Doping a metal (Ag, Al, Mn, Ni and Zn) on TiO₂ nanotubes and its effect on Rhodamine B photocatalytic oxidation

Xinghua Gao^{1,3}, Beihai Zhou^{1,2*}, Rongfang Yuan^{1,2}

¹Department of Environmental Engineering, School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

²Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

³CECEP Water Engineering Co. Ltd., China Energy Conservation and Environmental Protection Group, Beijing 100082, China

ABSTRACT

The effects of ion-doping on TiO₂ nanotubes were investigated to obtain the optimal catalyst for the effective decomposition of Rhodamine B (RB) through UV photocatalytic oxidation process. Changing the calcination temperature, which changed the weight fractions of the anatase phase, the average crystallite sizes, the BET surface area, and the energy band gap of the catalyst, affected the photocatalytic activity of the catalyst. The ionic radius, valence state, and configuration of the dopant also affected the photocatalytic activity. The photocatalytic activities of the catalysts on RB removal increased when Ag⁺, Al³⁺ and Zn²⁺ were doped into the TiO₂ nanotubes, whereas such activities decreased as a result of Mn²⁺ or Ni²⁺ doping. In the presence of Zn²⁺-doped TiO₂ nanotubes calcined at 550°C, the removal efficiency of RB within 50 min was 98.7%.

Keywords: Ion-doping, Photocatalytic oxidation, Rhodamine B, TiO₂ nanotubes

1. Introduction

Rhodamine B is a representative of xanthenes cationic dyes and is known for its stability [1]. It is harmful if swallowed and capable to cause irritation to the skin, eyes and respiratory tract. Photocatalytic oxidation is highly efficient in generating ·OH for the degradation of the pollutants [2].

Several techniques have been developed to treat RB. Ozone-ultra-violet (O₃/UV) photocatalytic oxidation is highly efficient in generating ·OH for the degradation of pollutants [2]. The choice of photocatalysis is essential in RB removal, and TiO₂ is a good candidate. TiO₂-photocatalyzed reactions are non-selective oxidation processes in a level of microgram per liter, and the use of TiO₂ is effective for inactive substrates [3]. Moreover, the presence of solid particles in TiO₂ can provide additional nuclei for bubble formation, thereby enhancing the degradation efficiency of pollutants [4].

Compared with its powder form, TiO₂ nanotubes have a larger Brunauer-Emmett-Teller (BET) surface area (S_{BET}), which is advantageous in one-electron oxidation during photocatalytic reactions [5, 6]. However, the relatively large bandgap of TiO₂ (3.2 eV) limits the efficiency of photocatalytic reactions because of the high re-

combination rate of photogenerated electrons and holes [7]. To solve this problem, metal ions were doped into the TiO₂ nanotubes to narrow the bandgap of TiO₂, as well as reduce the recombination rate of electrons and holes because of the generation of crystal defect caused by ion-doping [7–9]. In addition, the doped ions can act as shallow trapping sites for electrons and holes, and then reacted with H₂O₂, OH⁻ and O₂ to generate ·OH and O₂·- radicals.

In this study, the effect of metal ion-doping on the photocatalytic activity of TiO₂ nanotubes for RB removal via photocatalytic oxidation was investigated. Metal ions, including Ag⁺, Al³⁺, Mn²⁺, Ni²⁺ and Zn²⁺, were investigated, and Zn²⁺ was observed to be the optimum type. Characteristic analyses of the TiO₂ nanotubes were conducted to determine the factors that affect the photocatalytic activities of the catalysts.

2. Materials and Methods

2.1. Materials

P-25 TiO₂ was provided by the Degussa Corporation (Richfield Park, USA). The powder has an S_{BET} of 50 m²/g, an average crystallite

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* Corresponding author

Email: zhoubeihai@sina.com

Tel: +010-62334821 Fax: +010-62334821

size of 21 nm, and a crystal structure of 80% anatase and 20% rutile. RB (A.R.) was purchased from Beijing Chemical Reagent Company (China). Microporous membrane (0.45 μm) (MPM) was purchased from Agela Technologies (China).

