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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 (TEM), X-ray diffraction (XRD), ultraviolet-visible (UV-Vis), energy dispersive X-ray analysis (EDX) and photo-oxidation of methyl orange (MO) were used to characterize and evaluate the photocatalytic activity of improved TiO$_2$ films.

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 × 10$^{15}$, 1 × 10$^{16}$, 3 × 10$^{16}$ and 6 × 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$_2$PtCl$_6$ or AgNO$_3$ solutions with concentrations of 10$^{-3}$, 10$^{-4}$, 10$^{-5}$, 10$^{-6}$ and 10$^{-7}$ 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 $2\theta = 25.3^\circ$ 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 $1 \times 10^{-1}$ 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 ($1 \times 10^{-3}$ mol/L). In the case of transition metal ion implantation, the obvious change of field emission 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.

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 larger 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 $1 \times 10^{-3}$ mol/L. In radiochemical experiment, the solution with concentration under $1 \times 10^{-5}$ mol/L is called thin solution, and the solution with concentration above $1 \times 10^{-3}$ 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...