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Theoretical Kinetic Analysis of Heterogeneous Photocatalysis: The Effects of Surface Trapping and Bulk Recombination through Defects

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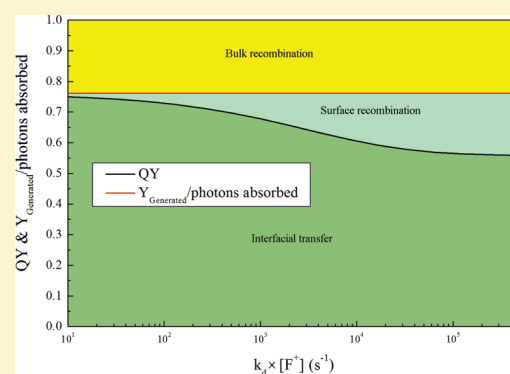
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ABSTRACT: A theoretical kinetic model is developed to study the functions of defects in photocatalysis, and the kinetic courses that are related to the defects on the surface and in the bulk are systematically analyzed. The analysis gives a description of the functions of the defects on the surface. It is found that increased speed of surface trapping leads to decreased photocatalytic performance. Surface trapping of electrons at defects is not sufficient to increase the photocatalytic activity, which is dependent on the kinetic courses that follow surface trapping, namely, surface recombination and interfacial transfer. The role of bulk defects as recombination centers is considered. The model gives a simple and general physical and mathematical treatment taking bulk recombination into consideration, based on which the effect of the bulk defects is analyzed.



1. INTRODUCTION

Doping other elements in TiO_2 has become an important route to increase the photocatalytic activity or use visible light^{1–5} in photocatalysis. The other elements form foreigner defects on the surface or in the bulk of TiO_2 . In addition, intrinsic defects such as oxygen defects, are reported to play an important role in photocatalysis.^{6,7} In photocatalysis under UV illumination, a “first increase and then decrease” dependence of photocatalytic activity on dopant concentration is always observed.^{8,9} It is stated that those defects form the trapping centers of photoinduced electrons and holes at low defect concentration and change to recombination centers in the case of high defect concentration. However, the physical mechanism of the trapping to recombination transformation is still unclear. It seems that it is difficult to elucidate experimentally the functions of defects in photocatalysis, and a theoretical kinetic analysis is needed. However, to date there have been very few theoretical studies. More importantly, defects, including foreigner defects and intrinsic defects, are prevalent in photocatalysts, so taking the effect of defects into account is extremely important for a theoretical kinetic analysis. However, almost all theoretical kinetic analyses have not considered the effect of defects. We now have numerous experimental studies that can support a detailed theoretical kinetic analysis of the functions of defects in photocatalysis. In this paper we establish a theoretical model to study the effects of defects in photocatalysis.

The defects on the surface and in the bulk should have different effects on photocatalysis because they have different chemical environments. Both types of defects are able to trap electrons or holes; however, the trapped electrons or the trapped holes will have different subsequent kinetic courses. The kinetic courses of the electrons or holes after trapping on the surface include interfacial transfer and surface recombination. For example, the holes can first be trapped by surface bound hydroxy groups (OH_s^- , a kind of defect) and then transferred to other substances through oxidation reactions. The electrons are considered to always transfer directly to O_2 in many theoretical analyses.^{10–13} This is true for perfect TiO_2 without any defects, but such a material does not exist. In fact, the defects on the surface of TiO_2 have an important effect on the interfacial transfer of electrons.^{6,14} For example, Gerischer et al. suggested that it is more likely that the electrons are first trapped by shallow defects on the surface and then transferred to O_2 .⁷ Here, the kinetic courses of electrons related to the surface defects are taken into consideration, including surface trapping, interfacial transfer and surface recombination, which apply equally to holes.