A photocatalytic reactor (60 mm diameter and 750 mm length), which was equipped with a 37 W 254 nm UV lamp (15 mm Dia. And 793 mm Lth.) purchased from Haili Lighting Equipment Company (China), was used in this experiment. O_2 , which was generated by an oxygenator (Yaao, China), was used to produce O_3 with the help of an ozone generator (Tonglin, China). O_3 was guided into the photocatalytic reactor through the bottom port, and the samples were acquired from the sampling port in the middle of the reactor.

2.2. Preparation of TiO_2 Nanotubes

One gram of P-25 TiO_2 was added into 16 mL of a 10 mol/L NaOH aqueous solution in a Teflon vessel. The mixture was then stirred for 2 h at room temperature. The mixture was then heated at 110°C for 24 h in an oven, and cooled to room temperature in air. The as-prepared precipitate ($\text{Na}_2\text{Ti}_3\text{O}_7$) was washed with distilled water to achieve a pH of 7 and then subsequently dispersed in a 0.1 mol/L HCl aqueous solution. After ultrasonication for 30 min, the precipitate was continuously washed to achieve a pH of 7 and then dried at 60°C. The nanotubes were prepared by calcining the precipitate at 400–600°C for 2 h.

The ion-doped TiO_2 nanotubes were prepared based on the aforementioned process except for adding AgNO_3 (0.0213 g), AlCl_3 (0.0167 g), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.0313 g), NiCl_2 (0.0162 g) or ZnCl_2 (0.0170 g) into the 10 mol/L NaOH solution. The amounts of doping ions which were added in the solution were 1.0% (atom percentage). According to the atlases of energy distribution, the doping concentrations of Ag^+ , Al^{3+} , Mn^{2+} , Ni^{2+} and Zn^{2+} ions were 0.251%, 0.618%, 0.498%, 0.459% and 0.372%, respectively. A 0.1 mol/L HNO_3 solution was used instead of an HCl solution for the preparation of Ag^+ -doped TiO_2 .

2.3. Characterization of TiO_2 Nanotubes

X-ray diffraction (XRD) patterns were collected using a Rigaku Dmax-RB diffractometer (Tokyo, Japan). The surface elemental composition of TiO_2 was recorded via X-ray photoelectron spectroscopy (XPS, AXIS ULTRA^{DLD}, Kratos Analytical, UK). Transmission electron microscopy (TEM) images were obtained using a HITACHI HT-7700 electron microscope (Tokyo, Japan). S_{BET} was measured using the Quadrasorb SI-MP apparatus (Quantachrome Instrument, USA). Diffuse reflectance spectroscopy (DRS) analyses were performed using a HITACHI U-3010 UV-vis scanning spectrophotometer (Tokyo, Japan).

2.4. Photocatalytic Activity Tests

Aqueous slurries were prepared by adding 0.15 g of TiO_2 -based photocatalyst to 1500 mL of 20 mg/L RB aqueous solution at pH 7. The aqueous slurries were stirred and bubbled with O_3 (1 L/min, 10%) for 30 min and then irradiated with a 254 nm UV lamp. Every 10 min, a 20 mL sample was acquired and mixed with 0.5 mL of 0.5 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ solution to stop the reaction. The sample was filtered through an MPM to separate the catalyst.

The concentration of RB was determined using a UV-visible spectrophotometer (DR5000, Hach).

3. Results and Discussion

3.1. Characterization of Photocatalysts

3.1.1. Morphology of the catalysts

Transmission electron microscopy was performed to observe the morphology of the catalyst. The morphologies of Zn^{2+} -doped TiO_2 nanotubes calcined at 550°C are shown in Fig. 1. The TiO_2 nanotube was successfully synthesized. Other ion-doped nanotubes shared a similar morphology (figure not shown). The TiO_2 nanotubes had an average diameter of approximately 10 nm with a hollow and open-ended structure, and the tube wall thickness was approximately 1 nm.

Fig. 1. TEM images of 550°C calcined Zn^{2+} -doped TiO_2 nanotubes.

3.1.2. XRD analysis

The XRD patterns of the un-doped and ion-doped TiO_2 nanotubes are shown in Figs. 3(a) and 3(b), respectively. The weight fractions of anatase in the anatase-rutile mixtures in the samples were calculated using Eq. (1) [10].

$$f = \frac{1}{1 + 1.265 \frac{I_R}{I_A}} \quad (1)$$

where f is the weight fractions of anatase in the mixtures, and I_R and I_A are the maximum X-ray diffraction peak intensities of rutile phase (110) and anatase phase (101), respectively. The weight fractions of anatase in various samples are listed in Table 1.

