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Determination of quantum yields in two-dimensional scattering systems

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Abstract

A simple method for the determination of photochemical quantum yields (Φ) in light scattering system is proposed. The method is applied for two-dimensional (2D) reactors, such as photocatalytic layers, where scattered light can exit only through the front or rear surfaces. The determination of Φ is based on the measurement of both product formation rate, R, and the transmitted light (I_T) in the 2D system, comparing two 2D reactors (layers with thickness L_1 and L_2, or suspensions with concentration C_1 and C_2), respectively. A good approximation of the quantum yield can be derived from the equation: $\Phi=(R_2 - R_1)/(I_{T(1)}-I_{T(2)})$, where the numbers in parenthesis refer to the given reactor. Satisfactory accuracy is obtained with "D_1" $= 0.6$–1 and "D_2" $= 1.2$–2, where "D_1" and "D_2" represent the respective apparent spectrophotometric absorbance of the 2D reactors. The method requires only a light intensity detector or a chemical actinometer. Systematic errors are discussed.

Keywords: Quantum yield; Photolysis; Light scattering; Layers; Titanium dioxide

1. Introduction

Although photochemistry of suspensions and nanocrystallite layers is being extensively investigated, the lack of standardized procedures makes it difficult to compare photochemical rates and yields even when the same materials are used. Most reports are lacking the information, which is required for calculation of quantum yields (Φ), such as absorbed light intensity (I_A). The situation is often complicated by light scattering, which makes it difficult to distinguish between absorbed and scattered light.

A conventional spectrophotometer measures the incident light (I_0) and the transmitted light (I_T), from which the optical absorbance, $D = \log(I_0/I_T)$. When light scattering is involved, most of it does not reach the detector, so that an apparent absorbance, "D" $> D$ is observed. Determination of quantum yield requires the knowledge of the amount of absorbed light, which usually is calculated as the difference between the light hitting the sample and the non-absorbed light. The later can be measured with the aid of an integrating sphere [1]. However, such device is not always available, and its use may involve systematic errors, e.g. when the layer reflects a significant part of the light towards the entrance aperture. Re-absorption of light reflected from the integrating sphere may also introduce systematic error, as similar reflections usually do not occur in the photochemical reactor (unless operated in the integrating sphere). Evaluation of radiation absorption in slurry photocatalytic systems and the importance to correct for scattered light has been recently discussed by Brandi et al. [2] Determination of quantum yields in scattering systems has been discussed by Serpone and Salinaro [3]. The proposed method involves an integrating sphere for high accuracy. Alternatively, study of the concentration effect in suspensions yields approximate values, although the backward scattering has been ignored in this treatment.

Here we propose a simple method for the determination of photochemical quantum yields in light scattering system, which does not require the use of an integrating sphere, and nevertheless shows reasonable accuracy. The principle is the measurement of the light exiting the reactor in the direction of the excitation light beam by placing the detector very near to the reactor. This assures that practically all the light, whether linearly transmitted or scattered in the direction of the detector be monitored.

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2. Experimental

A two-dimensional (2D) photochemical reactor is defined as a medium where photochemical reactions take place, with one dimension much smaller compared to the other two. The light hits the reactor at 90° to the plane defined by the large cross section. Under such conditions, the light absorption in any direction perpendicular to the incident beam is sufficiently large so that the unabsorbed scattered light can exit the reactor only through the front or rear surface. The most common 2D reactors are the flat-plate photo-reactor, [2] where the thickness (path-length) is less than 1/20 of any other dimension, photocatalytic TiO_2 layers, and reactors containing high concentration of colloid. The light beam must be considerably smaller than the cross section. If the quantum yield depends on absorbed light density, the beam must be much larger than the layer thickness, so that re-absorption of the scattered light outside the beam pattern can be neglected.

The light exiting through the rear surface was detected by actinometry [4] or by Ophir Optronics detector model PD300-UVSH, calibrated against the chemical actinometer.