It is well known that the presence of defects in bulk TiO_2 makes recombination much easier.^{9,15,16} Moreover, the electrons

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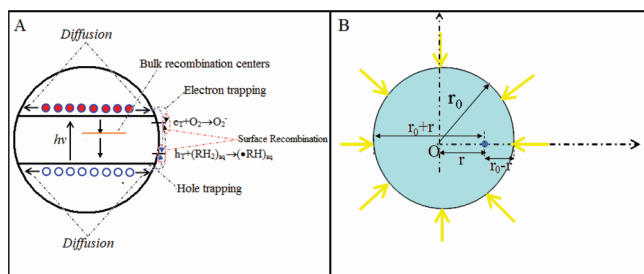


Figure 1. (A) Diagram of theoretical model with indirect bulk recombination and surface electron trapping considered. (B) Diagram of the light illumination and the coordinate system for establishing the hole continuity equation.

or holes trapped at bulk defects are localized in many cases. It is difficult for them to hop from one defect site to another site, so the unique fate of the trapped electrons or holes is recombination. From this viewpoint, the main kinetic course related to the bulk defects is recombination, which will result in decrease of the lifetimes of electrons or holes, as well as diffusion lengths. For example, photoelectrochemical measurement showed that the diffusion length of holes (L_p) in etched n -TiO₂ single crystal is about 10^{-6} cm, and the lattice defects introduced can reduce L_p to values of the order of 10^{-7} cm.¹⁷ This value is much smaller than the size of the TiO₂ nanoparticles used in photocatalysis, but bulk recombination has not been considered in the theoretical kinetic analyses until now.^{18–20} Thus, in the case of photocatalysts containing bulk defects, bulk recombination must be considered. Although the effect of bulk recombination on photocatalysis is well-known, how to include it in a theoretical kinetic analysis seems a difficult challenge. In this paper we give a simple method to deal with this problem.

We establish a theoretical kinetic model to study the functions of the defects in TiO₂ photocatalysis. The kinetic courses related to the defects on the surface and in the bulk, including surface trapping, surface recombination, interfacial transfer, and bulk recombination, are taken into consideration in the model. The effects of some kinetic factors, including the rate constant of surface recombination, the product of the rate constant of interfacial transfer and the dissolved oxygen concentration, the product of the rate constant of surface trapping and the surface defect concentration, and the effect of hole diffusion length on the photocatalytic activities are studied.

2. THEORETICAL MODELS

2.1. Model Description. Figure 1 shows diagrammatically the theoretical model, in which a spherical particle with radius r_0 is considered. As shown in Figure 1A, the electron–hole pairs generated in the TiO₂ particle after absorbing photons will diffuse to the surface, accompanied by indirect recombination via the defects in the bulk. On the surface electrons will first be trapped by the defects and then transfer to O₂ or recombine with holes in the valence band (VB). The holes will be captured by surface bound OH_s[−], then react with a dissolved organic molecule or recombine with the electrons in the conduction band (CB). As shown in Figure 1B, we consider a case in which the light uniformly illuminates radial directions of the spherical particle. To simplify the theoretical analysis, we select a coordinate system with the origin at the center of the spherical particle.

2.2. Photo Generation of Holes on Surface. For TiO₂ nanoparticles, diffusion is the dominant mode of transport of electrons and holes in the bulk. By consideration of the coordinate system in Figure 1B, the carrier continuity equation for holes in the steady state is

$$D_p \frac{d^2 p(r)}{dr^2} + \alpha I_0 (e^{-\alpha(r_0-r)} + e^{-\alpha(r_0+r)}) - \frac{p(r)}{\tau_p} = 0 \quad (1)$$

where D_p is the diffusion coefficient, $p(r)$ the density, and τ_p the lifetime of holes; r is the coordinate, α the absorption coefficient, and I_0 the photon flux. The general solution of formula 1 is

$$p(r) = C_1 e^{L_p^{-1}r} + C_2 e^{-L_p^{-1}r} - \frac{\alpha I_0 \tau_p e^{-\alpha r_0}}{\alpha^2 L_p^2 - 1} [e^{\alpha r} + e^{-\alpha r}] \quad (2)$$

where L_p , the square root of $D_p \times \tau_p$, is the diffusion length of holes. The boundary conditions of formula 2 are

$$\begin{cases} p(r_0) = p(-r_0) = p_s & (x = r_0, -r_0) \\ D_p \frac{\partial p(r)}{\partial r} \Big|_{x=0} = 0 & (x = 0) \end{cases} \quad (3)$$

where p_s is hole density on the surface.