Fig. 2 and Table 1 show that both anatase and rutile phases might exist in the TiO_2 nanotubes. When the calcination temper-

Fig. 2. XRD patterns of the TiO₂ nanotubes. (a) Un-doped TiO₂ calcined at 400°C to 600°C. (b) Ion-doped TiO₂ with different doped ions calcined at 550°C. “◆” refers to the anatase phase, “◇” refers to the rutile phase, and the words in red indicate the Bragg angles (2θ) of the characteristic peak of (101) crystal planes.

Table 1. Catalytic Properties of the TiO₂ Nanotube Samples

Calcination temperature / °C	Weight fractions of anatase phase / %				Indirect energy band gap / (eV)				BET surface areas / (m ² /g)			
	450	500	550	600	450	500	550	600	450	500	550	600
un-doped	78.8	82.6	83.4	76.9	3.26	3.24	3.24	3.22	237	169	123	99
Ag ⁺ -doped	82.0	83.1	84.6	75.8	3.18	3.13	3.12	3.02	100	62	56	48
Al ³⁺ -doped	78.3	86.8	86.0	88.3	3.24	3.23	3.22	3.21	199	143	123	108
Mn ²⁺ -doped	92.1	92.2	91.3	90.8	3.05	3.02	3.00	2.90	84	71	61	47
Ni ²⁺ -doped	84.0	87.4	88.5	88.8	3.09	3.07	3.06	3.01	89	58	48	46

ature was increased, the intensity of the anatase phase decreased, whereas that of the rutile phase increased. The dopant ions could substitute Ti⁴⁺ in the TiO₂ nanotubes lattice, which resulted in the deformation of the crystal lattice. As a result, broadening diffraction peak and decreasing peak intensity were observed.

Among the dopant ions, only Ag⁺ could be observed in the XRD patterns in the form of Ag₂O based on the characteristic peak of the (111) crystal plane of Ag₂O at 32.8° and the XPS spectra of Ag 3d [11]. Ag⁺ (ionic radius of 115 pm) could be observed because it had difficulty entering the TiO₂ lattice [12]. Ions were partially dispersed in the bulk of TiO₂ nanotubes [9]. The metallic oxides from other doped ions might also be formed on the surface of TiO₂. However, these oxides were not observed in the XRD patterns because their metal sites (0.5 wt.% – 2.0 wt.%) were expected to be below the visibility limit of X-ray analysis [13].

3.1.3. XPS analysis

The XPS analysis was performed to determine the surface composition and the chemical state of the elements in the ion-doped TiO₂ nanotubes calcined at 550°C (Fig. 3). Fig. 3(a) shows the XPS survey scan of the un-doped TiO₂, and Figs. 3(b) – 3(k) show the XPS spectra of Ag 3d, Al 2p, Cu 2p, Fe 2p, Mn 2p, Ni 2p, V 2p, Zn 2p, Ti 2p, and O 1s, respectively. The sharp XPS peaks for Ti, O, doped ions, as well as C and Na, are shown in Fig.

3(a). The presence of C was mainly attributed to carbon contamination when the samples were transferred to the XPS device [14]. The presence of Na 1s could be explained by the incomplete exchange of protons with Na⁺ during acid washing [9]. The results also indicate that a part of the catalyst still remained at the Na₂Ti₃O₇ nanotubes where a lot of Na existed [15].

Fig. 3(a) shows that the peak intensities of Ag₂O were much higher than those of other metallic oxides. Moreover, the Ag₂O peak could be observed in the XRD patterns of Ag⁺-doped TiO₂. Both observation results indicate that Ag₂O existed on the surface of the samples. The binding energies of Ag 3d, Al 2p, Mn 2p, Ni 2p and Zn 2p indicate that the doping ions existed as Ag⁺, Al³⁺, Mn²⁺, Ni²⁺ and Zn²⁺ in the TiO₂ crystal lattice (Figs. 3(a) – 3(e)).

