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Comparison of photocatalytic activity of TiO_2 film doped nonuniformly by Mn and Zn①

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Abstract: The thin films of TiO_2, doped by Mn or Zn with nonuniform distribution, were prepared by sol-gel method under process control. The actinic absorption of the catalyst thin films was evaluated by UV-vis spectrophotometry. And the activity of the photocatalyst was evaluated by photocatalytic degradation kinetics of aqueous methyl orange under UV radiation. The results show that the photocatalytic activity of the TiO_2 thin film can be evidently enhanced by Mn non-uniformly doping in the bottom layer and can be decreased by Mn doping in the surface layer. The activity of TiO_2 thin film can be evidently enhanced by Zn non-uniform doping in either the bottom or the surface layer. But the activity of TiO_2 is less affected by uniformly Zn doping. The different mechanisms for enhanced photocatalytic activity of Mn or Zn non-uniformly doped titanium dioxide film were discussed in terms of the separation of photon-generated carrier in the TiO_2 films.

Key words: TiO_2; Mn; Zn; non-uniform doping; photocatalysis
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1 INTRODUCTION

Heterogeneous photocatalysis attracts much attention as a friendly environment technique valuable for water and air purification. However, there are some problems in application, and one of the key problems is the low photon-quantum efficiency. From 1990s, the modification of TiO_2 by metal ions has become a hot topic, and the effect of metal (such as Cu, Fe, Ag, Au, Pt, W, V, Pb, Cr, Rh, Co and Ni) ions doping on photocatalytic activity of TiO_2 has been studied widely[1-4]. However, there were some contradictory reports on the activity of TiO_2 modified by metal ions. For example, Chot et al[4] considered that the activity of TiO_2 could be improved by Fe^{3+} doping, but Brezova et al[5] and Navio et al[6] revealed that Fe^{3+} was harmful to the activity of TiO_2. The photophysical mechanism of doped semiconductors is not always understood. According to the preparation process, the metal ion doping of TiO_2 should be defined as uniform doping, in other words, the distribution of metal ions in TiO_2 is uniform.

In the end of 2001, in order to improve the photocatalytic activity of the TiO_2 films, the authors proposed a new idea on TiO_2 modification, metal ions non-uniformly doping. It could not only promote the generation of current carriers, but also improve their separation. In this paper, the thin films of TiO_2, doped nonuniformly by Mn or Zn, were prepared by sol-gel method under process control. The different mechanisms for enhanced photocatalytic activity of the titanium dioxide film by non-uniformly Mn or Zn doping were discussed in terms of the separation of photon-generated carrier in the TiO_2 films.

2 EXPERIMENTAL

2.1 Preparation of Mn-doped, Zn-doped and pure TiO_2 films

The TiO_2-sol was prepared by the following method[7]: 68 mL tetra-butyl-ortho-titanate and 16.5 mL diethanolamine were dissolved in 210 mL absolute ethanol, and then stirred vigorously for 1 h (solution A). Under stirring, the mixture of 3.6 mL water and 100 mL absolute ethanol (solution B) was dropwise added into the solution A. The resultant alkoxide solution was left for 24 h in the dark, then the TiO_2-sol was formed.

The preparation of Mn/TiO_2-sol was similar to that of the TiO_2-sol. The difference was that

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some $Mn(NO_3)_2$(AR) was added into 3.6 mL H_2O and different concentration sols were formed when solution B was made. The Mn/TiO_2 sol contents were 0.23%, 0.57%, 0.80%, 1.15% and 1.72% (mass fraction), respectively. The Zn/TiO_2-sol was prepared by the same method with Zn$(CH_3COO)_2$(AR), and the contents of the Zn/TiO_2 sol were 0.14%, 0.41% and 0.96%, respectively.

