Calculation method of quantum efficiency to TiO$_2$ nanocrystal photocatalysis reaction

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Abstract: The quantum yield is an important factor to evaluate the efficiency of photoreactor. This article gives an overall calculation method of the quantum efficiency(Φ) and the apparent quantum efficiency(Φ_a) to the TiO$_2$/UV photocatalysis system. Furthermore, for the immobility system (IS), the formulation of the faction of light absorbed by the TiO$_2$ thin film is proposed so as to calculate the quantum efficiency by using the measured value and theoretic calculated value of transmissivity (T). For the suspension system(SS), due to the difficulty to obtain the absorption coefficient (α) of TiO$_2$ particulates, the quantum efficiency is calculated by means of the relative photonic efficiency (ζ_r) and the standard quantum yield ($\Phi_{standard}$).

Keywords: photodegradation reaction; quantum efficiency; apparent quantum efficiency; photonic efficiency; relative photonic efficiency; absorption coefficient

Introduction

The photocatalytic degradation of organic pollutants using TiO$_2$/UV is attracting considerable attention for the application to environmental problems (Fujishima, 2000; Hoffman, 1995; Ollis, 1993). Semiconductors TiO$_2$ has been shown to be an effective mental oxide due to its electronic structure, which is characterized by a filled valence band and empty conduction band. The process is initiated by the band-gap excitation of the TiO$_2$ under UV illumination. When a photo with energy of hν exceeds the band-gap energy, an electron is promoted from the valence band into conduction band. Photogenerated electrons are trapped by adsorbed oxygen molecules with high quantum yield to generate superoxide ion ($\cdot O_2^-$), which ultimately generates $\cdot$OH radical through series of processing. Photogenerated holes react with water absorbed on the surface of TiO$_2$ to produce $\cdot$OH radical or directly react with absorbed organics. $\cdot$OH radical also can oxide these pollutants.

Quantum efficiency is a very important factor to evaluate the reaction efficiency as a whole, which is controlled by the effectiveness of suppression of electron-hole recombination. However, it is a very difficult thing to measure quantum yield in heterogeneous photocatalytic system because of the problem of light scattering as well as other reaction condition. Until now, a comprehensive method is still inaccessible. So, there exists great necessity to build a scientific and reasonable method to describe the quantum efficiency of photocatalytic degradation reaction to organic compounds.

1   Model formulations

1.1   General formulations

Usually, quantum efficiency is defined as the ratio of the number of molecules undergoing a photocatalytic reaction to the number of quanta (N_{photon}), which are absorbed by photocatalyst.

$$\Phi = \frac{N_{molecule}(\text{mol/s})}{N_{photon}(\text{Einstein/s})} = \frac{V \cdot \dfrac{-d[C_{reactant}]|_{t=0}}{dt}}{I_{absorption}} = \frac{\text{initial rate of reaction}}{\text{rate of absorption of photos}}. \tag{1}$$

Where $I_{absorption}$ represents the irradiance of UV light incidence absorbed by catalyst TiO$_2$.

Since TiO$_2$ particles will absorb, scatter, or transmit light, photocatalyst can not absorb all the incident photo flux from a given source due to light scattering off TiO$_2$ particles (for suspension system) or transmit through the TiO$_2$ thin film (for immobility system). For this reason, the rate of absorption of

photos is very hard to assess accurately. Commonly, it is wise to adopt a simplified calculation method by introducing another factor. The apparent quantum efficiency is determined as a function of total incident light intensity. Hence, the apparent quantum efficiency, Φ_a, is got as the ratio of change of reactant in concentration per unit time divided by the total incident light flux from the source.

$$\Phi_a = \frac{\dfrac{-\,\mathrm{d}[\,C_{\mathrm{reactant}}\,]\,V}{\mathrm{d}t}}{\dfrac{\mathrm{d}[\,h\nu\,]_{\mathrm{incident}}}{\mathrm{d}t}}\,\bigg|_{t=0} = \frac{\dfrac{-\,\mathrm{d}[\,C_{\mathrm{reactant}}\,]\,V}{\mathrm{d}t}}{I_{\mathrm{incident}}}\,\bigg|_{t=0}\,. \tag{2}$$

Where I_{incident} is the total irradiance of UV light incidence.

