

TiO₂-coated optical fiber bundles used as a photocatalytic filter for decomposition of gaseous organic compounds

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Abstract

An optical fiber-based, filter-type photocatalytic reactor was designed and the decomposition reaction of gas phase isopropanol was studied using a recirculating reaction system. Compared to the conventional TiO₂-coated glass plate or honeycomb monolith, both higher efficiency of light utility and larger processing capacity were obtained. This good combination was achieved by employing both high input light intensities (1.6×10^{16} to 2.6×10^{17} quanta cm⁻² s⁻¹) and a large number of glass fibers (18000 pieces, 125 μm diameter) in the reactor, which makes it possible for the reaction to occur with a high reaction rates while maintaining a high quantum efficiency. These characteristics can be understood by considering a TiO₂-coated single fiber as a micro-reactor distributed with low photon flux, and the corresponding fiber bundles being composed of large number of such micro-reactors. © 2000 Published by Elsevier Science S.A.

Keywords: Photocatalysis; TiO₂-coated optical fibers; Isopropanol

1. Introduction

The capability of TiO₂-based photocatalysis to degrade a wide range of both gaseous and aqueous contamination makes it a promising candidate for use in air clean-up and water purification [1–3]. The strong decomposition power comes from the photo-generated holes and electrons which combine with surface adsorbed species such as water and oxygen to form highly reactive radical species (e.g. •OH and O₂⁻) [4–6]. These active radical intermediates can oxidize most organic compounds and some inorganic compounds (e.g. NO_x), yielding mostly carbon dioxide and dilute mineral acids (e.g. HNO₃) as the final products.

Since a photocatalytic reaction takes place on an irradiated TiO₂ surface, adsorption/or at least contact of the reactant on the TiO₂ surface is necessary for accomplishment of the reaction. This trait determines the low activated surface area-to-reaction volume ratio in conventional fixed-bed reactor systems (e.g. glass plates, glass beads), which usually results in mass transport limitation and thus restricts the processing capacity. In addition, the overall efficiency of light utility in a conventional photocatalytic system is generally

low due to the scattering and absorption of light by the reaction medium. Because UV light source usually represents a high cost element in the creation of photocatalytic treatment systems, improvement in light utility is important both for lowering cost and improving reaction efficiency.

A configuration that can meet both of these two demands was reported to be a TiO₂-coated optical fiber type reactor (OFR), which was first proposed and studied theoretically by Ollis and Marinangeli [7–9]. Snell's refraction law (Eq. (1)) provides the basic principle for understanding the characteristic of this type reactor [10]:

$$n_1 \sin \theta_i = n_2 \sin \theta_{\text{refr}} \quad (1)$$

where n_1 and n_2 are the refractive indices of medium 1 and medium 2, while θ_i and θ_{refr} are the incident angle in medium 1 and refracted angle in medium 2, respectively. When a light is incident from medium 1 on a medium 1/medium 2 interface, total internal reflection occurs when $n_1 > n_2$ and the incident angle θ_i is larger than $\arcsin(n_2/n_1)$. One of the examples is an optical waveguide, in which the light propagates to a distance place via total internal reflection on the fiber/air interface [10]. In the case of an optical fiber coated with TiO₂, however, since the refractive index of the TiO₂ coating (>2.4 in the near UV range) is larger

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than that of SiO₂ glass (~1.5), [11] total internal reflection does not occur at the SiO₂ glass/TiO₂ interface when the light is incident from the SiO₂ side at any angles. Therefore, the light flux in a TiO₂-coated glass fiber is divided into two parts, one part is reflected and the other is refracted into the TiO₂ phase. The reflected part transports light energy through the fiber with a loss of intensity after each contact with the interface. Provided that light loss in the fiber other than refraction is negligible, then all the incident light can be refracted into the TiO₂ phase to cause photocatalytic reactions if the fiber is long enough.

In recent years, use of OFR in waste water treatment has been reported by several research groups [11–16]. Hofstadler et al. [11] studied the photooxidation of 4-chlorophenol (4-CP) by TiO₂-coated fused-silica fibers (144 2 mm diameter) arranged in a tubular reactor (total volume, 0.22 l). A higher effective quantum yield (0.0002) than that obtained in a slurry reactor system (0.00005) was reported in their work. Hoffmann and Peill [12,13] designed a TiO₂-coated fiber optical cable reactor (0.227 l, 72 1 mm diameter fiber) for use in decomposition of 4-CP, pentachlorophenol (PCP), dichloroacetate (DCA) and oxalate, and reported a maximum effective quantum yield of 0.011 for the decomposition of 4-CP by optimizing the reaction parameters, e.g. incident light intensity, fiber length, fiber diameter, thickness of TiO₂ coating. The possibility of using solar energy instead of artificial UV source as the driving light was also studied by the same authors [15].