The doped or pure TiO_2 films were coated on the soda lime glass substrates, which was precoated with two SiO_2 layers, from the TiO_2 sol or Mn/TiO_2 sol by the following steps: 1) dipping-withdrawing at a speed of 2 mm/s; 2) drying at 100 ℃ for 10 min; 3) heating to 500 ℃ at a rate of 2 ℃/s; 4) keeping at 500 ℃ for 1 h, then cooling. The films of TiO_2 in different doping modes described in Table 1 were prepared by repeating the above steps.

Table 1 Doping modes of TiO_2

Sample	Composition
TT	2 layers SiO_2-sol + 4 layers TiO_2-sol + 4 layers TiO_2-sol
MM or ZZ	2 layers SiO_2-sol + 4 layers Mn/TiO_2-sol or 4 layers Zn/TiO_2-sol + 4 layers Mn/TiO_2-sol or 4 layers Zn/TiO_2-sol
MT or ZT	2 layers SiO_2-sol + 4 layers Mn/TiO_2-sol or 4 layers Zn/TiO_2-sol + 4 layers TiO_2-sol
TM or TZ	2 layers SiO_2-sol + 4 layers TiO_2-sol + 4 layers Mn/TiO_2-sol or 4 layers Zn/TiO_2-sol

The crystal form of the film was anatase, obtained by X-ray diffraction (XRD with D/MAX-ⅢA).

2.2 Photocatalytic activity test

The reactor was a glass cylinder (d = 70 mm, H = 240 mm), in which five pieces of glass with photocatalysis film were settled tightly near the inside container wall. Then, 400 mL aqueous methyl-orange (prepared by reverse osmosis treatment water, pH = 5.9, 10 mg/L) was added into the cylinder, and the solution was aerated for 30 min. A high-pressure mercury lamp (125 W, λ_p = 365 nm) was used as a light-house and preheated for 30 min. And then the high-pressure mercury lamp was put into the reactor center. The reactor was immersed in a thermostatic bath in order to obtain a constant temperature. The solution was sampled every 20 min. The concentration of aqueous methyl orange is determined through measuring the absorptive characteristic at 464 nm using a UV-visible spectrophotometer (UV-3010) within the scanning scope from 200 nm to 600 nm.

The photocatalytic decolorization of methyl orange is a pseudo-first order reaction and its kinetics can be expressed as follows[8]:

$$\ln(c_0/c) = K \cdot t_{illum}$$

where K is the apparent reaction rate constant, t_{illum} is the reaction time, and c_0 and c are the initial concentration and the reacting concentration of methyl orange, respectively.

3 RESULTS

3.1 Effect of doping mode

Fig. 1 shows the effect of Mn doping mode on the photocatalytic activity of TiO_2 films at the doping content of 0.80%. The sequence of activity of the TiO_2 films is MT> TT> TM> MM. The photocatalytic activity of MT films is better than that of TT, but those of MM and TM are evidently worse than that of TT. This phenomenon is similar to that of the TiO_2 doped by Mo[9].