By comparison with Eq.(1) and Eq.(2), although two equations are similar in form of formulation, Φ and Φ_a are really not identical factors to describe a same photoreaction system. It is apparent that Φ_a is surely smaller than Φ in numerical value, for bigger I_{incident} than $I_{\mathrm{absorption}}$. The apparent quantum efficiency (Φ_a) is much easier to approach, since I_{incident} can be measured expediently with a radiometer. However, the quantum efficiency(Φ) more actually reflects the extend to scattering, transmitting and refracting of the incident light by TiO₂ particulates or TiO₂ films, which is the true quantum efficiency. In the TiO₂/UV induced photocatalytic decomposition reaction system, there are mainly two different reaction modes. Here is given a detail discussion respectively.

1.2 Immobility system (IS)

In the immobility system, incident light may be absorbed, refracted, reflected by medium and transmitted through medium when illuminating TiO₂ film. The refractive index of the TiO₂ film was determined by property of surrounding medium and porosity of TiO₂, which can be described as the following equation.

$$n_{\mathrm{d,film}} = n_{\mathrm{d,medium}} \cdot x_{\mathrm{medium}} + n_{\mathrm{d,TiO_2}} \cdot x_{\mathrm{TiO_2}}\,. \tag{3}$$

Where x represents the compositional fraction of the pores and crystallite TiO₂ in the film and n_d is the refractive index. Generally, the porosity of the TiO₂ is approximate $45 \pm 7\%$ when its quantum size is at the range of tens to hundreds nanometer (Loudon, 1992). The medium often refers to aqueous solution, which is filled in the pores of TiO₂. Here we only consider the typical reaction model of the silica/TiO₂-film/aqueous solution system.
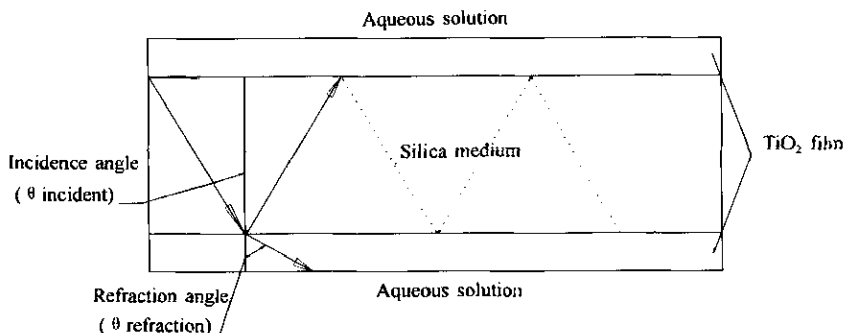

Fig.1   Increase in refraction angle and propagating distance with larger incident angle

Fig.1 shows influence of incidence angle on the propagating way and refraction angle in the interface of silica/TiO₂ thin film.

Obviously, in the silica/TiO₂-film interface, the critical angle can be calculated out.

$$\theta_c = \sin^{-1}(\,n_{\mathrm{d,silica}}/n_{\mathrm{d,TiO_2 film}}\,)\,. \tag{3.1}$$

Where $n_{d,silica}$ is $1.5 - 1.7$ for silica and $n_{d,TiO_2\,film}$ is the calculated value by using Eq.(3).