Theoretically, employment of an optical fiber reactor with large number of fibers enables reactions to occur in a high quantum efficiency domain characteristic of low incident light intensities while maintaining high reaction rates by employing high input light intensities [15]. Therefore, reduced mass transport limitations and higher processing capacities may be obtained. However, no sufficient experimental data have been provided so far to confirm the validity of this statement in the previous work, [11–16] in which relatively small number of glass fibers were used. In this regard, a filter-type photocatalytic reactor composed of large numbers of TiO₂-coated glass fibers (18 000 pieces, 125 μm diameter) was constructed in the present work. The photo-assisted oxidation reaction of gas phase isopropanol was studied using this reactor. Gas-phase isopropanol decomposition reaction was chosen based on the following two reasons. First, all those studies carried out in an OFR so far were aqueous systems, no efforts have been made on gas phase reactions. Second, this reaction has been extensively studied and thus sufficient data can be cited and compared [17–21]. A comparison of reaction efficiencies of the present reactor to a conventional honeycomb system was also made.

2. Experimental

Experiments were carried out in a recirculating batch-type reaction system (Fig. 1(a)). The whole configuration con-

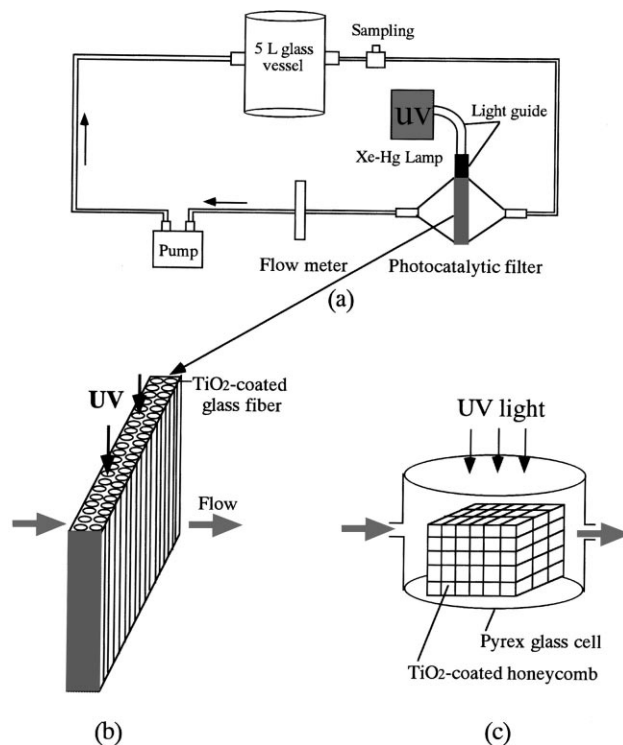


Fig. 1. Schematic diagrams of the experimental setup employed in the present work: (a) recirculating reaction system; (b) configuration of the optical fiber-based photocatalytic filter (reactor); (c) TiO₂-coated honeycomb-containing reactor.

sists of a light source, a photocatalytic filter (Fig. 1(b)), a recycling pump (Iwaki Pump. Co.), a flow meter (Kofloc. Co.) and a glass vessel used as a buffer (5 l). These parts were connected each other by gas-tight silicone tubes (8 mm. I.D.). The total volume of the reaction system is 5.6 l, and the flow rate used in the present work was 4.5 l/min.

The photocatalytic filter is composed of 18 000 TiO₂-coated optical fibers with 125 μm in diameter and 100 μm in length (Hoya Co.). These fibers were bundled into a filter-type reactor 88 mm × 6 mm × 105 mm (*L* × *W* × *H*) as depicted in Fig. 1(b). Photoactive TiO₂ layers of 2 μm thickness were coated on the fibers using a liquid solution of TiO₂ nano-particles (~7 nm in size). The pressure loss of the filter was found to be negligible below a flow rate of ~30 l/min. UV light was introduced to the optical fibers by a high-pressure Hg lamp (EX 250, Hoya-Schott. Co.) through an optical fiber light guide. The output light was centralized on 365 nm. To diminish the intensity, open-meshed thin metal sheets were used as neutral density filters. The input light intensity was measured using a UV power meter (TOPCON UVR-2).

