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Received 14th August 2019 Accepted 23rd August 2019 DOI: 10.1039/c9ra06323d rsc.li/rsc-advances A formation model of superoxide radicals photogenerated in nano-TiO₂ suspensions \dagger

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A formation model of $O_2^{\bullet-}$ produced in TiO₂ photocatalysis was established, and then a custom built continuous flow chemiluminescence (CFCL) system was used to confirm the model's reliability by monitoring the $O_2^{\bullet-}$ formation process. This model may give deeper insights into $O_2^{\bullet-}$ formation for TiO₂ and other photocatalysts.

In photocatalytic reactions, such as TiO₂, it is generally accepted that O_2 . is produced from the reduction of adsorbed oxygen by photogenerated electrons on the TiO2 surface.¹⁻⁵ O2^{•-} formation is a rate-limiting process in TiO₂ photocatalytic reactions,⁶ and thus determines the efficiency of TiO₂ photocatalytic reactions by promoting the separation of photogenerated electrons and holes. Moreover, O_2 is an intriguing active species, attracting a great deal of attention in recent years due to its unique role. Previous studies have confirmed that O2'- plays an essential role in the photodegradation of pollutants.7,8 Therefore, probing the dynamic formation of O₂^{•-} over the course of time under UV irradiation is conducive to better understanding TiO₂ photocatalytic reactions. We have successfully identified surface long-lived O2[•] photogenerated on TiO2 surface,9 however, the dynamic details of O_2 .⁻ formation in TiO₂ photocatalytic reactions still remain to be solved.

In photocatalytic reactions, $O_2^{\cdot-}$ is continuously undergoing the processes of formation and deactivation simultaneously. Many methods have been developed to determine the $O_2^{\cdot-}$, including electron spin resonance (ESR),¹⁰ spectrophotometric assays,¹¹⁻¹³ and fluorescence assays,^{14,15} but the $O_2^{\cdot-}$ could only be detected at discrete times, and thus the total quantity could only be given within the irradiation duration. Given these limitations, $O_2^{\cdot-}$ dynamic monitoring is a great challenge. Chemiluminescence (CL) is inherently sensitive and rapid due to the relative ease with which light emission is instantly generated through a chemical reaction when two or more reactants are mixed. These qualities of CL make it suitable for the dynamic study of O_2 ^{•-}, despite its characteristic instability. In a previous study, we were able to successfully develop a continuous flow chemiluminescence (CFCL) method for dynamic monitoring of the formation process of O_2 ^{•-} in TiO₂ photocatalytic reactions.¹⁶

For the formation mechanism of O_2 ⁻⁻ in TiO₂ photocatalytic reactions, it is generally accepted that O_2 ⁻⁻ formation occurs on TiO₂ surfaces by the following scheme:

$$\mathbf{O}_2 + \mathbf{S} \xrightarrow[k_{-1}]{k_1} \mathbf{O}_{2,s} \xrightarrow{k_f} \mathbf{O}_{2,s} \xrightarrow{\cdot} \xrightarrow{k_d} \mathbf{O}_2, \mathbf{H}_2 \mathbf{O}_2$$

where O₂ denotes the dissolved oxygen (DO) in solution, S denotes the oxygen adsorption site on TiO₂ surface, k_1 and k_{-1} denote the adsorption/desorption rate constant of O2 respectively, O_{21s} denotes the adsorbed oxygen on TiO₂ surface, k_f denotes the formation rate constant of O_2 ., $O_{2,s}$. denotes the O_2 formed on TiO₂ surface, and k_d denotes the rate constant of O2^{•-} decomposition. It was reported that DO was first adsorbed on the site of TiO2 surface following the Langmuir isotherm,⁶ and then the adsorbed O_2 was reduced to O_2 . by photogenerated electrons under UV irradiation. Meanwhile, the formed O2. was transformed into other species by side reactions, such as H₂O₂ or ¹O₂ which deactivated to O₂ quickly. Specifically, it is suggested by some research that O2^{•-} could be produced from the oxidation of H_2O_2 by valence-band hole (h⁺) or hydroxyl radical (\cdot OH) in solution, where H₂O₂ is produced by the two-step oxidation of water or the two-electron reduction of O2.17 It is insignificant in this study because the O2. detected by CFCL method is the long-lived superoxide adsorbed on TiO₂ surface which is produced from the reduction of O_2 by photogenerated electrons, not in solution according to our previous study.9 The process of O2. formation was illustrated concretely as follows: when TiO₂ semiconductor is irradiated, the photogenerated electrons transferring to the TiO₂ surface are captured by five-coordinated surface Ti⁴⁺ to form the Ti³⁺ (eqn

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form $O_2^{\cdot-}$ (eqn (2)).^{1,2,18}

