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Preparation and characterization of Zr doped TiO_2 nanotube arrays on the titanium sheet and their enhanced photocatalytic activity

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ABSTRACT

This paper described a new method for the preparation of Zr doped TiO_2 nanotube arrays by electrochemical method. TiO_2 nanotube arrays were prepared by anodization with titanium anode and platinum cathode. Afterwards, the formed TiO_2 nanotube arrays and Pt were used as cathode and anode, respectively, for preparation of Zr/TiO_2 nanotube arrays in the electrolyte of 0.1 M $Zr(NO_3)_4$ with different voltage and post-calcination process. The nanotube arrays were characterized by field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS) and UV–Vis diffusion reflection spectra (DRS). The photocatalytic activities of these nanotubes were investigated with Rhodamine B as the model pollutant and the results demonstrated that the photocatalytic efficiency of Zr doped TiO_2 nanotubes was much better than that of TiO_2 nanotubes under UV irradiation. Zr/TiO_2 nanotube arrays doped at 7 V and calcined at 600 °C (denoted as TiO_2-7 V-600) achieved the best photocatalytic efficiency and the most optimal doping ratio was 0.047 (Zr/Ti). TiO_2-7 V-600 could be reused for more than 20 times and maintained good photocatalytic activities.

1. Introduction

TiO_2 nanotube have received considerable attention in recent years because of its higher surface area, better adsorption ability and higher photocatalytic activity in comparison with TiO_2 powders [1]. Hydro-thermal method has been widely used to prepare TiO_2 nanotube [2,3]. However, TiO_2 nanotubes prepared with such method are difficult to be recovered and reused and also are limited in the applications. Nowadays there is a creative way to solve this problem, which is to prepare oriented nanotubes on substrates and create ordered arrays. Many developed methods have been reported [4,5] and anodic oxidation is a simple, cheap and straight-forward method to prepare highly ordered TiO_2 nanotube arrays on Ti substrate [6,7]. It has been found that the morphology of TiO_2 nanotube arrays prepared by anodic oxidation is affected by the anodization voltage and time, electrolyte composition and temperature, etc. [4,8–11]. Owing to their tight coherence to the Ti substrate and recyclable property, TiO_2 nanotube arrays prepared by anodization have been widely studied in photoelectrocatalysis [12], dye-sensitized solar cells [13], and water splitting [14,15] in recent years.

During the procedure for improving the photocatalytic activity of TiO_2, various methods such as element doping [16–21], noble metal deposition [22,23], surface modification [24] and semiconductor composition [25] have been carried out, among them, doping element into TiO_2 lattice is an effective way [16–21]. It has been found that some metals such as transitional metals Zn, Cr and Fe doping can improve the separation rate of photo-induced electrons and holes and enhance the photocatalytic activity of TiO_2 [19,21,26]. Nonmetal doping such as Si, F, C, N can either increase the photocatalytic efficiency [27] or extend the absorb band to visible light regions [28–30].

Zr and Ti are both IV B elements and have the similar atom semidiameters (Ti, 2 Å; Zr 2.16 Å) and the same valent state (+4). Both oxides TiO_2 and ZrO_2 are n-type semiconductors with similar physicochemical properties. Therefore, it is possible for Zr atom to enter into the TiO_2 lattice and substitute for Ti atom. Both of our previous work [31,32] and others' research [33,34] have demonstrated that incorporating Zr^{4+} into TiO_2 can introduce lattice defects and lead to higher photocatalytic activity than that of pure TiO_2.

The goal of present study is to prepare Zr doped TiO_2 nanotube arrays on Ti sheet and further investigate their photocatalytic efficiencies.

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2. Experimental

2.1. Experimental materials

Titanium sheets (0.2 mm thick, 10 × 20 mm size) with 99.6% purity (Beijing, China) were polished with metallographic abrasive paper, and then were degreased by sonicating in acetone, isopropanol and methanol, respectively. The sheets were air-dried after rinsing with deionized water. Pt electrode was obtained from Shanghai Ruosull Technology Co. Ltd. Acetone, isopropanol, methanol, NaF, H_3PO_4, $Zr(NO_3)_4$ and Rhodamine B were all of analytical grade. Deionized water was selfmade in laboratory.