Fig. 3(f) shows that binding energies of 458.15 eV to 459.00 eV for TiO₂ nanotubes correspond to the peaks of Ti 2p_{3/2}, whereas binding energies of 464.05 eV to 464.90 eV correspond to Ti 2p_{1/2}. The binding energy of Ti 2p indicates that Ti was incorporated into the lattice of TiO₂ as Ti⁴⁺. The Ti 2p binding energy of the ion-doped TiO₂ nanotubes increased compared with that of pure TiO₂ because the electrons in the conduction band of TiO₂ may be transferred to the doped metal ions on the surface of TiO₂, which resulted in a decrease in the outer electron cloud density of Ti ions [8].

Fig. 3. XPS spectra of the TiO₂ nanotubes: (a)-(f) XPS spectra of Ag 3d, Al 2p, Mn 2p, Ni 2p, Zn 2p and Ti 2p, respectively.

3.1.4. BET surface area analysis

The catalytic efficiencies of the TiO₂ nanotubes are related to the S_{BET} of the catalyst [16, 17]. As summarized in Table 1, the S_{BET} of TiO₂ nanotubes decreased with increasing calcination temperature. The decrease in S_{BET} could be attributed to the aggregation of nanotubes, which resulted in a closely coagulated structure [17].

Table 1 indicates that the S_{BET} of ion-doped TiO₂ nanotubes was more or less smaller than that of un-doped TiO₂ nanotubes, particularly for Ag⁺-, Mn²⁺-, and Ni²⁺-doped TiO₂ nanotubes. The S_{BET} decreased when metal ions were doped because of partial pore blockages and framework defects [9].

The S_{BET} of TiO₂ nanotubes was significantly larger than that of P-25 TiO₂. This finding is attributed to the inner and outer

surfaces of the layered-tubular structure, which is one of the special qualities of this catalyst [6].

3.1.5. UV-vis DRS analysis

The UV-vis DRS analysis was performed on the catalysts to obtain the energy band gaps (E_g) (Fig. 4). The E_g of the catalysts are calculated [18] and shown in Table 1.

Fig. 4(a) shows that E_g decreased with increasing calcination temperature. This trend occurred because the E_g of rutile TiO_2 (3.0 eV) was narrower than that of anatase TiO_2 (3.2 eV), and the rutile phase of TiO_2 began to form when the calcination temperature was increased. The E_g of un-doped TiO_2 nanotubes was between 3.30 and 3.22 eV, which was a little higher than that of anatase TiO_2 in powder form. This blue shift was due to the quantum size effect on different morphologies of the catalysts [19]. The reflectance spectra of ion-doped TiO_2 slightly shifted toward a longer wavelength (red shift) compared with those of un-doped TiO_2 , and the E_g of ion-doped TiO_2 was visibly narrower. The results show that the doped elements involved were indeed integrated into the lattice of the TiO_2 nanotubes, thereby altering the crystal and electronic structures of the TiO_2 nanotubes [20]. The reduction in E_g of the TiO_2 nanotubes allows the excitation of the catalyst at a lower irradiation power. Thus, the photocatalytic activity of the catalyst is enhanced [19].

3.2. Photocatalytic Activity of the Catalysts

As shown in Fig. 5(a), the highest catalytic activity for the un-doped TiO_2 nanotubes was observed at a calcination temperature of 500°C, with an RB removal efficiency of 98.1%. The S_{BET} , crystalline phases, crystallinity, and E_g of TiO_2 nanotubes were considered as crucial factors that affect the photocatalytic activity of the catalyst. When the calcination temperature was increased, the S_{BET} decreased (see Table 1). The S_{BET} could affect the photocatalytic activities of the catalyst because a larger S_{BET} indicates that more pollutants are adsorbed onto the surface of the catalyst, and more areas become available for electron-hole pair separation. The anatase phase exhibited a higher photocatalytic activity compared with other phases. Although the S_{BET} of TiO_2 nanotubes calcined

at 450°C were larger, the crystalline phases were predominantly amorphous, which resulted in low photocatalytic activity, and broadened E_g of TiO_2 . For TiO_2 nanotubes calcined at 550°C, and 600°C, although the main crystalline phases were anatase, the amount of rutile phase increased, and the S_{BET} decreased; thus, the overall efficiencies were low.