The isopropanol and acetone concentrations were measured using a GC (Shimadzu Model GC-9A) equipped with a 5 m PEG 1000 column and a flame ionization detector, using N₂ as the carrier gas. The CO₂ concentration was measured using the same model GC equipped with a methanizer and a 2 m active carbon column, also using N₂ as

the carrier gas. Gas phase isopropanol with a concentration of ~ 5 vol.% collected in a gas-tight bag was obtained by passing synthesized pure air through a isopropanol liquid reservoir at room temperature. Measured quantities of the isopropanol-containing gas were then injected into the reaction system using a syringe. UV irradiation was started after the adsorption equilibrium was reached in the system.

In a comparison experiment, the optical fiber-based filter was replaced by a TiO₂-coated ceramic honeycomb monolith reactor (Fig. 1(c)), while keeping the other parts of the reaction system unchanged. The honeycomb monolith 106 mm \times 38 mm \times 20 mm ($L \times W \times H$), obtained from Ishihara Sangyo. Co.) used in the present work has square channels of width 1.1 mm, with a total apparent surface area of ~ 2490 cm². Coating of TiO₂ photocatalytic layer on the honeycomb monolith was carried out by dipping the support into a well mixed ethanol slurry of 3.6 wt.% TiO₂ (p-25) for about 20 s. Small amount of tetraethylorthosilicate was added to the mixture to act as a binder between the support and TiO₂. In order to prevent the possible blockage of the channel by the TiO₂ particles, a handy blower was used to remove the slurry remaining in the channel and also to dry the coatings. After this operation was repeated nine times, the sample was annealed in a muffle furnace for 1.5 h at 450°C under ambient conditions. Thus, the obtained monolith support has a deposition amount of TiO₂ ~ 0.43 mg/cm², which is close to the value coated on the optical fiber reactor (~ 0.39 mg/cm²).

3. Results and discussion

Fig. 2 shows a typical experimental data set for the concentration changes of gas-phase isopropanol, acetone, and CO₂ as a function of irradiation time with an input UV light intensity of 60 mW/cm² and an initial isopropanol concentration of 21 ppmv. The decrease of the isopropanol concentration

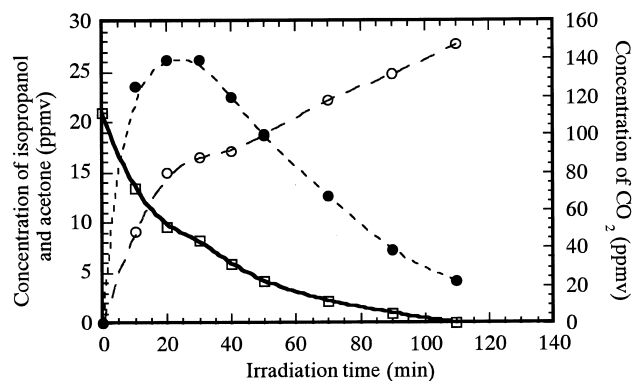


Fig. 2. Concentration changes of gas phase isopropanol, acetone, and CO₂ as a function of the irradiation time during the decomposition of isopropanol. Incident light intensity, 60 mW/cm²; initial isopropanol concentration, 21 ppmv; (□), isopropanol; (●), acetone; (○), carbon dioxide.

can be fitted very well with exponential decay function, indicating that the decomposition reaction follows the first-order kinetics. With the decomposition of isopropanol, increased concentrations of both acetone and CO₂ were detected. Our previous work showed [17] that, at low light intensities (< 45 μ W/cm²), isopropanol decomposed to acetone with a conversion of 100%, and no generation of CO₂ was measurable within the experimental error. At higher light intensities, however, the formed acetone could be further degraded to CO₂ [18]. Since a higher incident light intensity was used in this experiment, measurable amount of CO₂ was formed. In addition, the successive type degradation reaction from isopropanol to CO₂ (i.e. isopropanol \rightarrow acetone \rightarrow CO₂) results in a “mountain-type” curve for the concentration change of acetone (Fig. 2).

It is noteworthy that, since UV illumination was started after the adsorption equilibrium was reached in the reaction system, the pre-adsorbed isopropanol on TiO₂ was first decomposed to form acetone. With the decomposition of pre-adsorbed isopropanol, the adsorption equilibrium was broken and thus the gas-phase isopropanol also became adsorbed and decomposed. As the consequence, the quantity of acetone formed in the initial 10 min (~ 24 ppmv) was greater than that of isopropanol (~ 8.0 ppmv) decomposed in the same time interval because the data shown in Fig. 2 just represented the gas-phase concentration change. As will be seen in the next section, this recognition is important for us to calculate the quantum efficiency more correctly by using the number of generated acetone molecules instead of the number of isopropanol molecules decomposed.