2.2. Experimental methods

2.2.1. Preparation of TiO_2 nanotube arrays

The anodic oxidation was accomplished with a 30 V potentiostat (JWY-30G, Shijiazhuang, China) using titanium sheet as anode and platinum as cathode. The distance between two electrodes was 3 cm in all experiments. The electrolyte was composed of 0.14 M NaF and 0.5 M H_3PO_4 [35]. The anodic oxidation was carried out at 20 V for 30 min. After electrolysis, titanium sheet was rinsed with deionized water and then air-dried.

2.2.2. Preparation of Zr doped TiO_2 nanotube arrays

In this step, Ti sheet with TiO_2 nanotube arrays was used as cathode and platinum as anode. The electrolyte was 0.1 M $Zr(NO_3)_4$ and the voltage was adjusted to 3, 7, 10 and 15 V, respectively. The distance between two electrodes was kept as 3 cm. The entire electrochemical process was maintained for 1 h. After then, Ti sheet was rinsed by deionized water and dried in air.

2.2.3. Calcination

Ti sheets with Zr/TiO_2 and TiO_2 nanotube arrays were calcined in air for 2 h at the temperature of 400, 500, 600 and 700 °C, respectively. In order to easily exhibit the corresponding preparation and calcination methods of the TiO_2 nanotubes, they were denoted as TiO_2-*x*-*y* or TiO_2-*y*, where *x* stands for the voltage of electrochemical process and *y* stands for calcining temperature. For example, TiO_2-3 V-400 indicates TiO_2 nanotube arrays were doped at 3 V and then calcined at 400 °C, while TiO_2-400 were pure TiO_2 nanotube arrays calcined at 400 °C.

2.2.4. Characterization

The morphological features of the nanotube arrays were assessed using a field emission scanning electron microscope (S-4800 FESEM, Hitachi, Japan). The crystal structure was characterized by an X-ray diffractometer (DX-2000, Cu$K\alpha$ radiation, 35 kV, λ=1.5418 Å). The X-ray photoelectron spectroscopy (XPS) measurements were performed by an Axis Ultra spectrometer (KRATOS ANALYTICAL Ltd., England). UV–Vis DRS were carried out using a U-3010 (Hitachi). Fine $BaSO_4$ powder was used as baseline and the spectra were recorded in a range of 250–800 nm.

2.2.5. Photocatalytic activity measurements

Photocatalytic reaction equipment was described in Fig. 1. Oxygen flowed into the 10 mL Rhodamine B solution at a rate of 0.2 L/min. TiO_2 nanotube arrays on titanium sheet were fixed in the middle of the solution and faced to the lamp. Dark reaction was done at the same conditions without irradiation. Rhodamine B degradation under UV irradiation without catalyst was also tested.

The concentration of Rhodamine B was detected at 550 nm every 10 min during the whole irradiation by a 722 UV–Vis spectrophotometer. The reaction constants were calculated after deducting the dark reaction and degradation of Rhodamine B without catalyst.

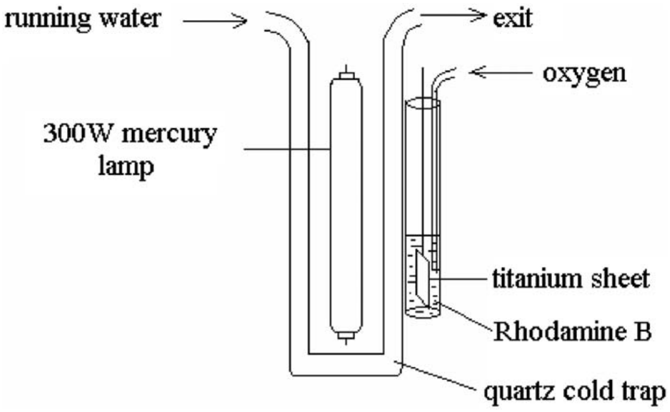

Fig. 1. Photocatalytic reaction equipment.

