A simple technique to determine quantum yield for UV photocatalytic decomposition studies

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Abstract−In this article a simple but effective method to calculate the quantum yield in heterogeneous photocatalysis is addressed. The amount of photons absorbed by coated photocatalyst was obtained with a portable radiometer, optical fiber (diameter 1 mm) and a purpose-built, fabricated accessory, as well as converted isopropyl alcohol, as the probe substance, with gas chromatography and a designed reactor system which determined a first order rate constant. Quantum yield was calculated under the assumptions that all the irradiated photons from one end of the fiber were either absorbed by the photocatalyst or transmitted to the other end and that the peak wavelength of the spectrum of the used UVBLB lamp represented the irradiated light. The resulting quantum yields with four different photocatalysts were in the range of 10-30% under specified reaction conditions of initial isopropyl alcohol concentration of 240 volume ppm, coated length of 10 cm, and initial transmitted light intensity of 20-25 $\mu W/cm^2$.

Key words: Quantum Yield, Heterogeneous Photocatalysis, Optical Fiber, Test Method

INTRODUCTION

Under ultraviolet (UV) illumination, photocatalysis reveals several functions that proceed in the purification of contaminated air and water, including deodorization, removal of harmful volatile organic compounds (VOCs) [Kim and Lee, 2001], sterilization and antibacterial actions, and also in the self-cleaning and antifogging actions. These functions of photocatalysis have attracted significant research attention to investigate potential commercial applications in the future. The effect of photocatalysis, however, is not easily envisaged and hence proper and official evaluation methods have yet to be confirmed, even though some recent efforts have been made in the fields of nitric oxide removal, antibacterial activity, and self-cleaning performance in Japan [Takeuchi, 2004] and standardization of light source and dye decolorization in Korea [Na et al., 2005] All of these methods except the light source were focused on using prepared photocatalytic materials, rather than a photocatalyst itself, in which or on which the photocatalyst is added by coating, impregnation, mixing, etc. Even for the efficiency or yield of photocatalyst in liquid-phase decomposition of a probe material, values in the literature have discrepancy that might be due to the systematic difference caused from different test setups used by different groups.

In this communication a novel test method for a photocatalyst in the form of powder or sol is introduced. This method is intended for application by handlers of powder or sol photocatalysts and is capable of supplying investigators in academies and institutes with an appropriate tool to compare photocatalysts that are prepared differently.

EXPERIMENTAL PROCEDURE

1. Chemicals

Isopropyl alcohol (IPA) was used as the probe compound for measuring activity because the conversion of IPA to acetone does not involve chain reactions [Fujishima et al., 2000]. P25 TiO_2 powder was generously given by Degussa and used throughout this study. Other photocatalysts that were also used to check the applicability of this method included the Hombikat series (UV 100, K01 and T) supplied by Sachtleben Chemie GmbH Duisburg and LT prepared in our laboratory.

2. Apparatus

The apparatus included a 15 W UVBLB (from GE, USA) light source and a portable radiometer (UM-10 & UM-360 Minolta Co. Japan). An accessory was fabricated to measure the light intensity from the opposite side of the illuminated optical fiber without any interference from exterior light (Fig. 1). Quartz optical fiber with 1 mm diameter was purchased from Mitsubishi Rayon (Japan).

The probe material and occasional by-products of acetone and carbon dioxide were analyzed by gas chromatography with flame ionization detector (GC/FID, HP 5890 and HP 6890 with a methanizer). The reactor for photocatalytic decomposition of IPA was fabricated as shown in Fig. 2. The reactor was constructed out of glass with in a tubular shape a diameter of 3 cm and a length of 25 cm (total volume ca. 177 cm^3).