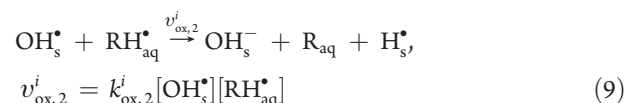
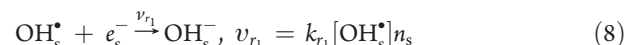
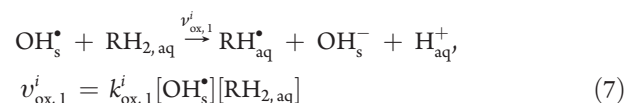
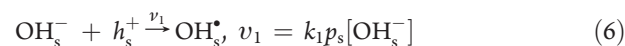
The photo generation rate of holes on the surface is

$$y_{\text{generated}} = -D_p \frac{dp(r)}{dr} \Big|_{x=r_0} = v_p C_1 (e^{-L_p^{-1}r_0} - e^{L_p^{-1}r_0}) + \frac{\alpha_2 L_p^2 I_0 e^{-\alpha r_0}}{\alpha_2 L_p^2 - 1} (e^{\alpha r_0} - e^{-\alpha r_0}) \quad (4)$$

where v_p , the square root of D_p/τ_p , is the diffusion rate of holes. The two integration constants C_1 and C_2 are

$$C_1 = C_2 = \frac{p_s + \frac{\alpha I_0 \tau_p e^{-\alpha r_0}}{\alpha^2 L_p^2 - 1} (e^{\alpha r_0} + e^{-\alpha r_0})}{e^{-L_p^{-1}r_0} + e^{L_p^{-1}r_0}} \quad (5)$$

2.3. Surface Recombination and Interfacial Charge Transfer. 1. For Holes.



Equation 6 shows hole trapping by the surface-bound OH_s[−]. Equation 7 is the photo-oxidation of dissolved RH_{2, aq} by OH_s[•], and the product RH_{aq}[•] can be further oxidized to R_{aq} according to eq 9. Equation 8 is the surface recombination of holes and electrons via OH_s[−]. According to a previous study¹⁷ it is considered that $v_{\text{ox},2}^i$ equals $v_{\text{ox},1}^i$.

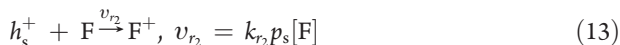
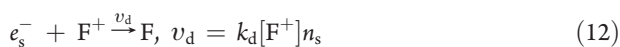
In the steady state

$$\frac{d[\text{OH}_s^*]}{dt} = v_1 - 2v_{\text{ox},1}^i - v_{r1} = 0 \quad (10)$$

It follows that

$$[\text{OH}_s^*] = \frac{k_1 p_s [\text{OH}_s^-]}{2k_{\text{ox},1}^i [\text{RH}_{2,\text{aq}}] + k_{r1} n_s} \quad (11)$$

II. For Electrons.



Equation 12 shows trapping of electrons on TiO_2 surface by the surface defects (F^+), and the product (F) can regenerate F^+ via surface recombination (eq 13) and interfacial transfer (eq 14) with rates v_{r2} and v_{red} , respectively.

Under steady-state conditions

$$\frac{d[\text{F}]}{dt} = v_d - v_{r2} - v_{\text{red}} = 0 \quad (15)$$

and

$$[\text{F}] = \frac{k_d [\text{F}^+] n_s}{k_{r2} p_s + k_{\text{red}} [\text{O}_2]} \quad (16)$$

The overall surface recombination rate is the sum of v_{r1} and v_{r2} . The rate of interfacial transfer of holes must be equal to that of electrons under steady state photocatalytic reactions, i.e.

$$2v_{\text{ox},1}^i = v_{\text{red}} \quad (17)$$

Combining the above equations gives

$$n_s = \frac{-b + \sqrt{b^2 + 4acp_s + 4adp_s^2}}{2a} \quad (18)$$

with

$$\begin{cases} a = k_{r1} k_{\text{red}} k_d [\text{F}^+] [\text{O}_2] \\ b = 2k_{\text{ox},1}^i k_{\text{red}} k_d [\text{F}^+] [\text{O}_2] [(\text{RH}_2)_{\text{aq}}] \\ c = 2k_{\text{ox},1}^i k_1 k_{\text{red}} [\text{OH}_s^-] [(\text{RH}_2)_{\text{aq}}] [\text{O}_2] \\ d = 2k_{\text{ox},1}^i k_{r2} k_{\text{red}} [\text{OH}_s^-] [(\text{RH}_2)_{\text{aq}}] \end{cases} \quad (19)$$

Equations 18 and 19 define the relationship between electron density (n_s) and hole density (p_s) on the surface.