 $-Ti^{4+}-OH + e \rightarrow -Ti^{3+} + OH^{-}$ (1)

$$-\mathrm{Ti}^{3^{+}} + \mathrm{O}_{2,s} \rightarrow -\mathrm{Ti}^{4^{+}} \cdots \mathrm{OO}^{\bullet -}$$
⁽²⁾

$$O_2^{\bullet-} + h^+ / \cdot OH \to {}^1O_2 \tag{3}$$

$$O_2^{*-} + e + H^+ \to H_2O_2$$
 (4)

$$O_2^{\cdot -} + O_2^{\cdot -} + H^+ \to H_2O_2 + O_2$$
 (5)

Meanwhile, O_2 ^{•-} formed also undergoes a decaying process possibly *via* the following three pathways (eqn (3)–(5)): (1) oxidation by h⁺ or •OH, (2) further reduction by e, or (3) selfdisproportionation in solution. Therefore, the number of O_2 ^{•-} determined in photocatalytic reactions at any irradiation time (*t*) is what the total quantity of formed O_2 ^{•-} subtract those decomposed *via* the aforementioned side reactions from t_0 s to *t* s upon irradiation. The formula can be expressed as follows:

$$\left[\mathbf{O}_{2}^{\cdot-}\right]_{t} = \int_{t_{0}}^{t} d\left[\mathbf{O}_{2}^{\cdot-}\right]_{f} / dt - \int_{t_{0}}^{t} d\left[\mathbf{O}_{2}^{\cdot-}\right]_{d} / dt$$
(6)

In this equation, the t_0 and t of the lower and upper limit of the definite integral represent the starting and ending time of UV irradiation respectively. Based on the formation process of O2. mentioned above, the net rate of O2. formation at any time in photocatalytic reactions can be obtained as shown in eqn (7.1). The first term of the right side of the eqn (7.1) represents the formation rate of O2^{•-}, and it is a second-order reaction with respect to the concentration of -Ti³⁺([Ti³⁺]) and adsorbed oxygen ($O_{2,s}$). k_f is a second-order formation rate constant. The second term (eqn (7.1)) represents the decay rate of O_2 ., among which k_d is a second-order decay rate constant, [X] represents the concentration of e, h^+ , \cdot OH or $O_2^{\cdot-}$ in terms of eqn (3)–(5). It is generally believed to contain the aforementioned three pathways. We have previously confirmed that the O₂^{•-} adsorbed on TiO₂ surface is thermodynamically favored.⁹ Therefore, the two former pathways (eqn (3) and (4)) dominated the decay process under UV irradiation. These processes were considered to be pseudo-first-order due to the constant of h^+ , $\cdot OH$ and e under steady-state irradiation. So $k'_d(k'_d = k_d \times [X])$ is the pseudo-first-order apparent rate constant (eqn (7.2)). $[O_2]_s$ is equal to oxygen coverage on TiO_2 surface (θ) by the number of adsorption sites ([S]) according to Langmuir isotherm (eqn (7.2)), in which θ is related to the DO concentration in solution ([O₂]), adsorption constant (k_1) , desorption constant (k_{-1}) , and formation rate constant of $O_2^{\cdot -}(k_f)$ (eqn (7.3)).

$$\frac{d[O_2^{\cdot}]}{dt} = k_f [Ti^{3+}][O_2]_s - k_d [X][O_2^{\cdot}]$$
(7.1)

$$=k_{\rm f} \left[{\rm Ti}^{3+} \right] \theta[{\rm S}] - k'_{\rm d} \left[{\rm O}_2^{\, \cdot -} \right] \tag{7.2}$$

$$=k_{\rm f} [{\rm Ti}^{3+}] [{\rm S}] \frac{k_1 [{\rm O}_2]}{k_1 [{\rm O}_2] + k_{-1} + k_{\rm f}} - k_{\rm d}' [{\rm O}_2^{\cdot-}] \qquad (7.3)$$

It has been reported that the electron transfer from TiO_2 to O_2 is the rate-limiting step in TiO_2 photocatalytic reaction.^{6,19-21} Upon this, k_f is far less than $k_1[O_2]$ and k_{-1} . Furthermore, the $[O_2]$ in solution is low, and thus $k_1[O_2]$ is far less than k_{-1} . If such speculation is true, the eqn (7.3) can be eventually transformed into the following:

$$\frac{d[O_2^{\cdot-}]}{dt} = k_f [Ti^{3+}][S]K_1[O_2] - k'_d [O_2^{\cdot-}]$$
(8)

where $K_1 (K_1 = k_1/k_{-1})$ is the adsorption equilibrium constant of $[O_2]$. Assuming that $[O_2^{\cdot -}] = mCL + n$, which is a linear relationship between $O_2^{\cdot -}$ concentration and CL intensity, the eqn (8) can then be converted into the following:

$$\frac{d[mCL+n]}{dt} = k_{\rm f} [{\rm Ti}^{3+}] [{\rm S}] K_1 [{\rm O}_2] - k'_{\rm d} [mCL+n]$$
(9)

Finally, the eqn (10) representing the formation model of $O_2^{\cdot-}$, with respect to time as the independent variable and CL intensity as the dependent variable, would be obtained by integrating these variables with the eqn (9) from t_0 to t:

$$CL = \frac{k_{f}K_{1}[Ti^{3+}][S][O_{2}]}{mk'_{d}} \left(1 - e^{-k'_{d}(t-t_{0})}\right) + \frac{n}{m}$$
(10)