3. Results and discussions

3.1. Morphology of TiO_2 and Zr/TiO_2 nanotube arrays

After anodic oxidation for 30 min, highly ordered nanotube arrays were fabricated on Ti sheet. Fig. 2(a) and (b) were the top and cross-sectional views of annealed TiO_2 nanotubes from FESEM analysis. Fig. 2(c) was the top-view of Zr/TiO_2-7 V-600. These images showed that the nanotubes in TiO_2 layer had an average diameter of 70 nm and approx 400 nm in length. The wall thickness was about 20–30 nm. Zr-doping did not change the morphology of nanotube arrays significantly, which indicated a uniform doping of Zr into TiO_2 nanotubes.

3.2. XRD analysis

Fig. 3 showed XRD spectra of TiO_2 and TiO_2-7 V nanotube arrays that were annealed at different temperatures. Nanotube arrays were amorphous before calcinations. Crystals were formed during annealing [36]. Anatase phase was the main style when calcined at 400 °C, rutile phase appeared when annealing temperature increased to 600 and was dominant at 700 °C.

Two peaks of 27.4°(110) and 36.0°(101) were chosen to calculate the lattice constants of TiO_2 and Zr/TiO_2 at the temperature of 600 and 700 °C. The results were presented in Table 1. Because the diameter of Zr atom is larger than that of Ti atom, when Zr substituted for Ti into the TiO_2 lattice, the lattice constants became larger.

3.3. XPS analysis

The XPS spectra of TiO_2-7 V-600 before and after calcinations were shown in Fig. 4. The surfaces of the samples were composed of Ti, O, Zr and C contaminants (a). There were obvious zirconium signals in the samples. Zr 3*d* peak (b) existed at 182.0 and 184.2 eV, which was very close to the binding energy of Zr 3*d* peaks in ZrO_2 (182.2 and 184.7 eV [37]), indicating Zr was in the oxidation state of +4. O 1*s* peaks before and after calcinations were shown in Fig. 4(c) and (d). Before calcinations, O 1*s* peak could be fitted by two peaks, a main peak at 530.0 eV, ascribed to Ti–O bond and the additional peak at 531.3 eV related to O–H [38]. After calcinations, the two peaks moved to 529.6 and 531.9 eV,

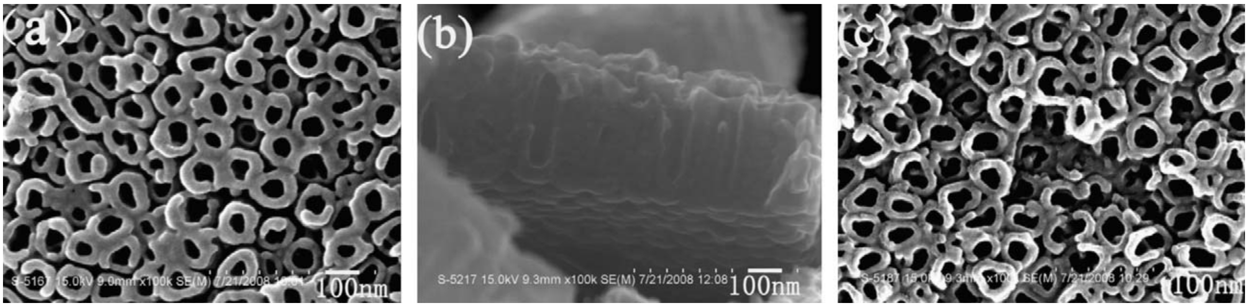

Fig. 2. FESEM images of TiO_2-600 nanotube arrays. (a) Top-view, (b) cross-sectional view and (c) top-view of Zr/TiO_2-7 V-600.