A 20-cm length of optical fiber was cut and two holders with a 1 mm-hole in the middle were placed and fixed at both ends of the optical fiber with a binder. After the holders were confirmed to be strictly bonded to the fiber, both ends were polished sequentially with a variable-speed rotational sander until the transmitted light intensity reached 20-25 $\mu W/cm^2$. A clad of up to a 10-cm length of the middle part of the fiber was removed thoroughly by heat, and then the removed part underwent a rinsing procedure with distilled water. The total weight of the prepared substrate and light intensity transmitted were measured separately. This measurement needed to be repeated after the photocatalyst was coated by using either
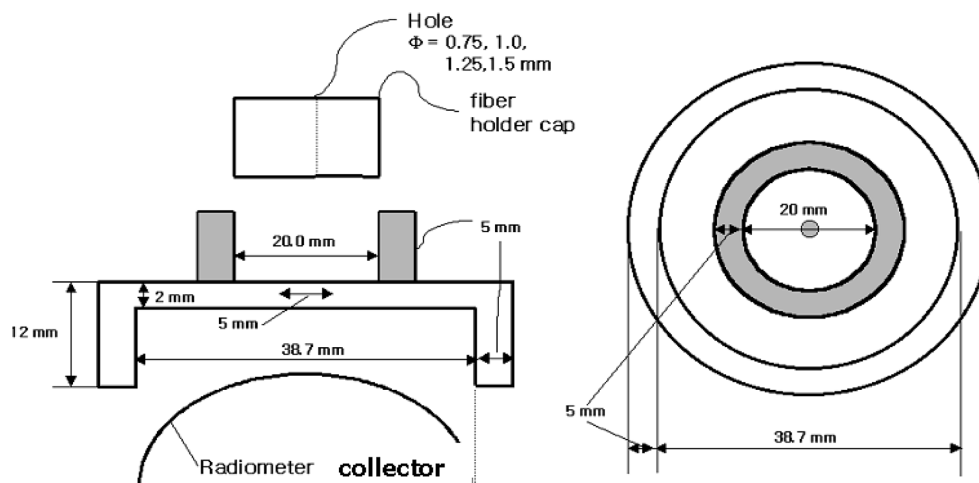
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Fig. 1. Accessory to measure the light intensity emanating from the opposite end to the illuminated optical fiber.

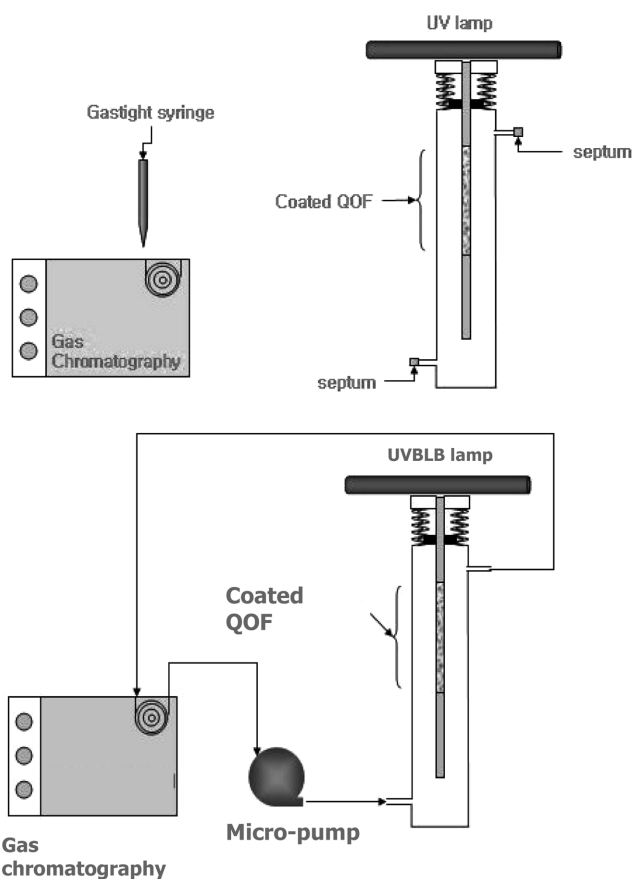**Fig. 2. Reactor and reaction system for the test method (top: batch type, bottom: on-line type).**

Fig. 3. Principle of light transmission and absorption through optical fiber.

ppm. The reaction was instigated by turning the UV lamp on and analysis samples were taken three times at 5-min intervals.