2.4. Continuity Condition on the Surface and Quantum Yield. Under steady-state photocatalysis, the rate of photogeneration of holes on the surface must be equal to the sum of the rates of surface recombination and interfacial transfer. As shown in eq 20, they are functions of p_s .

$$y_{\text{generated}}(p_s) = y_{\text{consumed}}(p_s) \quad (20)$$

$y_{\text{generated}}(p_s)$ can be obtained from eq 4, and $y_{\text{consumed}}(p_s)$ is $v_{r1} + v_{r2} + v_{\text{red}}$. By use of this continuity condition, the interfacial transfer, surface recombination, and bulk recombination rates

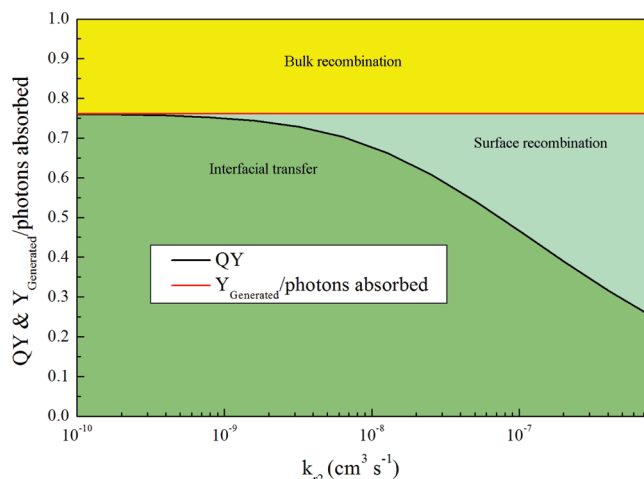


Figure 2. Dependences of QY and hole generation ratio on the rate constants of surface recombination. ($k_{r2} = 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, $I_0 = 1.0 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, $[\text{OH}_s^-] = 3.0 \times 10^{14} \text{ cm}^{-2}$, $r_0 = 10 \text{ nm}$, $k_{\text{ox},1}^i \times [(\text{RH}_2)_{\text{aq}}] = 10 \text{ s}^{-1}$, $k_1 \times [\text{OH}_s^-] = 3.0 \times 10^6 \text{ s}^{-1}$, $k_{r1} = 1.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, $k_d \times [\text{F}] = 1.0 \times 10^4 \text{ s}^{-1}$, $k_{\text{red}} \times [\text{O}_2] = 0.1 \text{ s}^{-1}$, $L_p = 1.0 \times 10^{-6} \text{ cm}$.)

can be calculated. Finally, the quantum yield (QY) of the photocatalytic reactions is

$$\text{QY} = \frac{v_{\text{red}}}{\int_{-r_0}^{r_0} \alpha I_0 e^{-\alpha(r_0-r)} dr} \quad (21)$$

3. RESULTS AND DISCUSSION

In this model, there are three kinetic courses, namely, surface trapping, surface recombination, and interfacial transfer, that are related to the surface defects as shown in formulas 12, 13, and 14. Surface trapping is the initial step of surface recombination and interfacial transfer. It is reported that surface trapping will change the lifetime of electrons or holes. The rate constant of surface recombination (k_{r2}) will decrease if the lifetime of the electrons increases. Figure 2 shows the dependence of QY on k_{r2} , and it can be seen that QY decreases when k_{r2} increases. The hole generation ratio (the hole generation speed on the surface divided by the photons absorbed) is also shown in Figure 2. This ratio is smaller than 1 due to bulk recombination, and it is almost independent of k_{r2} indicating that surface recombination has almost no effect on hole generation in bulk TiO_2 . The results show that reducing k_{r2} can effectively limit surface recombination, which can result in increasing the speed of interfacial transfer because the bulk recombination rate is almost unchanged.