Photocatalytic activity was also affected by ionic radius, valence state, and configuration. The photocatalytic activities of the catalysts on RB removal increased when Ag^+ , Al^{3+} and Zn^{2+} were doped into the TiO_2 nanotubes, whereas such activities decreased as a result of Mn^{2+} or Ni^{2+} doping. In the presence of Zn^{2+} -doped TiO_2 nanotubes calcined at 550°C, the removal efficiency of RB within 50 min was 98.7%. The catalytic activity was affected by the following factors. First, the existing impurity band can reduce the recombination of photoinduced electron-hole, which can transfer electrons more efficiently to the oxygen adsorbed on the surface of TiO_2 nanotubes [21]. Second, the weight fractions of the anatase phases of the catalyst were larger than those of un-doped TiO_2 nanotubes, the E_g of the nanotubes were narrower, and the S_{BET} of the catalyst were smaller (see Table 1). Third, the ionic radii of the doped ions affected the photocatalytic activities.

For Ag^+ , the ionic radius was significantly larger than that of Ti^{4+} (60.5 pm). Ag^+ was observed on the surface of TiO_2 . The electrons continuously transferred from TiO_2 to Ag_2O , which allowed the pollutant with negative charges to be easily adsorbed by the TiO_2 crystals. The weight fraction of the anatase phase of the catalyst was larger than that of the un-doped TiO_2 nanotubes, and the E_g of the catalyst was narrower. Therefore, the catalytic activity of Ag^+ -doped TiO_2 increased.

The photocatalytic activity increased when Al^{3+} was doped into the catalyst. The ionic radii of Al^{3+} (53.5 pm) was smaller than that of Ti^{4+} ; thus, the ions were easily substituted in the lattice. Two doped ions replaced two Ti^{4+} ions, and one O^{2-} hole appeared. The shape of the crystal changed, which facilitated the generation of electron-hole pairs. The weight fraction of the anatase phase of the catalyst increased after ion-doping, and the E_g was narrower. Therefore, the photocatalytic activities of Al^{3+} -doped TiO_2 nanotubes increased.

Fig. 4. UV-vis diffuse reflectance spectra and energy band gap of TiO_2 nanotubes: (a) un-doped TiO_2 calcined at 450-600°C; (b) 550°C calcined ion-doped TiO_2 nanotubes with different doped ions.

Fig. 5. Removal of 20 mg/L RB in the presence of different TiO₂ nanotubes: (a) un-doped TiO₂; (b) Ag⁺-doped TiO₂; (c) Al³⁺-doped TiO₂; (d) Mn²⁺-doped TiO₂; (e) Ni²⁺-doped TiO₂; (f) Zn²⁺-doped TiO₂.

When Mn²⁺ and Ni²⁺ ions were added, the photocatalytic activity of the catalyst decreased. Mn²⁺ and Ni²⁺ ions, whose ionic radii were 67 and 69 pm, respectively, had a slight difficulty in entering the lattice, therefore, MnO and NiO were generated on TiO₂ nanotubes. The formation of MnO or NiO could hinder the separation of electrons and holes. In addition, the S_{BET} of Mn²⁺- and Ni²⁺-doped TiO₂ were extremely small. Therefore, the photocatalytic activities of the Mn²⁺- and Ni²⁺-doped catalysts were limited.

The ionic radii of Zn²⁺, which was 74 pm, was slightly larger than that of Ti⁴⁺. ZnO might be formed on the surface of the TiO₂. The combination of TiO₂ with the doped metallic oxide results in the generation of Ti³⁺. The electrons were transferred to Ti³⁺ and then to the oxygen, which could reduce the probability

for recombination between electrons and holes. In addition, the photogenerated holes left in the valence band would have more opportunity to participate in the oxidizing reactions because photogenerated electrons can be effectively scavenged by Zn²⁺ ions [22]. Therefore, the removal efficiencies increased.

4. Conclusions

Ion-doped TiO₂ nanotubes were successfully synthesized for RB removal. The ions were effectively incorporated into the TiO₂ lattice, except for Ag⁺. When the ions were doped and the calcination temperature was increased, the S_{BET} of TiO₂ decreased, and the E_g of ion-doped TiO₂ became visibly narrower. The photocatalytic

activities of catalysts on RB removal could be increased when Ag^+ , Al^{3+} and Zn^{2+} were doped into the TiO_2 nanotubes, and the Zn^{2+} -doped TiO_2 nanotubes had the highest catalytic activity because of the effects of the weight fractions of the anatase phase, S_{BET} , E_g , and the doped ions. When Mn^{2+} and Ni^{2+} were used as dopants, the photocatalytic activity of the catalyst decreased.

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