In eqn (10), k_f , K_1 , k'_d , [S], [O₂], *m*, and *n* are constants under certain conditions. The coefficient $((k_{\rm f}K_1[{\rm Ti}^{3+}][{\rm S}][{\rm O}_2]/(mk'_d)) + n/m)$ represents the theoretical maximum CL intensity (CL₀) corresponding to the steady-state concentration of $O_2^{\cdot-}$ when t is infinite in irradiated TiO_2 suspensions. Herein t_0 is the time when irradiation starts for 50 s, due to the disturbance of background signal within the first 50 s of irradiation. According to eqn (10), given that $k_{\rm f}, K_{\rm 1}$, and k_d are determined by the intrinsic property of TiO₂ photocatalyst regardless of experimental conditions, CL₀ is dependent on [Ti³⁺], [S], [O₂] and [X], which are closely related to experimental conditions. In photocatalytic reactions, [Ti³⁺] relies on the number of photogenerated electrons highly dependent on I; [S] is the total surface area of TiO_2 in suspension, closely related to $[TiO_2]$; $[O_2]$ is dependent on [DO] in TiO_2 suspensions; [X], the aforementioned concentration of h^+ , $\cdot OH$ and e, is also dependent on I.

In order to verify the formation model of O_2 ., we fit the different CL curves with eqn (10) by changing [TiO₂], *I*, and [DO]. As shown in Fig. 1(a–i), the CL curves from different [TiO₂], *I* and [DO] were well-fit by eqn (10) with high correlation coefficients ($R^2 > 0.99$), indicating that the model could simulate dynamic process of O_2 . formation. Furthermore, according to the O_2 . formation model (eqn (10)), CL intensity is linearly correlated to [S], [Ti³⁺], and [O₂], indicating that CL intensity could increase linearly with the increase of [TiO₂], *I* and [DO] within set limits. In order to verify this assumption, CL intensity at 300 s, 600 s, 900 s, 1200 s and + ∞ under different [TiO₂], *I* and [DO] conditions in TiO₂ suspensions was calculated by eqn (10) (Table S1†). Then the CL intensity from different [TiO₂], *I* and [DO] at different time points were linearly fit (Fig. S1–



Fig. 1 CL curves of luminol (50 μ M) with photo-irradiated TiO₂ suspensions (pH = 11) under different experimental conditions: TiO₂ concentration (a-c), irradiation intensity (d-f), DO concentration (g-i). The black lines represent experimentally measured values and the red lines are the fitted values.

3[†]), and the R square values were calculated and summarized in Table 1. For instance, the CL intensity with TiO₂ concentration of 0.02 mg mL $^{-1}$, 0.05 mg mL $^{-1}$ and 0.1 mg mL^{-1} at 300 s, 600 s, 900 s, 1200 s and $+\infty$, respectively, had good linear fit with high correlation coefficients ($R^2 > 0.99$), except at $+\infty$ ($R^2 = 0.903$), confirming that CL intensity increased linearly with the increase of [S] as indicated by eqn (10). There was also a good linear relationship between CL intensity and I with high correlation coefficients ($R^2 > R^2$) 0.9), except at $+\infty$ ($R^2 = 0.821$), indicating that CL intensity increased linearly with the increase of [Ti³⁺]. At different [DO], the corresponding R^2 values were also high ($R^2 > 0.95$), indicating that CL intensity was also linearly dependent on $[O_2]$. Overall, the formation model of O_2 . could adequately describe the dynamic process of O_2 .⁻ formation in photoirradiated TiO₂ suspensions.

In the present work, a formation model of O_2 .⁻ in TiO₂ photocatalytic reactions was established. According to the model, the O_2 ⁻⁻ formation was closely related with [TiO₂], [DO] and I, under which the dynamic process of O_2 . formation was successfully simulated by the model with high correlation coefficients ($R^2 > 0.9$), thereby confirming the model validity. This model can explicitly provide details on O₂^{•-} formation which determines the photocatalytic efficiency in TiO₂ photocatalytic reactions, and give deeper insights into designing high-efficiency TiO₂ photocatalysts. In accordance with this model, Feng et al. reported the selfdoped Ti³⁺ enhanced TiO₂ photocatalyst for hydrogen production through the reduction of the TiO₂ surface using a one-step combustion method.22 Furthermore, this model may have significant implications for other photocatalysts with respect to O_2 .⁻ formation.

Table 1	The calculated	value of R	square u	pon different	experimental	conditions a	at different	irradiation time
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Time (s)	TiO_2 concentration (mg mL ⁻¹)	Irradiation intensity $(mW cm^{-2})$	DO concentration $(mg mL^{-1})$	
300	0.998	0.921	0.999	
600	0.999	0.946	0.982	
900	0.998	0.960	0.971	
1200	0.994	0.972	0.968	
$+\infty$	0.903	0.821	0.977	

Conflicts of interest

There are no conflicts to declare.

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