RESULTS AND DISCUSSION

This test method is based on the theory that optical fiber can transmit light by the difference in refractive index between the core and clad material. Once the clad is removed and a photocatalyst with a higher refractive index than that of the core is coated on the clad-removed part, the transmitted light can be refracted and absorbed by the coated photocatalyst (Fig. 3). This phenomenon was clearly noted in the experiments of varying conditions such as the kind and diameter of optical fiber, and stripped and coated length were adapted (Fig. 4). Clad stripping reduced the transmitted light slightly (<10%) without any remarkable decrease in stripped length. The small decrease in transmitted light could be attributed to possible defects or dust on the core surface. Increased fiber diameter widened the surface for light collection, thereby increasing the light intensity trans-

5 wt% sol in powder form or as-received sol. These measuring procedures determined the amount of coated photocatalyst and the light intensity absorbed by the coated photocatalyst. The prepared substrate was then ready to be inserted into the tubular reactor for the IPA conversion. The desired amount of IPA in the liquid phase (0.136 μl) was injected into the reactor and the total reaction system (batch type or on-line type with micro-pump) was allowed to settle to equilibrium for an hour with a desired IPA concentration of 240 volume
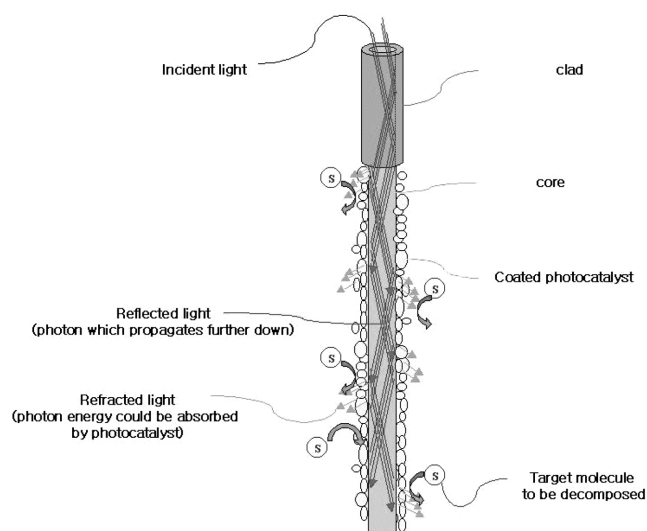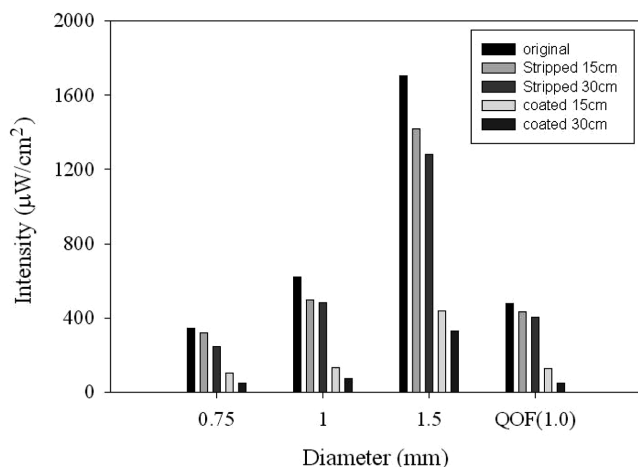
Fig. 4. Variation in transmitted light intensity with respect to the conditions of optical fiber (coated with 5 wt% P25 sol).

mitted. In the coated photocatalyst, the light intensity transmitted decreased sharply, indicating the absorption of light by the coated photocatalyst. Therefore, after the first order rate constant and absorbed light intensity were measured, the quantum yield (ϕ) [Serpone and Salinaro, 1999] was calculated by Eqs. (1) through (4).