In order to get information whether an optical fiber-based photocatalytic reactor like that used in the present work possesses advantages (e.g. larger processing capacity, higher efficiency of light utility) over a conventional reaction system or not, the decomposition reaction of isopropanol at various initial concentrations and various incident light intensities were investigated. Studied isopropanol concentration ranges from 10 to ~ 1000 ppmv, and the incident light intensity from 9.0 mW cm⁻² s⁻¹ (1.6×10^{16} quanta cm⁻² s⁻¹ at wavelength of 365 nm) to 140 mW cm⁻² s⁻¹ (2.6×10^{17} quanta cm⁻² s⁻¹). Relatively high light intensities were used in order to demonstrate the potential advantages of the OFR system more clearly. Fig. 3 shows log-log plots of the initial degradation rates (the average concentration changed in the initial 10 min, R) of isopropanol at different initial concentrations versus the number of input photons. It is known from our previous study that, [18] for a conventional TiO₂-coated glass plate (as a photocatalyst), at light intensities greater than $\sim 2.0 \times 10^{16}$ quanta cm⁻² s⁻¹, the decomposition reaction of isopropanol becomes completely mass transport-limited and the reaction rate does not show any light intensity-dependence at concentrations below 100 ppmv. However, when using our designed TiO₂-coated glass fiber bundles as a photocatalytic reactor, no such a limitation was observed in the same range of light intensities and

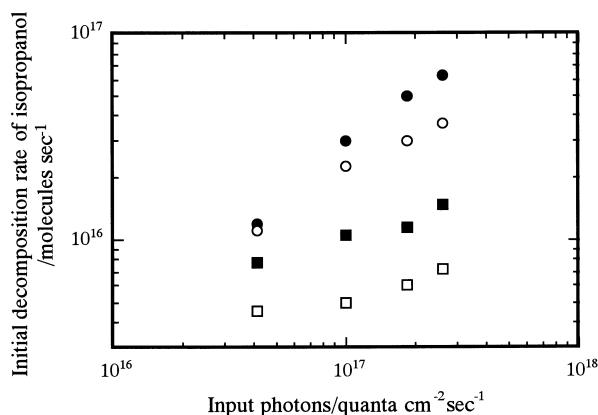


Fig. 3. Dependence of the isopropanol decomposition rate on the number of input photons. The initial isopropanol concentrations were (●), 1000 ppmv; (○), 600 ppmv; (■), 200 ppmv; (□), 50 ppmv.

concentrations (Fig. 3). It was found that, at all concentrations studied in the present work, the initial decomposition rates of isopropanol increase with increasing input photons. Greater slope values were obtained at higher isopropanol concentrations, indicating that the reaction becomes more light intensity-dependent at higher concentrations. These results demonstrate that employment of an optical fiber-based reactor can really reduce mass transport limitation and thus enhance the reaction rate at a certain light intensity (compared to the conventional systems). Since mass transport limitation tends to lower the processing capacity of a certain photocatalytic reaction system in practical applications, the results obtained in this study showed great possibility to enhance the processing capacity by employing an OFR reactor and using high light intensities. It is worth noting that because the decomposition rate also showed some extent of concentration-dependence at a certain light intensity (Fig. 3), the degradation reaction of isopropanol under the present experimental conditions is neither completely surface reaction-limited nor completely mass transport-limited, but lies in a transition regime between them.

Fig. 4 shows semi-log plots of input photons versus the apparent quantum yield (QY) for the gas-phase decomposition reaction of isopropanol at concentrations of 1000 and 50 ppmv, respectively. It is known that the real QY value of a photochemical reaction should be calculated based on the number of molecules transformed per absorbed photon. In the present work, however, in order to demonstrate the overall efficiency of light utility, the total input photons instead of the adsorbed ones were used, and thus the obtained QY is called apparent quantum yield. The apparent QY values were calculated using the following equation:

$$QY = \frac{\text{number of generated acetone molecules} + (1/3) \text{ number of CO}_2 \text{ molecules}}{\text{number of total input photons}} \quad (2)$$

Since part of the acetone formed from the decomposition of isopropanol is further degraded to CO₂ and this process