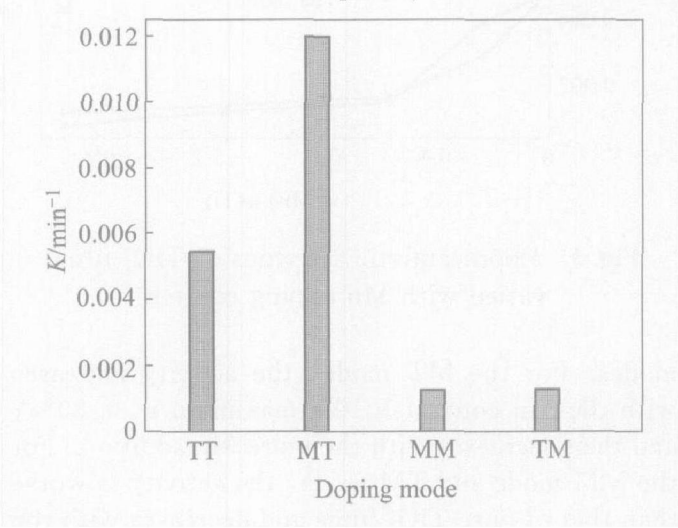

Fig. 1 Effect of Mn doping mode on photocatalytic activity of TiO_2 films

Fig. 2 shows the effect of Zn doping mode on the photocatalytic activity of TiO_2 films at the doping content of 0.41%. The sequence of activity of TiO_2 films is ZT > TZ> ZZ> TT. The photocatalytic activity of ZT films is better than that of TT; and that of Zn doping in the surface layer is better. The activity of the films is little affected by Zn uniformly doping (ZZ).

3.2 Effect of doping content

Fig. 3 presents the apparent kinetics parameter (K) of methyl orange degradation as a function of the Mn-doped content under different doping modes. For the MT mode, the activity increases

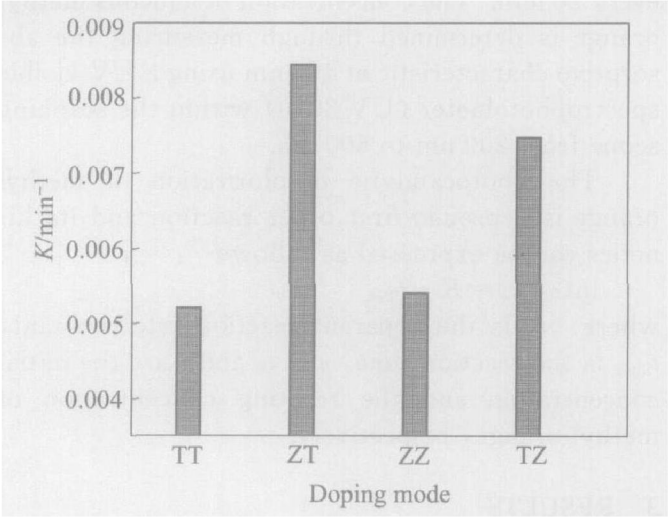

Fig. 2 Effect of Zn doping mode on photocatalytic activity of TiO_2 films

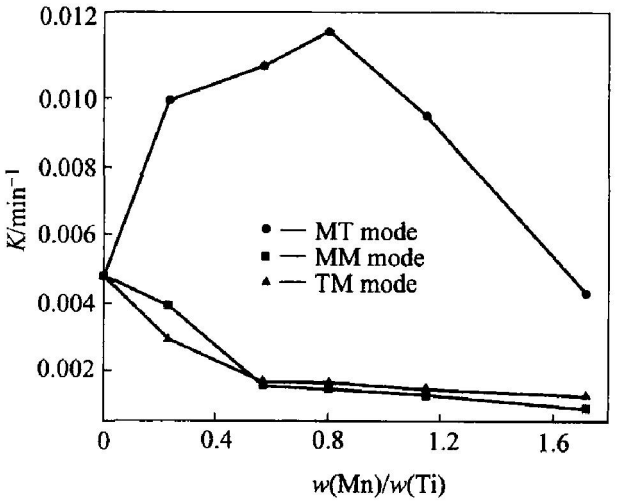

Fig. 3 Photocatalytic activities of TiO_2 films varied with Mn doping content

with the Mn content to the maximum at 0.80%, and then decreases with the more Mn addition. For the MM mode and TM mode, the activity is worse than that of pure TiO_2 films and decreases with the Mn addition all the while.

Fig. 4 presents the apparent kinetics parameter (K) of methyl orange degradation as a function of the Zn doped content under different doping modes. For the ZT mode and TZ mode, the activity increases with the Zn content to the maximum at 0.41%, and then decreases with the more Zn addition. For the ZZ mode, the activity is little affected by the doping content.