In addition to the lifetime of electrons or holes, surface trapping will also change the speed of interfacial transfer. The related kinetic factor is the product of the rate constant of electron interfacial transfer and O_2 concentration, $k_{\text{red}} \times [\text{O}_2]$. Figure 3 shows the relationship between QY and the values of $k_{\text{red}} \times [\text{O}_2]$. It can be seen that QY increases with increase of $k_{\text{red}} \times [\text{O}_2]$. The relationship between the hole generation ratio and the value of $k_{\text{red}} \times [\text{O}_2]$ is also shown in Figure 3: the hole generation ratio is also independent of the values of $k_{\text{red}} \times [\text{O}_2]$. It follows that increase of $k_{\text{red}} \times [\text{O}_2]$ contributes to increase of QY through limiting surface recombination.

It is not surprising that photocatalytic activity will increase as surface trapping increases the lifetime and interfacial transfer of

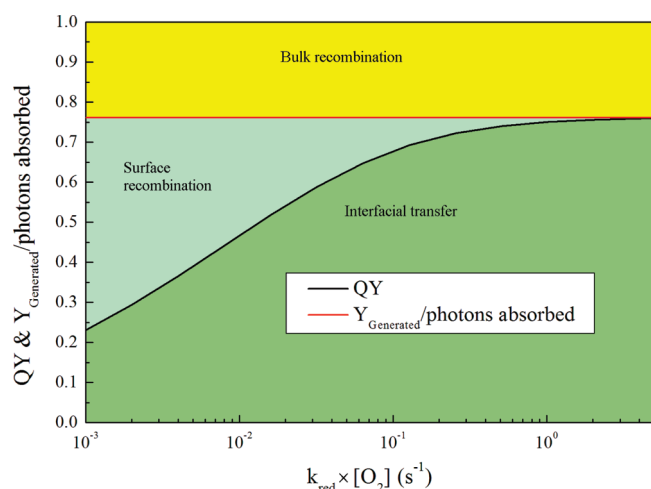


Figure 3. Dependences of QY and hole generation ratio on the product of the rate constant of interfacial transfer and oxygen concentration. ($k_{r_2} = 1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $k_{r_1} = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $I_0 = 1.0 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, $[\text{OH}_s^-] = 3.0 \times 10^{14} \text{ cm}^{-2}$, $r_0 = 10 \text{ nm}$, $k_{\text{ox},1} \times [\text{RH}_{2,\text{aq}}] = 10 \text{ s}^{-1}$, $k_1 \times [\text{OH}_s^-] = 3.0 \times 10^6 \text{ s}^{-1}$, $k_{r_1} = 1.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, $k_d \times [\text{F}] = 1.0 \times 10^4 \text{ s}^{-1}$, $L_p = 1.0 \times 10^{-6} \text{ cm}$.)

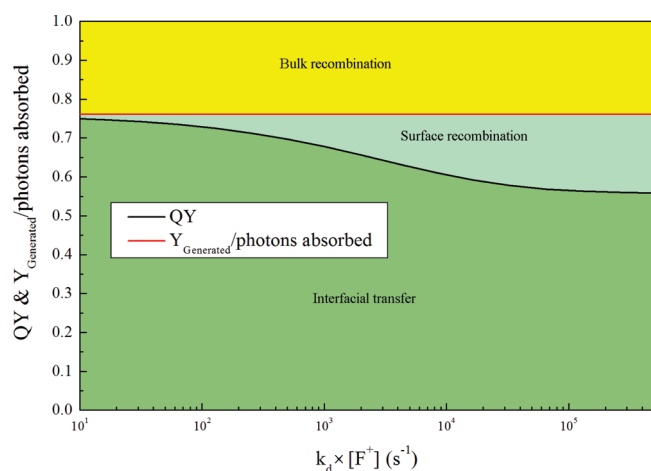


Figure 4. Dependences of QY and hole generation ratio on the product of the rate constant of electron trapping and the concentration of defects on surface. ($k_r = 1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $k_{r_1} = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $I_0 = 1.0 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, $[\text{OH}_s^-] = 3.0 \times 10^{14} \text{ cm}^{-2}$, $r_0 = 10 \text{ nm}$, $k_{\text{ox},1} \times [\text{RH}_{2,\text{aq}}] = 10 \text{ s}^{-1}$, $k_1 \times [\text{OH}_s^-] = 3.0 \times 10^6 \text{ s}^{-1}$, $k_{r_1} = 1.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, $k_{\text{red}} \times [\text{O}_2] = 0.1 \text{ s}^{-1}$, $L_p = 1.0 \times 10^{-6} \text{ cm}$.)