The thickness of TiO_2 film is only at the range of hundreds of nanometers, which do not have large resistance for light transmittance. When the incidence angle ($\theta_{incident}$) is below the critical angle (θ_c), light will propagate in a frustrated total reflection (FTR) mode in the silica medium so that light only can transmit a short distance in the medium. Just because of the exiting refraction at the interface, most of the light is lost out of the TiO_2 film and transmits into outside aqueous medium. All these factors result in a low quantum yield.
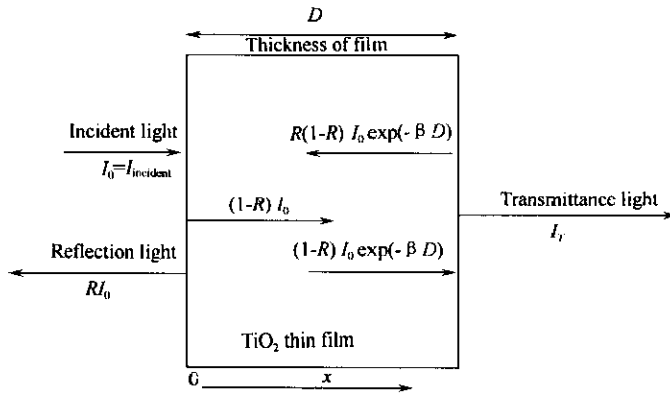

Fig.2   The absorption and reflection in the TiO_2 thin film

When the incident angle is no smaller than the critical angle (θ_c), the light will propagate with the attenuated total reflection (ATR) mode in the silica medium. The below is given the formulation to calculate the fraction of incident light absorbed by TiO_2 films. Fig.2 shows the absorption and reflection of light in the TiO_2 thin film under ideal situation.

At a given wavelength (λ), there is a certain relationship among absorptivity (A), reflectivity (R) and transmissivity (T; Miller, 1999).

$$A + R + T = 1; \quad A = \lg(1/T);$$

$$I_T = (1 - R)\int_0^D dI_x = (1 - R)^2 I_0 \exp\left(-\int_0^D \beta_x dx\right) = (1 - R)^2 I_0 \exp(-\beta \cdot D),$$

$$T = I_T/I_0 = (1 - R)^2 \exp(-\beta D).$$

Where β is the absorbency coefficient of TiO_2 thin film, and D is the thickness of film.

From the above equations, it is easy to get the following equation.

$$(1 - R) + 2\lg(1 - R) - \beta D - (1 - R)^2 \exp(-\beta D) = 0. \tag{4}$$

Provided a complete uniform thin film, in theory, $I_{absorption}$ will be calculated out through the R factor, which can be worked out by solving the Eq.(4).

$$I_{absorption} = I_0 - RI_0 - I_T = I_0(1 - R)[1 - (1 - R)\exp(-\beta D)]. \tag{4.1}$$

The above is the ideal situation. In fact, the flux of light incident had some certain spectral distribution on band-pass ranges. And so, the fraction of light absorbed by the various TiO_2 films at each wavelength should be calculated as:

$$[(I_0 - I_T)/I_0]_{\lambda,film} = \eta \cdot (1 - T)_{\lambda,film} \cdot (I_\lambda/I_{\lambda,max})_{filter}.$$
$$I_{\lambda,max} = I_{,measured} \tag{5}$$

Where the first term, $[(I_0 - I)/I_0]_{\lambda,film}$, is the faction of light absorbed by the TiO_2 film at a given wavelength, and the term $I_{\lambda,max}$ is the integral light intensity with respect to overall wavelength distribution, which was assumed to be equal to the factual measured light intensity ($I_{,measured}$). I_λ is the light intensity at the wavelength of λ. The efficiency factor, η, is approximate $0.90 - 0.98$ according to respective film material, carrier and photoreactor shape, which represents absorption efficiency as considering the reflection loss from the different interface. The term, T, represents the percent transmittance of TiO_2 films coating on carrier (silica) versus wavelength.

1.3 Suspension system (SS)

In the suspension system, TiO₂ particulates are also not capable of absorbing all the incidence photo flux from a given source due to the light scattering off the particle surface. $I_{absorption} = \alpha I_{incident}$, where α is the absorption coefficient. The intensity of light scattered by the suspension depends on the refractive indices of the scattering film/particle (n_1) and the surrounding medium (n_0). For the materials making up a typical photocatalytic system in heterogeneous photocatalysis, n_0 is 1.33 for H_2O or correlative value for aqueous solution. And n_1 is 3.87 for rutile TiO₂ or 2.5 – 3.0 for anatase TiO₂ at wavelength range of 310 to 380 nm. When $n_0 \approx n_1$, the extent of scattered light is negligible. But when $n_1 > n_0$, light is expected to be highly scattered, with losses of above 50 percentage of the light flux occurring. As a result, the percentage of photons absorbable appears to be in a wide range.