4 DISCUSSION

Heterogeneously photocatalytic oxidation is a surface reaction, and its efficiency depends on the separation of the photon-generated carrier and the quantity of the hole on the film surface to react with the organic substance or H_2O absorbed on the

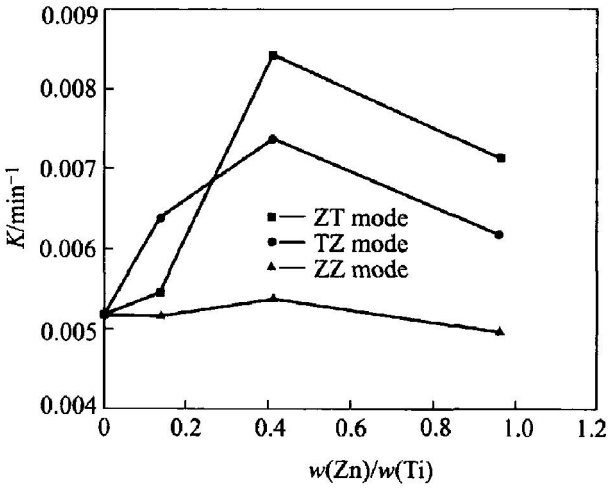

Fig. 4 Photocatalytic activities of TiO_2 films varied with Zn doping content

surface[10]. Based on the above principle, the mechanism of the activity of the TiO_2 films affected by Mn or Zn doping is discussed as follows.

4.1 Doping mode analysis

For Mn-doped films, because the radius of Mn is close to that of Ti, Mn ion can be easily embedded into the crystal lattice, and replace the Ti ion in the lattice point. Mn ion exists as Mn^{4+} after Mn-doped TiO_2 is treated at 500 ℃[11]. The configuration of extra-nuclear electron of Mn^{4+} is $3s^2 3p^6 3d^3$, which is prone to return to that of $3s^2 3p^6 3d^5$ (Mn^{2+}) (a stably-associated one with the half-filled subshells ($3d^5$)).

For the MT mode, when the films are heat-treated, there will be a content gradient from the bottom layer to surface layer in the film, due to the diffusion and migration of Mn ions. With UV radiation, there are photon-generated carriers within the semiconductor. The Mn^{4+} in the bottom layer becomes the electron acceptor, and the photon-generated electrons transfer from the surface layer to the bottom layer in the films. Thus the N-type field of PN junction is formed in the bottom layer of the doped TiO_2 film, and P-type field is formed in the surface layer (Fig. 5). The whole systematic Fermi level is the same, but band near interface forms current carrier potential barrier[12, 13]. The potential barrier suppresses recombination of the electron-hole pairs. In the photocatalytic oxidation reaction, when the holes on the surface are consumed, the holes in the film will migrate to the surface layer due to the effect of the electric field of potential barrier, so the concentration of holes in the surface layer remains affluent and photocatalytic oxidation activity is enhanced. For the TM mode, it will form the reverse electric field in the interface. So the holes on the surface are fewer than those in TT mode. Because the holes are ma-

jor factor in the photo-catalytic oxidation reaction, the photocatalytic oxidation activity is lower than that of pure TiO_2. For the MM mode, the sites of dopant ions may become electron-hole recombination centers, which greatly decreases the lifetime of charge carriers. Furthermore it can not form potential barrier, accordingly the photocatalytic oxidation activity decreases.