The accuracy of the approximation method was tested by comparison to measurements in integrating sphere, Labsphere, 15 cm diameter. In the latter case, the total non-absorbed light including all transmitted and scattered light was measured in the integrating sphere. The backwardly scattered light (I_{BS}), which includes the light exiting the reactor through the front surface, or reflected at the front surface, was calculated as the difference between the total non-absorbed light and the total transmitted light (I_{T}). Note that the detector at close proximity to the reactor measures the total transmitted light, including forwardly scattered light (I_{FS}). An irradiated 2D scattering reactor is shown in Fig. 1.

TiO_2 layers were prepared using Ishihara's STS-01 or STS-21 titania-suspensions. The STS-01 product is a suspension containing 40% of TiO_2 (60 nm aggregate diameter, primary particles 7 nm diameter). The STS-21 is a suspension containing 40% of TiO_2 (200 nm aggregate diameter, primary particles 20 nm diameter). The surface areas of these titania are 300 and 50 m^2/g, respectively. The photocatalysis of CH_3OH using TiO_2 layers and the detection of the product HCHO are described in reference [5].

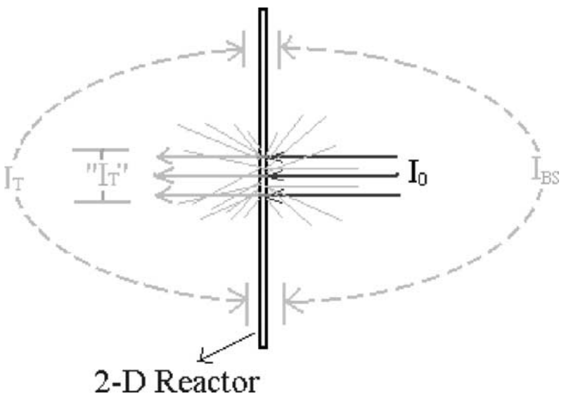

Fig. 1. The illuminated 2D scattering reactor.

3. Results and discussion

The determination of Φ is based on the measurements of product formation rate (R, mole/s) and the transmitted light in two 2D reactors differing by the thickness of the photocatalytic layer. The quantum yield corresponding to the light intensity $I = I_{\mathrm{T}(1)}–I_{\mathrm{T}(2)}$ (einstein/s) is calculated from Eq. (1), where the numbers in parenthesis refer to the given layer. The transmitted light is measured using an actinometer at close proximity to the 2D reactor.

$$\Phi = \frac{(R_2 - R_1)}{(I_{\mathrm{T}(1)} - I_{\mathrm{T}(2)})} \qquad (1)$$

Good agreement with the results of an integrating sphere (correcting for re-absorption of scattered light) has been obtained using pairs of layers with "D_1" = 0.6–1 and "D_2" = 1.2–2, respectively.

In order to understand the significance of Eq. (1) imagine the comparison between two layers with thickness L_1 and L_2 and apparent absorbance "D_2" ~ 2"D_1", "D_1" being in the range 0.6–1. Precise determination of Φ requires the knowledge of the absorbed light intensity, which equals to the incident light intensity less the total non-absorbed light intensity. In most measurements of quantum yields, the backward scattered and reflected light is ignored because its measurement is complicated. On the other hand, the method described here eliminates the need to know the back scattering because it depends only little on the thickness of the 2D reactor under the conditions described. Note that in the second layer, there is relatively little back-scattered light from distances larger than L_1, which avoid re-absorption. The method described here ignores only this small fraction of scattered light. The transmitted light is different in the two reactors, but it can be easily measured as described above. Thus the systematic error in absorbed light intensity introduced by using Eq. (1) is relatively small.