The above is only a simple method to estimate the $I_{absorption}$. How to accurately calculate the quantum yield is still a big problem.

1.3.1 Simplified mode

As a consequence of the fact that some needed parameters are very difficult to be attained, the above methods are proposed only to make a fundamental evaluation to photocatalytic efficiencies. If these parameters are not evaluated accurately, the calculating outcome maybe has a significant deviation to the real value. So, a more useful term, photonic efficiency, ζ, is proposed to compare process photoreaction efficiencies. Photonic efficiency (ζ) describes the number of transformed reactant molecules or formed product molecules divided by the number of photonic at a given wavelength.

$$\zeta = \frac{N_{molecules}(mol/s)\, reactant\ or\ product\ molecules}{N_{photos}(Einstein/s)\, incident\ inside\ reactor\ cell} \quad (6)$$

Where the parameter, N_{photo}, is also hard to be worked out. So, another useful term, the relative photonic efficiency (ζ_r) is raised, which is related to a standard photocatalyst and a standard degraded object in photocatalyzed process (Gimenez, 1999).

It is reasonable to assume that the initial photodegradation of phenol is chosen as the standard process and Degussa P25 TiO₂ as the standard photocatalyst. And so, the photonic efficiency (ζ_r) is defined as following:

$$\zeta_r = \frac{\dfrac{dc_{substrate}}{dt}}{\dfrac{dc_{phenol}}{dt}}\bigg|_{t=0} = \frac{r_{substrate}}{r_{phenol}}\bigg|_{t=0}. \quad (7)$$

In the Eq.(7), both initial rate should be obtained under exactly the same conditions. Ultimately, ζ_r can be converted into the quantum yield (Φ) once a standard quantum yield ($\Phi_{standard}$) for a given photocatalyst and a given substrate has been determined by using the following equation.

$$\Phi = \zeta_r \Phi_{standard}. \quad (8)$$

1.3.2 Mode solution

The below is the way to calculated out the standard quantum yield ($\Phi_{standard}$). In this area, Serpone had made a detail study to estimate the fraction of light absorbed in Degussa P25 TiO₂ by using an integrate sphere (Serpone, 1996; 1997). It is very reasonable to follow Serpone' experimental method to calculate out the quantum yield of similar compounds. According to the definition of above quantum yield, the standard quantum yield can be described as:

$$\Phi_{standard} = N_{phenol}/N_{photo} = N_{phenol}/I_{absorption} = [V(r_{phenol})]/[\alpha \cdot I_{incident}]. \quad (9)$$

Where V is the volume of reactor cell, and r_{phenol} represents the rate of disappearance of phenol. For 1g/L TiO₂ loading (m_0) and total 3.058 Einstein/min incident photon flux (I_0) to degradation of

phenol, the initial absorption coefficient (α_0) was 0.1385. Supposed that there exited certain linearity relationship between them under the same incident photo flux and the total absorption still abides by Lambert-Beer' Law, the absorption coefficient (α) with different TiO_2 loading can be described as: $\alpha_0 = \alpha \cdot [I_i/I_0]$. With regarding to incident light intensity, we assume that it is no influence to the absorption coefficient within the appropriate experimental range. As a result, the absorbed photo flux just linearly varies with incident light. Integrating above two factors, the absorption coefficient can be expressed as:

$$\alpha = \alpha_0 \cdot [I_i/I_0] \cdot [m_i/m_0], \tag{10}$$

$$\alpha_0 = 0.1385, \quad I_0 = 3.058 \text{ (Einstein/min)},$$

where I_i and m_i represent factual values respectively, I_0 and m_0 are the referenced values. α is the real absorption coefficient.