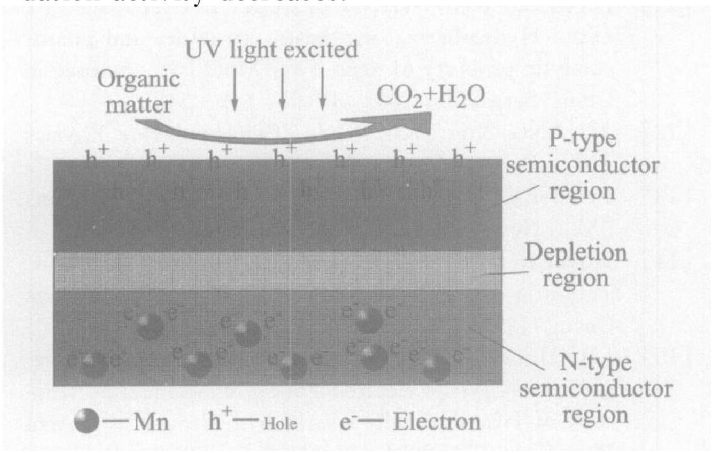

Fig. 5 Schematic diagram of photocatalytic process in MT mode

For Zn-doped films, the radius of Zn ion is bigger than that of Ti, and it is difficult for the Zn ion to be embedded into crystal lattice. So the cluster of ZnO is formed in the TiO_2 films. And ZnO has the characteristic of better electron-withdrawing[14].

For the ZT mode, there is also a Zn concentration gradient from the bottom layer to the surface layer in the film. With UV radiation, the electrons in the surface layer accumulate into the bottom layer of the films and leave behind the holes in the surface layer. In the same way, the concentration of holes in surface layer remains affluent, so the photocatalytic oxidation activity is enhanced.

For the TZ mode, the electrons on the surface increase, but the cluster of ZnO on the surface maybe form the effect of "Pt Island" analogously[15], which makes the electrons and holes separate effectively on the surface(Fig. 6), so the oxidation activity of the films is also enhanced. For the ZZ mode, it can not form electric potential in the film, then the oxidizing and reducing potential of TiO_2 and ZnO have a little difference, so the photocatalytic oxidation activity of the films in the ZZ mode has been less affected.

4.2 Doping content analysis

For the MT and ZT modes, when Mn or Zn doping content in the bottom layer is low, the depletion layer can not form. So the photo-generated carrier can not be separated effectively in the titanium dioxide films[16]. Because more dopants in the bottom layer could decrease concentration gradient

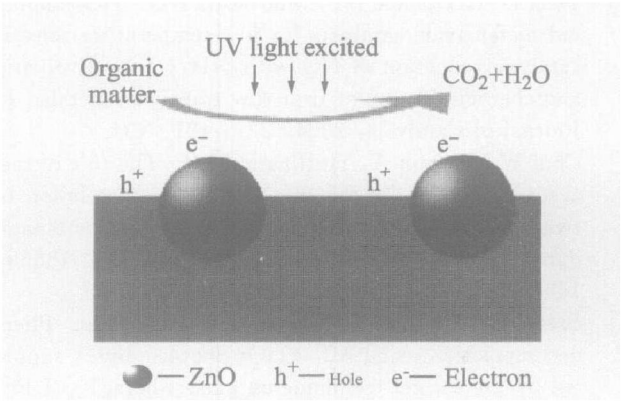

Fig. 6 Schematic diagram of photocatalytic process in TZ mode

of dopant due to the driving force from field-aided diffusion in the process of heat treatment, there would be a maximum width of space-charge region along with an optimal dopant concentration. So there exists an optimal doping content in MT or ZT film on the photocatalytic activity. For the TM mode and MM mode, the electron-hole recombination centers increase with the doping content, which greatly decreases the lifetime of charge carriers. So the quantity of the effective carriers migrating to the surface of the films decreases, and the photocatalytic activity decreases evidently.

For TZ mode, in the similar manner, there exists an optimal charge separation on the surface, so there also exists an optimal content on the photocatalytic oxidation activity.

5 CONCLUSIONS

1) For Mn-doped TiO_2 films, the MT mode can enhance the photocatalytic activity evidently. However, the activity of the films decreases in the TM mode or MM mode.

2) For Zn-doped TiO_2 films, the photocatalytic activity of the films is enhanced evidently by the ZT mode or TZ mode. But the photocatalytic oxidation activity of the films in the ZZ mode has been less affected.

3) The optimal content of TiO_2 films doped non-uniformly by Mn in MT mode is about 0.80%, and that by Zn in ZT and TZ mode is about 0.41% (mass fraction).

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