Fig. 2 shows the scattering pattern of STS-21 TiO_2 layer as a function of thickness, taken with the aid of an integrating sphere. The total non-absorbed light is measured with the aid of the integrating sphere, where the absorbing sample is placed at the center. This non-absorbed light includes light scattered in all directions, as well as transmitted light. It is possible to calculate the separate components of the non-absorbed light by combining the integrating sphere measurements with the data of total transmitted light I_{T} (using the actinometer or detector as described above) and spectrophotometric data. The spectrophotometer measures only the light transmitted in the original direction of the excitation light beam "I_{T}". Fig. 2 shows the variation of the different light patterns as a function of the apparent

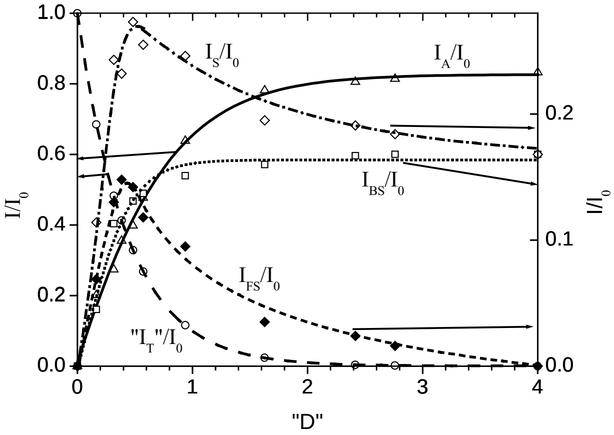

Fig. 2. The light pattern after hitting a thin layer of TiO_2. The fractions of the scattered light (I_S/I_0 (-·-·-)), absorbed light (I_A/I_0 (—)), apparent transmitted light ("I_T"/I_0 (– – –)), backwardly scattered light (I_{BS}/I_0, (···)) and the forwardly scattered light (I_{FS}/I_0 (- - -)) as a function of the apparent absorbance "D" in STS-21 TiO_2 layers, 340 nm.

absorbance of STS-21 TiO_2 layer, namely: (a) Light transmitted along the original beam direction, "I_T". This light reaches the spectrophotometer detector. (b) The forwardly scattered light, I_{FS}, which is detected by a detector at close proximity (together with "I_T") but not by the far positioned spectrophotometer detector. (c) The backwardly scattered light, I_{BS}, which is the difference between the total non-absorbed light detected by the integrating sphere and the total transmitted light, measured by the detector at close proximity to the sample. (d) The total scattered light, I_S, which is the difference between the total non-absorbed light and "I_T". (e) The absorbed light, I_A, which is the difference between the incident light and the total non-absorbed light.

I_{BS} reaches a near plateau value above "D" = 1. From Fig. 2, the error introduced by neglecting the increase of I_{BS} upon changing "D" from 0.6 to 1.2 is only 7%.

3.1. Comparison with other methods for determination of Φ

(A) When the apparent absorbance, as measured by spectrophotometer is not corrected for scattered light, a relative systematic error equal to I_S/I_A is introduced.

(B) When the transmitted light $I_T = I_0 – I_A – I_{BS}$ is measured, ignoring I_{BS}, introduces a systematic error equal to I_{BS}/I_A.

(C) The present method introduces a systematic error amounting to $\Delta I_{BS}/\Delta I_A$, where the Δ sign stands for the difference in the respective function for the two layers.

The relative error in light absorption under the different approximations is shown in Fig. 3 as a function of the layer extinction. The calculation is based on the experimental results shown in Fig. 2.

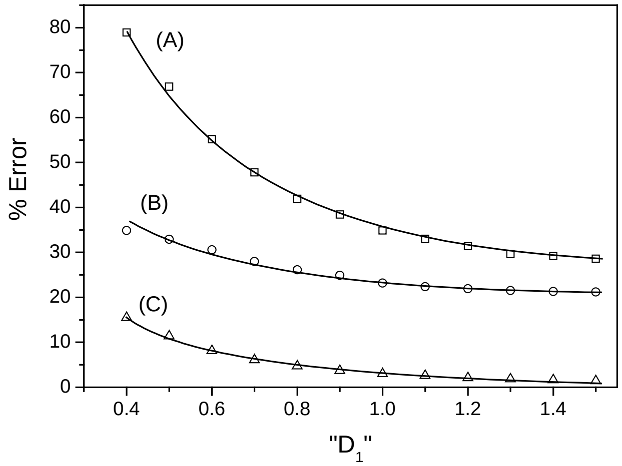

Fig. 3. Errors in the measurements of approximate light absorption compared to integrating sphere measurements (STS-21 TiO_2 layer). (A) No correction for scattering; (B) No correction for the backward scattering; (C) The present two-layer method. The relative error is based on comparison with the absorption measured with the aid of an integrating sphere.