According to the different α, the value of $I_{\text{absorption}}$ can be rationally adjusted as well as Φ_{standard}. Then, under analogous experimental condition, through the measurement of degradation rate of the objective reactant, the quantum yield (Φ) of respective substrate can be calculated out by using Eq.(7) and Eq.(8).

2 Experimental section

2.1 Experimental condition

The photo flow 3.08×10^{-6} Einstein/min (1 Einstein = 1 mol of photons); TiO_2 loading is 1.00 g/L; The initial concentration of phenol is 50 mg/L.

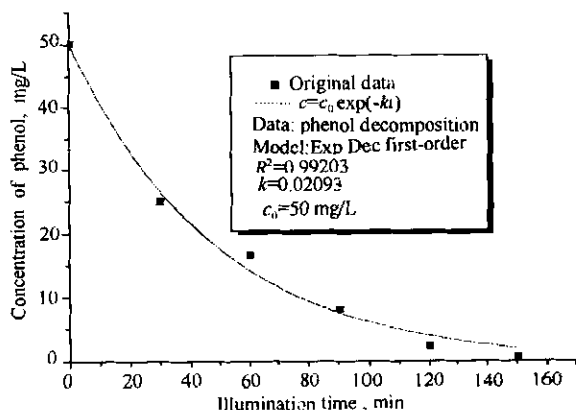Fig.3 shows variation of phenol concentration as function of illumination time.

Fig.3 Decrease of phenol concentration (c) dependence on UV illumination time (t)

The photocatalytic degradation kinetics of many organic compounds in TiO_2 suspension under UV radiation have often been modeled using the simple Langmuir-Hinshelwood equation. And the degradation rate is followed Pseudo first-order reaction kinetics for the studied concentration rage, which can be expressed as the form of $c = c_0 \exp(-kt)$ (Emeliine, 1999).

Where c_0 is the initial concentration of phenol, k is the apparent first-order rate constant and t is the UV illumination time.

$$c = 50 \cdot \exp(-0.02093t). \tag{11}$$

Eq.(11) is determined by means of non-linear curve fitting.

The parameter (k) and initial rate of degradation (r_0) can be obtained from the above data process.

$k = 0.02093 \text{ min}^{-1}$

$$r_0 = -\frac{dc}{dt}\Big|_{t=0} = (-c_0) \cdot (-k) \cdot \exp(-kt)\Big|_{t=0} = c_0 \cdot k = 1.0415 \text{mg} \cdot L^{-1} \cdot min^{-1}. \tag{12}$$

Similar outcome can be obtained with the same method to process the data of other analogous compounds' decomposition.

$$\Phi_{\text{standard}} = \frac{\nu \cdot r_{\text{phenol}}}{\alpha \cdot I_{\text{incident}}} = \frac{\nu \cdot \gamma_0}{\alpha \cdot I_{\text{incident}}} = 0.1275,$$

$$\Phi = \zeta_r \Phi_{\text{standard}} = \Phi_{\text{standard}} \times (r_{\text{substrate}}/r_{\text{phenol}}). \tag{13}$$

If not considering the absorption coefficient of incident light, the apparent quantum yield is equal to, $\Phi_a = \alpha\Phi_{standard} = 0.0177$, which seems much smaller than the standard quantum yield because most incidence photons can not completely absorbed by TiO_2 particles. So, under different reaction condition or with different calculation method, there have great deviations to quantum yields even with the same reaction system. Such kinds of comparisons on respective quantum yields are unmeaningful.

3   Conclusion

From the definition of quantum efficiency, the calculation equations of quantum efficiency and apparent quantum efficiency are proposed. The absorption coefficient is the key factor to the calculated absorption incident intensity and photoefficiency. For the immobility system, a direct calculating method is present by means of measured value and theoretic calculated value of transmissivity respectively. For the suspension system, by introducing a new factor of the relative photonic efficiency, a simplified model is proposed for calculating quantum yield, which is also suited for the immobility system by modifying the standard quantum yield and related parameters. Moreover, the quantum yields of the same compounds even have significant deviations with different calculation methods and reaction condition.

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