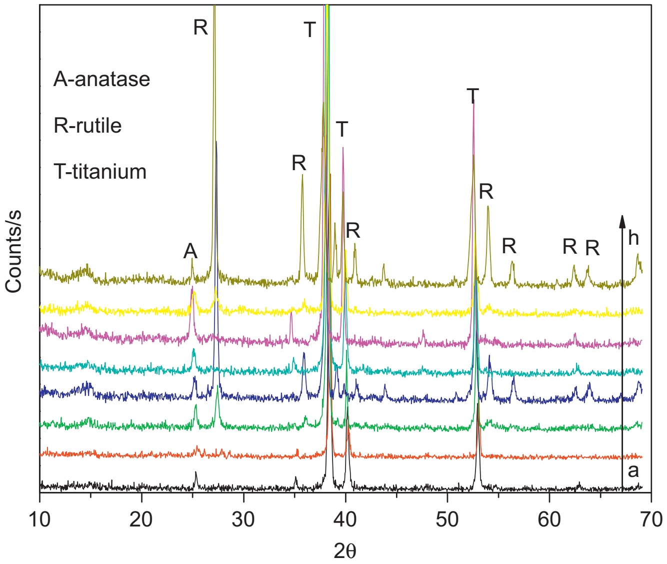

Fig. 3. XRD spectra of (a) TiO_2-400, (b) TiO_2-500, (c) TiO_2-600, (d) TiO_2-700, (e) TiO_2-7 V-400, (f) TiO_2-7 V-500, (g) TiO_2-7 V-600 and (h) TiO_2-7 V-700.

Table 1
Lattice constants of TiO_2 and Zr/TiO_2 at 600 and 700 °C.

	a=*b*	*c*
TiO_2-600	0.44588	0.29024
Zr/TiO_2-600	0.44671	0.29047
TiO_2-700	0.44623	0.29082
Zr/TiO_2-700	0.44969	0.29190

respectively, and a new peak of 530.7 emerged, this was assigned to O–Zr link [39].

Intriguingly, the concentration of Zr on the surface of TiO_2 was enhanced with the increase of doping voltage—the Zr/Ti ratios derived from XPS analysis were 0.028, 0.047, 0.061 and 0.120, respectively, corresponding to the voltage from 3, 7, 10 to 15 V.

3.4. *UV–Vis diffuse reflection spectra analysis*

Fig. 5 showed UV–Vis diffuse reflection spectra of different samples after calcining at 600 °C. The absorbance spectra of doped TiO_2 nanotubes were similar to that of pure TiO_2 nanotubes. All the samples exhibited a broad band absorption in ultraviolet regions (<400 nm) and showed no obvious peaks. Compared with pure TiO_2 nanotubes, TiO_2-3 V-600 and TiO_2-7 V-600 exhibited higher absorption, while TiO_2-10 V-600 and TiO_2-15 V-600 showed lower absorption in ultraviolet regions. All the samples also showed some visible light absorbance (>400 nm), which was possibly caused by the color of titanium.

3.5. *Results of photocatalytic activity*

After deducting the dark reaction and photodegradation without catalyst, the degradation of Rhodamine B with catalyst was in accordance with first-order kinetics by the linear transform equation $\ln(C_0/C_t)=kt$. In which, C_0 is the initial concentration of Rhodamine B, C_t is the instant concentration of Rhodamine B, k is kinetic constant, and t is time interval. The corresponding kinetic constants were presented in Table 2. It was found that all samples calcined at 600 °C exhibited higher photocatalytic efficiencies because of the formation of the mixed crystalline structure, which indicated that 600 °C was the most optimal annealing temperature both for pure TiO_2 and Zr/TiO_2 nanotube arrays. This result was in agreement with previous report [27] that mixed crystalline structure exhibits more efficient photocatalytic activity. Rhodamine B had been degraded more than 90% in 40 min by all of the photocatalysts calcined at 600 °C. All doped TiO_2 nanotube arrays exhibited higher photocatalytic activities than that of pure TiO_2 nanotube arrays.