The rate of converted probe material, N_{cpr}, was calculated as follows:

$$N_{cpr} = \frac{V_{IPA} \times d_{IPA}}{MW_{IPA}} \times k \tag{1}$$

where V_{IPA} is the volume amount of injected IPA (ml), d_{IPA} the density of IPA (g/ml), MW the molecular weight of IPA (g/mol), and k the first order rate constant (s^{-1}).

The amount of photon energy absorbed by the coated photocatalyst, N_{aph}, was obtained by the following equation:

$$N_{aph} = \frac{E \times A_d}{U_\lambda} \tag{2}$$

where E is the measured difference in the light intensity transmitted before and after the photocatalyst was coated ($\mu W/cm^2$), A_d the area of the light collector part of the radiometer (cm^2), and U_λ the mole photon energy of the representative wavelength λ (J/mol photon), where U_λ can be obtained by:

$$U_\lambda = \frac{hc \times N_A}{\lambda} \tag{3}$$

where h is the Planck constant ($6.6260755 \times 10^{-34}$ J·s), c the speed of light in a vacuum (3×10^8 m/s), N_A the Avogadro number (6.0221367×10^{23} mol^{-1}), and λ the representative wavelength of the light source used (368 nm).

Finally, the quantum yield for IPA conversion can be calculated with the following equation:

$$\phi = \frac{N_{cpr}}{N_{aph}} \tag{4}$$

As an example, with an inserted amount of IPA of 0.068 μl, an absorbed light intensity of 21.5 μW/cm², and k set to 0.0000583 s^{-1}, N_{cpr} by Eq. (1) is 5.18228×10^{-11} mol/s and N_{aph} is 4.15×10^{-10}, pro-

ducing a quantum yield of 12.5%. This result is reasonable in comparison with that of another scientific article [Zhang et al., 1998] which reported a photonic efficiency (based on the irradiated light intensity) of ca. 5% in homogeneous photocatalysis.

With this procedure, the effect of various parameters was examined including initial IPA concentration, weight percent of P25 sol, coated length, reaction type (batch or circulation), and different photocatalysts. Blank runs were performed before main studies on various parameters, resulting in no change in IPA concentration when either light or photocatalyst was absent in the system. The IPA photocatalytic decomposition turns out to follow first order reaction and the reaction rate increases with increase in initial IPA concentration up to ca. 500 ppm and then levels off beyond that concentration. Increasing initial IPA concentration decreased the rate constant but increased the quantum yield overall (the reaction rate increases). This was attributed to the difference between the amount of decreasing rate constant and that of the increasing initial IPA concentration, i.e., the increasing initial IPA concentration overwhelmed the decreasing rate constant. This effect also applied to the type of system, whereby the on-line system enlarged the total reactor volume caused by the connecting tube, thereby decreasing the initial IPA concentration. Hence, the on-line system showed lower quantum yield than the batch type. The coated thickness showed a gradual increase depending on the weight percent of P25 sol (ca. 200, 600, 1,000 and 1,400 nm for 1, 5, 10 and 15 wt%, respectively), but as far as ease of handling is concerned, 5 wt% sol seemed to be adequate. The coated length seemed to be optimized at 10 cm because the photons were not able to travel farther than 10 cm with photocatalyst coated due to their small light intensity input (ca. 20 μW/ cm²). The amount of coated photocatalyst apparently increased the quantum yield by 60% when 7 wt% P25 sol (ϕ=ca. 40%) was used compared with 5 wt% P25 sol (ϕ=ca. 25%). The experiments demonstrated good reproducibility and thus good coincidence (Fig. 5). Gradual detection of acetone during the photodecomposition of IPA confirmed the photocatalytic conversion of IPA rather than its adsorption or leakage.