electrons or holes. However, it is not known what will happen if the surface trapping cannot change the lifetime of electrons or holes and interfacial transfer; hence we need to consider the effect of surface trapping speed. Figure 4 shows the dependences of QY and hole generation ratio on the product of the rate constant of electron trapping and the concentration of surface defects, $k_d \times N_t$. According to formula 12, $k_d \times N_t$ is an important kinetic parameter that decides the trapping speed of electrons on the TiO_2 surface. QY shows an obvious decrease as $k_d \times N_t$ increases. As hole generation is almost independent of $k_d \times N_t$, the increase of surface trapping is mainly consumed by surface recombination and cannot contribute to interfacial transfer. This result means that increase of electron trapping speed will

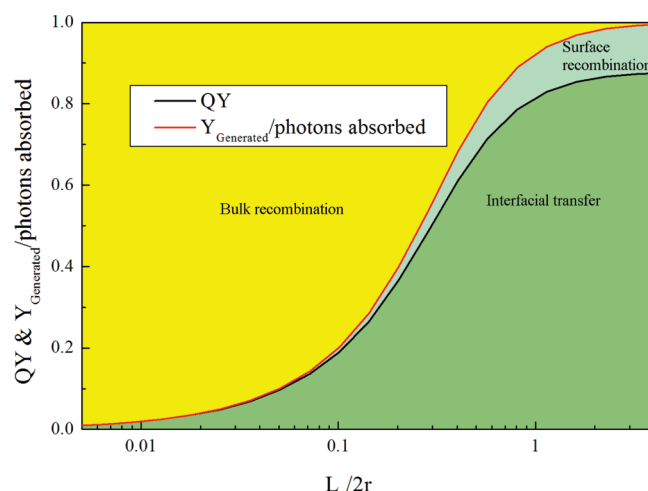


Figure 5. Dependences of QY and hole generation ratio on the hole diffusion length. ($k_{r_2} = 1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $k_{r_1} = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $I_0 = 1.0 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, $[\text{OH}_s^-] = 3.0 \times 10^{14} \text{ cm}^{-2}$, $r_0 = 10 \text{ nm}$, $k_{\text{ox},1} \times [\text{RH}_{2,\text{aq}}] = 10 \text{ s}^{-1}$, $k_1 \times [\text{OH}_s^-] = 3.0 \times 10^6 \text{ s}^{-1}$, $k_{r_1} = 1.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, $k_d \times [\text{F}] = 1.0 \times 10^4 \text{ s}^{-1}$, $k_{\text{red}} \times [\text{O}_2] = 0.1 \text{ s}^{-1}$.)

have negative effects if the lifetime of electrons and interfacial transfer cannot increase. As discussed above, QY is commonly decided by the surface trapping speed and its effect on the kinetic courses of electrons or holes after trapping. Only surface trapping that is able to increase the lifetime and the interfacial transfer speed of electrons or holes can increase QY. From this viewpoint, surface trapping is a necessary but not decisive kinetic course for increase of QY. Whether QY can be increased or not is dependent on the subsequent kinetic courses, i.e., surface recombination and interfacial transfer.

Compared to the surface defects, we consider the case of bulk defects as recombination centers. In the present model, the hole diffusion length, L_p , is an important parameter related to the kinetic course of bulk recombination. Figure 5 shows the dependences of QY and hole generation ratio on $L_p/2r_0$ ($2r_0$ is the nanoparticle diameter). The result shows that decrease of L_p will greatly increase bulk recombination, resulting in decrease of interfacial transfer. Because of high bulk recombination, hole generation will become the rate-determining step for low L_p values. When $L_p/2r_0$ is greater than 1, bulk recombination becomes very small due to the fact that almost all of the holes can migrate to the surface in their lifetime. Generally, the defects are on the surface for low defect concentrations because the introduction of defects on the surface is much easier than in the bulk. Some defects can enter the bulk at high defect concentrations, so recombination via bulk defects in photocatalysis will become important for high concentrations of defects.