Based on the experimental results, Zr-doping induced the increase of the photocatalytic efficiency. The reason may result from two aspects. On the one hand, Zr doping into the TiO_2 lattice results in relatively larger lattice strain. To offset this strain, lattice oxygen, especially surface oxygen atom can escape from the lattice and exist as a hole trap [21]. On the other hand, Zr-doping introduces a few defects into a TiO_2 matrix, it is preferential for electrons to be trapped on Zr^{4+} than on Ti^{4+}, these defects can play the role of trapping centers to inhibit charge recombination and improve the photoactivity [33,34].

Compared with the other doped TiO_2 nanotube arrays, TiO_2-7 V exhibited higher photocatalytic activity at all temperatures. TiO_2-7 V-600 achieved the highest efficiency, which was 1.55 times than that of pure TiO_2-600. Moreover it was found that the most optimal doping amount of zirconium into TiO_2 was Zr/Ti 0.047. Generally, when the doped zirconium amount is small (from TiO_2-3 V to TiO_2-7 V), zirconium can enter into the lattice of TiO_2 entirely during the calcining process and act as defect positions, through which the separation rate of photo-excited electrons and holes is improved. As a result, the photocatalytic efficiency of doped TiO_2 nanotubes is improved. However, when the amount of zirconium increases over a certain amount (TiO_2-7 V to TiO_2-15 V), some of them are unable to enter into the TiO_2 lattice.

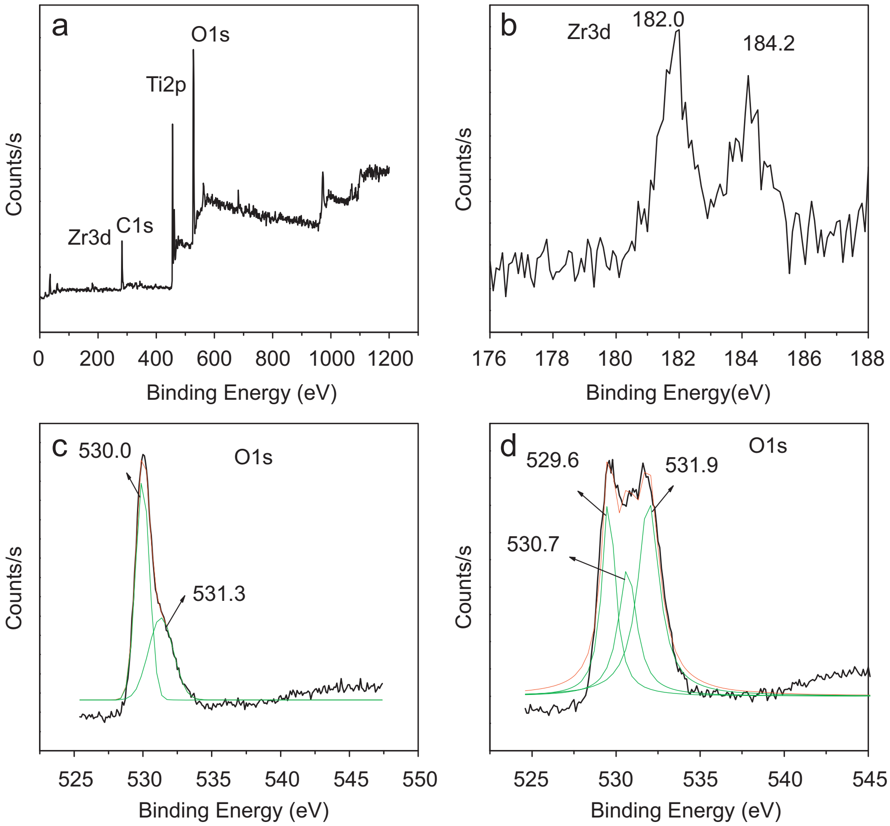

Fig. 4. XPS spectra of TiO_2-7 V-600. (a) Survey spectra, (b) Zr 3*d* spectra, (c) O 1*s* spectra before calcining and (d) O 1*s* spectra after calcining.