To summarize, the method tested here is now described in terms of the preparation of test piece, IPA conversion test and calculation.
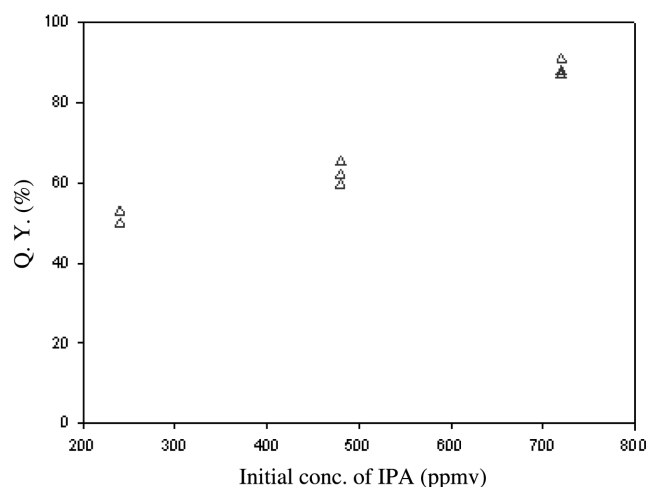

Fig. 5. Reproducibility of the proposed test method with 7 wt% P25 sol (10 cm of the total 20 cm-optical fiber was coated).

1. Preparation of Test Piece

Cut the optical fiber to the desired length. Attach the holder of 'teflon' to both ends with a binder that does not affect the GC peaks of IPA and acetone. Keep it overnight under room condition to fix. Polish both ends of the test piece to obtain 20-25 $\mu W/cm^2$ at one end after UVBLB irradiation to the other end. After removal of the clad by heat, wash thoroughly and dry it for an hour or longer at 80 °C. Coat the photocatalyst with 5 wt% sol or similar to the surface of the clad-removed part of the test piece. Weigh the test piece and measure the light intensity under UVBLB irradiation before and after coating. Then, dry the test piece for two hours or longer at 80 °C.

2. Procedure

Mount the test piece on the reactor. Inject 0.136 mL of IPA to obtain 240 volume ppm. Wait for 60 minutes for equilibrium to be reached. Turn on the UVBLB to start the reaction. Take three samples at 5-min intervals and record the GC data. Finally, calculate the quantum yield using the obtained first order rate constant and absorbed light intensity.

CONCLUSION

The proposed test method is a unique procedure to measure the quantum yield in heterogeneous photocatalysis. The use of this method, or a modified version, promises to give researchers in academies, institutes, and industries consistent data on the quantum yield, thereby allowing precise comparison of different photocatalysts in the photodecomposition of simple gaseous compounds. This proposed method also allows the quantum yield for various probe materials to be determined. The reasonable quantum yield results obtained from this method verified the accuracy of the proposed test procedure and indicated a potential for future application in research and industrial activity with photocatalysts.

ACKNOWLEDGMENTS

NOMENCLATURE

c   : the speed of light in vacuum [3×10^8 m/s]

N_A : the Avogadro number [6.0221367×10^{23} mol^{-1}]
λ : representative wavelength of the light source used [368 nm]
A_d : area of the light collector part of the radiometer [cm^2]
d_{IPA} : density of IPA [g/ml]
E   : measured difference in the light intensity transmitted before and after the photocatalyst was coated [$\mu W/cm^2$]
IPA   : isopropyl alcohol
GC/FID : gas chromatography with flame ionization detector
k   : first order rate constant [s^{-1}]
MW   : molecular weight of IPA [g/mol]
N_{aph} : the amount of photon energy absorbed by the coated photocatalyst
N_{cpr} : the rate of converted probe material
U_λ : mole photon energy of the representative wavelength λ [J/mol photon]
V_{IPA} : volume amount of injected IPA [ml]
VOCs : volatile organic compounds
h   : the Planck constant [6.6260755×10^{-3} J·s]
ϕ : quantum yield (the amount of reactant consumed to the amount of photons absorbed by the photocatalyst

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