3.2. On the accuracy of calculated quantum yield

The scattering albedo of STS-21 TiO_2, $\omega = (\beta - \mu)/\beta$ (where β is the extinction coefficient in the scattering system and μ the absorption coefficient, namely the extinction coefficient corrected for light scattering) has been reported as 0.562 at 355 nm [1]. Most of the scattering materials have lower albedo than STS-21 TiO_2, and are expected to show better accuracy.

In systems where the quantum yield is independent on light intensity, the systematic error in Φ due to scattered light results from erroneous values of I_A. On the other hand, when the quantum yield is a square root function of the absorbed light density, the error in quantum yield is considerably smaller. The distribution of quantum yields along the light path in the latter case introduces a problem in defining the absorbed light density. The average quantum yield, which is measured by the present method (or any other method yielding correct or nearly correct values), is a weighted average of the absorbed light density. It cannot be attributed to the arithmetic average light density, because the light intensity decreases non-linearly with the distance within TiO_2 layer. In our previous work [5], a specific parameter K_d was introduced as a measure of the photochmical efficiency. The relation between the quantum yield and K_d ($s^{1/2}g^{1/2}einstein^{-1/2}$) is given by Eq. (2), [5] where $A = 2.3K_d^2\varepsilon_A I_0$.

$$\Phi_{exp} = \frac{\begin{array}{c}2\Phi_{max}(A^{0.5}(1-10^{-0.5D}) \\ +\ln[(1+A^{0.5}10^{-0.5D})/(1+A^{0.5})]\end{array}}{A(1-10^{-D})} \quad (2)$$

Table 1
Φ_{HCHO} in photocatalytic oxidation of methanol

	Integrating sphere	Present method	No I_S correction
STS-01			
I_A (einstein/s)	7.3×10^{-11}	7.3×10^{-11}	7.3×10^{-11}
R (mole/s)	5.91×10^{-11}	6.06×10^{-11}	5.18×10^{-11}
Φ	0.81	0.83	0.71
STS-21			
I_A (einstein/s)	2.6×10^{-10}	2.6×10^{-10}	2.6×10^{-10}
R (mole/s)	1.51×10^{-10}	1.46×10^{-10}	1.12×10^{-10}
Φ	0.58	0.56	0.43

Aqueous solution of 2 M CH_3OH at pH 7 treated by photocatalytic TiO_2 layers type STS-01 and STS-21 at 340 nm. Layers' absorbance was 0.8 and 1.6, respectively.

A simplified Eq. (3) yields similar values of K_d.

$$\Phi_{exp} = \frac{\Phi_{max}}{(1 + K_d (I_{d,1}^{1/2})_w)} = \frac{\Phi_{max}}{(1 + 2A^{0.5}(1 - 10^{-1.5D})/3(1 - 10^{-D}))} \qquad (3)$$

Eqs. (2) and (3) were derived by examining the distribution of absorbed light density along the light path, while ignoring the density distribution in the cross-section. The inhomogeneous distribution of absorbed light density in the plane perpendicular to the light path affects the calculation of K_d. If the cross-section of the beam is very small, the re-absorption of scattered light outside the beam pattern may cause considerable inhomogeneity of the density distribution in the cross-section. However, in most works with thin layers the cross-section of the light beam is much larger than the layer thickness, and light scattered at directions parallel to the layer surface is reabsorbed within a relatively very short distance so that its uniformity is not distorted.

Values of I_A and Φ calculated by the present method are compared to the results obtained under similar conditions using an integrating sphere (Table 1). The comparison shows good agreement between the two methods.

Acknowledgements

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