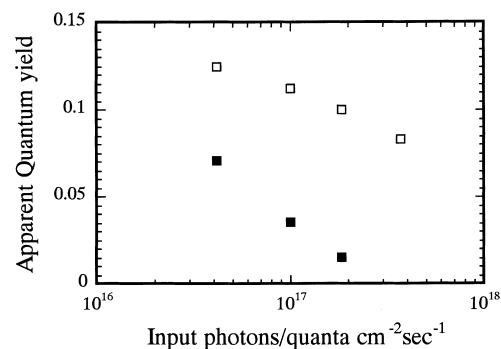


Fig. 4. Apparent quantum yields for the photocatalyzed decomposition reaction of gas phase isopropanol as a function of input light intensity obtained using an optical fiber-based reactor. (□), 1000 ppmv; (■), 50 ppmv.

also consumes photons, a second term in the numerator of Eq. (2) is included. A factor “1/3” being incorporated is because complete decomposition of one molecule acetone produces 3 moles CO₂. It can be seen from Fig. 4 that, in both cases, typical types of *I*-QY curves were obtained, i.e. the QY value decreases with increasing incident light intensity due to the faster electron (e⁻)-hole (h⁺) recombination reaction (a second-order process) compared to the surface charge transfer process (a first-order process) at high light intensities [16]. However, compared to the conventional plate-type photocatalytic reactor, [17] higher QY values were achieved at the same range of incident light intensities in the present work. For example, at the condition of light intensity 4.1×10^{16} quanta cm⁻² s⁻¹ and initial isopropanol concentration 1000 ppmv, a QY value of ~0.125 was obtained in the present study. This value is much higher than that (<0.01) obtained in the conventional system [17]. This indicates that higher efficiency of light utility can be achieved by employing the optical fiber type reactor.

The advantages of an optical fiber-based reactor is further demonstrated by comparing it with a TiO₂-coated commercially available honeycomb monolith as a photocatalytic reactor. The results obtained in the both cases are shown in Fig. 5, in which the log-log plots of the isopropanol degradation rates (R) at an initial concentration of 200 ppmv versus the number of input photons were presented. In contrast to the case of OFR, in which the decomposition rate of isopropanol increase relatively rapidly with increasing input photons, no obvious light intensity-dependence of the decomposition rate was observed when using a honeycomb-type reactor. This implies that at the light intensities studied in the present work, the decomposition reaction of isopropanol is mass transport-limited in a honeycomb reactor, similar to the case of a TiO₂-coated plate-type reactor. The corresponding QY values were also lower than that obtained in the OFR. For example, at the input light intensity of 4.1×10^{16} quanta cm⁻² s⁻¹, the QY value of the OFR is ~0.10, higher than that of ~0.03 obtained in the honeycomb reactor.

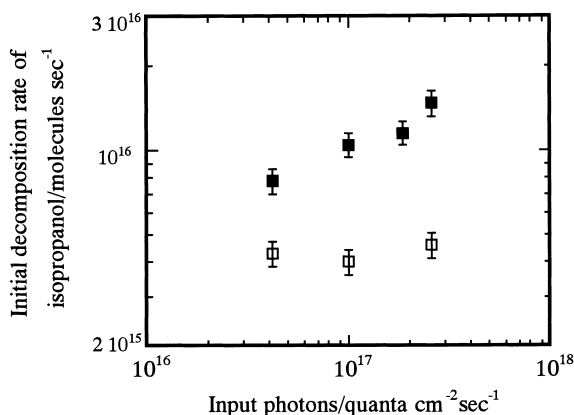


Fig. 5. Dependence of the decomposition rates of isopropanol on the input photons. Initial concentration, 200 ppmv; (■), data from the optical fiber-based reactor; (□), data from the TiO₂-coated honeycomb monolith.