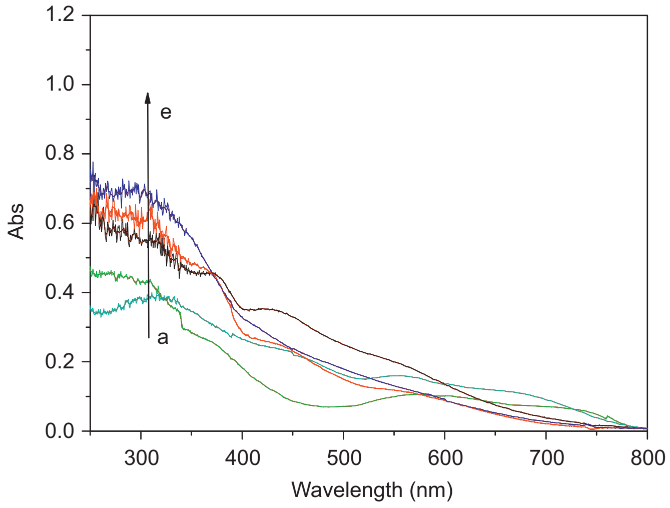

Fig. 5. UV–Vis diffuse reflection spectra of (a) TiO_2-15 V-600, (b) TiO_2-10 V-600, (c) TiO_2-600, (d) TiO_2-7 V-600 and (e) TiO_2-3 V-600.

Table 2
Kinetic constants for Rhodamine B degradation.

Temperature (°C)	TiO_2	TiO_2-3 V	TiO_2-7 V	TiO_2-10 V	TiO_2-15 V
400	0.04270	0.05219	0.06464	0.05843	0.05808
500	0.05350	0.05451	0.05915	0.05475	0.05364
600	0.06048	0.06556	0.09354	0.06594	0.06372
700	0.05465	0.05573	0.05774	0.05792	0.05960

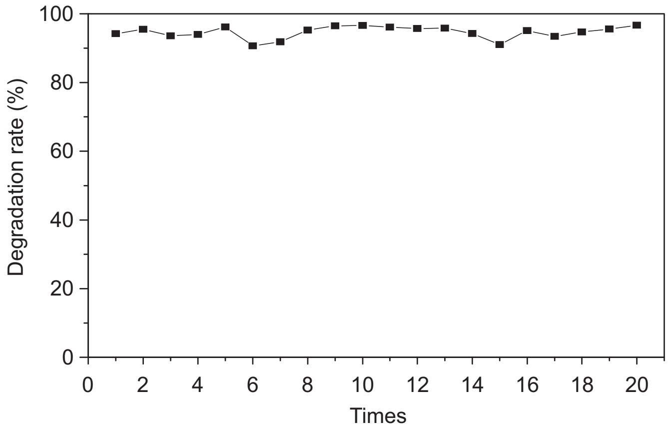

Fig. 6. Repeating photocatalytic experiments of TiO_2-7 V-600.

This part of zirconium acts as recombination sites on the surface of TiO_2 nanotube arrays. Hence, the photocatalytic efficiency decreased along with the further increase of doping amount of zirconium [31].

3.6. *Stability test*

To evaluate the stability of catalysts, the photocatalytic test of the TiO_2-7 V-600 nanotube arrays were repeated for up to 20 times. The results were demonstrated in Fig. 6. As can be seen, the photocatalytic ability of the nanotube arrays did not change significantly after reusing for more than 20 times. This indicated that the Zr/TiO_2 nanotube arrays prepared in the present study had good photocatalytic stability and could be reused.

4. Conclusions

Zr/TiO_2 nanotube arrays have been successfully fabricated by two-step electrochemical process. Calcining process facilitated Zr entering into TiO_2 lattice. The photocatalytic results proved that Zr doping was able to increase the photocatalytic efficiency and the most optimal doping ratio was 0.047 (Zr/Ti). Meanwhile the experimental results demonstrated that the nanotube arrays fabricated in the present study had good photocatalytic stability and could be reused for many times.

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