.5 | 2.3 | 3.9 | 2.3 |
| | 6 | 10.7 | 1.7 | 3.1 | 1.8 |

Note: $k = 0.006\ 3$ h$^{-1}$ for $TiO_2$ annealed at 450°C for 240 min.

modified by electron beam irradiation will be the best when the size of noble metal particles is appropriate. If the concentration of impregnating solution further increases, the size of the noble metal particles enlarges accordingly, and the photocatalytic efficiency decreases. In Fig. 3, a large amount of tiny particles smaller than 2 nm were produced by electron beam irradiation when the concentration of impregnating solution was high. A large part of surface area of $TiO_2$ films was covered by such tiny particles, so the surface area that can be irradiated by visible light decreased too, which reduced the photocatalytic efficiency of $TiO_2$ films modified by electron beam irradiation. The virtue of electron beam irradiation is that noble metal particles can be reduced and deposited in a short time, and the size of noble particles prepared by this method is smaller than that by traditional photodeposition method. The results of Li and Li [5] showed that sub-energy-levels could be produced between the band gaps of $TiO_2$ by the dispersion of noble metal particles, which was proved by the experimental results of UV-Visible spectra and photodegradation by visible light excitation.

The photocatalytic efficiencies of implanted $TiO_2$ films are listed in Table 2 for comparison with pure $TiO_2$ film. The results show that the rate constants $k$ of $V/TiO_2$ and $Cr/TiO_2$ films are related to the implanted ion fluences. The maximum degradation was found at the fluence of $1 \times 10^{16}$ cm$^{-2}$. The values of $k$ at this point are about 2.9 ($V/TiO_2$) and 2.5 ($Cr/TiO_2$) times of that of pure $TiO_2$ film, and are enhanced to 4.0 ($V/TiO_2$) and 3.6 ($Cr/TiO_2$) times of that of pure $TiO_2$ film after annealing process. However, it should be noticed that the $k$ decreases after annealing, so the photocatalytic efficiencies of $V/TiO_2$ and $Cr/TiO_2$ actually decrease rather than increase after annealing process. In the previous work [6], this phenomenon was not noticed for the weak visible light irradiation (1,400 LUX) and short experimental time (8 h).

Yamashita et al.'s experiment [8,9] and Nishikawa et al.'s calculation [17] proved that implanted $V^+$ could replace the position of $Ti^{4+}$ in the $TiO_2$ lattice, and then the band structure of $TiO_2$ was changed. This structure will endow the films with the capability of absorbing visible light. The band gap of $TiO_2$ decreases with the increase in the implanted transition metal ions, so the photocatalytic efficiency of $TiO_2$ films increases with the increase in fluence. However, the $V^+$ ions also serve as the recombination centers for the photo-induced electrons and holes, which counteract the decrease in band gap. When the fluences of implantation are above the optimal value, the photocatalytic efficiency reduces.

Annealing process can make more implanted $V^+$ replace the $Ti^{4+}$ [8,9], and reduce band gap of implanted $TiO_2$ films, which can be proved by the red shift of UV-Visible spectra. However, the photocatalytic efficiency of implanted $TiO_2$ films is determined by not only band gap of $TiO_2$, but also the absorbing ability of light. When the implanted $TiO_2$ films were annealed, its photocatalytic efficiency was declined in fact (Table 2).

## 4 Conclusions

The red shift in UV-Visible spectra of $TiO_2$ films takes place by beam irradiation (the implantation of transition metal ions and the deposition of noble metal particles by electron beam irradiation), and the photocatalytic efficiency of modified $TiO_2$ films is enhanced. Therefore, the method of beam irradiation is an effective way to produce visible light responsive $TiO_2$ films. The photocatalytic efficiency of $TiO_2$ films modified by the deposition of noble metal particles using electron beam irradiation is influenced by the concentration of impregnating solution. The photocatalytic efficiency of the implantation of transition metal ions is influenced by the fluences of implanted ions. There is an optimal value of $k$ in both cases.

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