In the photocatalysis of the doped TiO_2 under the illumination of UV light, it is always observed that the photocatalytic activity first increases and then decreases with the increase of defect concentration. The present model gives a reasonable explanation for this experimental result. For low-level doping, the presence of defects may effectively increase the lifetime of electrons or holes (as trapping centers) but cannot greatly influence the surface trapping speed, so the photocatalytic activity will increase as defect concentration increases. For high level doping, surface trapping and bulk recombination will become fast, so they will become the main factors that influence the photocatalytic reactions, resulting in decrease of photocatalytic activity.

Table 1. Summaries of the Photocatalytic Results about Doped TiO₂ Photocatalysts

doped element	preparation method	crystalline phase	doped range (%)	light source	decomposed substance	optimum doped concentration (%)
Mo ²⁴	hydrothermal	A	0–1.0	UV (365 nm)	orange II-dye	0.15
Sr ²⁵	sol–gel	A	0–1.0	UV (365 nm)	2,4 DNP	0.1
V ²⁶	sol–gel	A	0–10	UV+Visible	ethene	5
Ce ²⁷	sol–gel	A	0–30	UV (254 nm)	methylene blue	0.3
Fe ²⁸		A	0–0.1	UV (362 nm)	ethylene	0.005
La ²⁹	hydrothermal	A	0–5	UV (365 nm)	phoxim	0.2
Nb ³⁰	sol–gel	A	0–2.0	UV (365 nm)	2-mercaptobenzothiazole	1.2
Mn ³¹	sol–gel	A + R	0–0.1	UV (370 nm)	indanthrene BR violet	0.06
Fe ³²	thermal hydrolysis	A	0.31–0.39	UV (365 nm)	methylene blue	0.35
Sm ³³	sol–gel	A	0–0.5	sun light	diuron	0.3
S ³⁴	hydrothermal	A + R	0–2.0	UV (365 nm)	methyl orange	1.5

We compare our theoretical analysis with some published results of the doped TiO₂ photocatalysis. First, let us consider the surface modification and doping, in which case almost no doped element can enter TiO₂ bulk. Tada et al. used a chemisorption-calcination cycle (CCC) method to prepare Fe-surface-modified TiO₂ photocatalyst and studied their photocatalytic activity.²¹ The Fe-TiO₂ photocatalysts show high photocatalytic activity of 2-naphthol under the illumination of UV light, and it was seen that the photocatalytic activity first increases and then decreases with the increase of Fe loaded concentration. The authors thought that the Fe ions could effectively separate the photoinduced electrons and holes at low loading levels. However, they would cause the drop of Fermi level to lower the reducing power of the excited electrons or the rise in the top of the surface d sub-band to reduce the hole oxidation power, and thus the photocatalytic activity falls. Choi et al. prepared Fe-doped TiO₂ quantum dots and studied their photocatalytic activity under the illumination of UV light.²² They also found that the photocatalytic activity of Fe-doped TiO₂ samples first increases and then decreases with the increase of doped Fe concentration. They thought that the Fe ions would form the trapping centers for photoinduced electrons or holes at low doping level and can effectively prolong their lifetime. However, high-level Fe doping increases the probability of the tunneling recombination. For the Fe-doped TiO₂ quantum dots with the size of 3–4 nm, the doped Fe ions should mainly locate on the TiO₂ surface, and the Fe ions that can enter the TiO₂ bulk can be ignored. The present research shows that even if the Fermi level dropping, the Fe 3d sub-band rising, and the tunneling recombination do not take place significantly, the photocatalytic activity of doped TiO₂ photocatalysts may also first increase and then decrease with the increase of doped concentration, as illustrated in Figures 2 and 4. As for the bulk doping, it is considered that the doped impurities mainly form recombination centers.²¹ For example, Zhang et al. studied the effect of particle radius on the photocatalytic activity of Fe-doped TiO₂.²³ It was observed that the optimum Fe doped concentration decreases with the increase of particle radius. This may be due to the fact that the increase of particle radius will reduce the specific surface area, resulting in the increase of the concentration of Fe ions that enter TiO₂ bulk. Because of the increase of bulk recombination, the optimum doped concentration of highest photocatalytic activity will decrease accordingly with the increase of particle size. This experimental result is in accordance with the present theoretical analysis. Table 1 summaries the data of photocatalytic activity of some published papers, including the transition metal, rare earth