The interesting thing is why higher efficiency of light utility and larger processing capacity can be concurrently achieved at such high light intensities as studied in the present work when using a TiO₂-coated optical fiber bundles as a photocatalytic reactor. As described above, in the same range of light intensities, the decomposition reaction of isopropanol already becomes completely mass transport-limited and the effective QY values are lower in a conventional plate-type reactor system [17,18]. This “abnormal” phenomenon can be understood from the unique configuration of such a reactor. The photocatalytic reactor used in this work was composed of 18 000 glass fibers. Therefore, although high input light intensities were used, photons entering each fiber were small. Supposed that the input photons from the reactor window (8.8 cm × 0.6 cm in area as shown in Fig. 1(b)) enter uniformly into the fiber bundles, then photons entering one fiber were calculated to be only $\sim 4.8 \times 10^{12}$ quanta s⁻¹ and $\sim 7.1 \times 10^{13}$ quanta s⁻¹, corresponding to total input light intensities of 1.6×10^{16} and 2.6×10^{17} quanta cm⁻² s⁻¹, respectively. Since TiO₂ was coated on the outside of each fiber, one TiO₂-coated glass fiber can be taken as a micro-reactor. The TiO₂ coating is activated by absorbing the photons refracted out of the fiber. This means that the photocatalytic reaction in an optical fiber-based reactor is practically driven by the photons in a single fiber. Increase in fiber number density decreases the number of photons to which a fiber’s photocatalytic coating is exposed. If it is further supposed that the photons input into a single fiber are totally and uniformly refracted into the TiO₂ layer along the length of the fiber, then the photons incident on per unit surface of TiO₂ (i.e. the light intensity incident on the TiO₂ coating) are 1.2×10^{13} and 1.8×10^{14} quanta cm⁻² s⁻¹, respectively, corresponding to the lowest and highest input light intensities studied in this work. Therefore, the reaction could be considered to take place in a lower light intensity region in the conventional reactor. As the consequence, mass transport limitation was avoided, and higher efficiency of light utility were obtained.

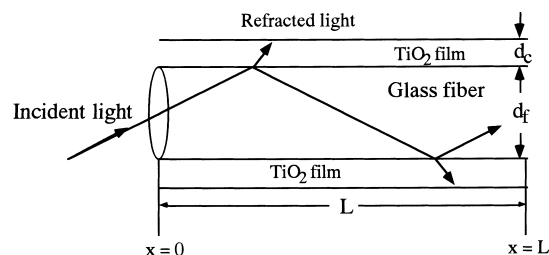


Fig. 6. Schematic diagram of light propagating in a TiO₂-coated optical fiber.

Meanwhile, since the real reactor was composed of large number of such micro-reactors, higher reaction rates and greater processing capacity can thus be concurrently achieved by employing high input photons.

However, it should be pointed out that the virtual situation is quite complicated because the light decays exponentially along the axial direction of a TiO₂-coated optical fiber (Eq. (2)) [7,13].

$$I_{\text{fiber}}(x) = I_{\text{input}} e^{-\alpha x} \quad (3)$$

where $I_{\text{fiber}}(x)$ is the amount of light remaining in the fiber at position x (see Fig. 6), I_{input} is the light in the fiber at position $x = 0$; and α is a loss coefficient that is a function of the optical and physical properties of the fiber and the TiO₂ coating. As a consequence, the distribution of photons refracted into the TiO₂ coating are not uniform along the fiber. Near the input side of the fiber, larger quantity of photons were refracted; while at the end side of the fiber, only smaller photons were refracted. As the result, reactions occurring near the input side usually bear characteristics of the high light intensity region; while reactions occurring at the end side of the fiber bear more characteristics of the low intensity region. A virtual reaction may contain characteristics from both of the regions. In the former case, part of the photons may be lost in the form of “leaking” light due to excess of photons, which tends to lower the light utility efficiency. The latter case may results in insufficient activation of the TiO₂ coating (depending on its thickness), which thus lower the reaction rates. It is obvious that, the nonuniformity of the photon distribution in the fiber and TiO₂ layer may severely lower the reaction efficiency and thus prevent the potential advantages of an OFR system being presented clearly.

Design and optimization of the operation parameters are crucial for acquiring a high efficient OFR. For example, Hoffmann et al. [12,13] have demonstrated and discussed the effect of several parameters on the operation efficiency of an OFR system. These parameters included fiber length, fiber diameter, fiber number, TiO₂ coating thickness and the incident angle of light, etc. By optimizing these parameters, a higher effective QY value for the oxidation of 4-CP in aqueous solution was achieved than that of a slurry and a non-optimized OFR systems. However, only modification of the above parameters can not solve the foregoing inherent

problem, i.e. the nonuniformity of photon distribution in a fiber. Taking account of the fact that distribution of photons in a TiO₂-coated optical fiber is a function of the refractive indices of both TiO₂ and the glass fiber, [7,13] one possible solution to this problem may be the use of optical fibers with refractive indices changed downward the length of the fiber. Combined with the optimization of other parameters, achievement of relatively uniform distribution of light along the fiber and the TiO₂ coating may become possible, and thus further improvement of light utility and processing capacity is anticipated. Related investigation is under way.

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