metal, alkaline earth metal, and nonmetal doped TiO₂ prepared using different method. Those experiments all show that the photocatalytic activity first increase and then decrease with the increase of doped concentration under the illumination of UV (UV + visible) light. There is an optimum doped concentration for the TiO₂ to present the best photocatalytic activity. In a conclusion, although the photocatalytic activity is also affected by other factors, for example, the specific surface area, particle size, and crystallinity phase, the present theoretical analysis gives a reasonable dynamic explanation of the photocatalytic mechanism of the doped TiO₂ photocatalysts under the UV light illumination.

4. CONCLUSIONS

A theoretical kinetic model is developed to study surface trapping and bulk recombination through defects, in photocatalysis under UV light illumination. All of the kinetic courses related to the defects, including surface trapping, surface recombination, interfacial transfer, and bulk recombination, are analyzed in detail. This model gives a clear picture of the functions of surface trapping. It is proved that increase of surface trapping speed alone cannot increase QY. Whether QY increases or not is decided by the kinetic courses that follow surface trapping, i.e., interfacial transfer and surface recombination. Another important point is that the model provides a simple method for including bulk recombination in theoretical kinetic studies of photocatalysis and gives a physical and mathematical description of bulk recombination. The comparison between the published results of doped TiO₂ photocatalyst and our theoretical analysis shows that the present research provides a reasonable explanation of the doped photocatalysis. We hope that this theoretical kinetic model can be used to direct future studies of doped TiO₂ photocatalysis.

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ABBREVIATIONS

I_0 =incident photonic flux ($\text{cm}^{-2} \text{s}^{-1}$)
 $[\text{RH}_{2,\text{aq}}]$ =pollutant concentration (cm^{-3})
 D_p =hole diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
 $p(r)$ =hole concentration (cm^{-3})
 p_s =hole concentration on TiO_2 surface (cm^{-3})
 n_s =electron concentration on TiO_2 surface (cm^{-3})
 α =absorption coefficient (cm^{-1})
 L_p =hole diffusion length (cm)
 τ_p =hole lifetime (s)
 r_0 =particle radius (nm)
 $j_{\text{generated}}$ =rate of hole photo generation on surface ($\text{cm}^{-3} \text{s}^{-1}$)
 v_p =rate of hole transport in TiO_2 bulk ($\text{cm} \text{s}^{-1}$)
 C_1, C_2 =integrated constants for carrier continuity equation
 v_1 =trapping rate of surface holes by bridging oxygen ($\text{cm}^{-3} \text{s}^{-1}$)
 $v_{\text{ox},1}$ =photo oxidation rate of $(\text{RH}_2)_{\text{aq}}$ in the case of hole IT transfer ($\text{cm}^{-3} \text{s}^{-1}$)
 $v_{\text{ox},2}$ =photo oxidation rate of $\text{RH}_{\text{aq}}^\bullet$ in the case of hole IT transfer ($\text{cm}^{-3} \text{s}^{-1}$)
 v_{r_1} =surface recombination rate via bridging oxygen ($\text{cm}^{-3} \text{s}^{-1}$)
 v_{d} =electron trapping rate by the impurities on the surface ($\text{cm}^{-3} \text{s}^{-1}$)
 v_{r_2} =surface recombination rate via impurities on the surface ($\text{cm}^{-3} \text{s}^{-1}$)
 v_{red} =electron transfer rate from the impurities to oxygen molecule ($\text{cm}^{-3} \text{s}^{-1}$)
 QY =quantum yield for interfacial transfer
 F^+ =signal of impurities on TiO_2 surface

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