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Photodecomposition of phenol by silica-supported porphyrin derivative in polymer microchannel chips

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Abstract

Silica gel beads (diameter ∼10 μm) covalently modified with metal-free monopyridyltriphenylporphyrin (PyTPP) via a silane coupling reagent ($PyTPP-SiO_2$) were introduced into a polymer microchannel and, the microchip was applied to photodecomposition of phenol under solution-flow conditions. The photodecomposition yield of phenol in the microchannel was dependent on the solution-flow rate (ν) and increased with decreasing ν. At $\nu = 0.5$ μL/min, the decomposition yield was as high as 93% with the reaction time of 42 s, while that in a bulk aqueous $PyTPP-SiO_2$ suspension was 73% with the reaction time of 2 h. In the microchannel chip experiments, furthermore, the yield increased with decreasing the thickness of the solution-flow layer above the $PyTPP-SiO_2$ particles. On the basis of optical trapping-absorption microspectroscopy of single $PyTPP-SiO_2$ particles before and after the photoreaction, we discuss characteristics of the photoreaction in the microchannel accommodated with $PyTPP-SiO_2$ particles.
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Keywords: Polymer microchannel chip; Singlet oxygen; Microspectroscopy; Photodecomposition; Silica-supported catalyst

1. Introduction

Dye-sensitized oxidation of chemicals via singlet molecular oxygen has been studied extensively and applied to many research fields: synthetic organic reactions, photodegradation of polymers and environmental materials, and so forth [1–4]. Generally, xanthene dyes, porphyrins, and phthalocyanines are employed as a sensitizer, since these compounds possess both high absorption coefficients in the visible region and the excited triplet-state energies capable of transferring the electronically excited-state energy to molecular oxygen in the ground state, giving rise to generation of singlet molecular oxygen: $^1\Delta_g$ [3]. Among the related researches, photosensitized oxidation of both inorganic (sulfide, thiosulfate, and so on) [5,6] and organic environmental materials (phenol derivatives, *N*-heteroaromatics, and so on) [7–10] has received interests, since the reaction provides a versatile means to decompose the materials under visible light irradiation. Conventionally, a photosensitized reaction has been conducted in a homogeneous solution. However, a homogeneous system is disadvantageous in respect to separation of a sensitizer from the reaction mixture, and thus, the sensitizer is not reusable. In order to overcome such drawbacks, immobilized photosensitizers have been also employed: rose bengal on Merrifield polymers and Amberlite [11,12], ruthenium(II) complexes on Sephadex [13], phthalocyanine derivatives on zeolites [8], and so on [14]. Griesbeck and Bartoschek also reported that various olefins were oxidized selectively by porphyrin-loaded polystyrene beads via a singlet oxygen mechanism [15]. Although such inhomogeneous systems are certainly advantageous in respect to separation and recycling of the sensitizer, the photooxidation efficiency becomes frequently lower than that in the relevant homogeneous system, owing to the low diffusion rates of a substrate, O_2, and/or singlet oxygen in the solid catalysis phase. Clearly, a new experimental approach is desired to achieve efficient inhomogeneous photosensitized oxidation reactions, and an application of a microchannel chip to such reactions would be a possible candidate.

Microchannel chips have spread widely in chemical and biological researches during the past decade and, the research areas are expanding very rapidly [16–18]. In chemistry, microchannel chips have been employed as analytical and synthetic tools. Although the number of the report is still limited, photochemical reactions have been also explored by using microchannel chips [19–25]. As an example, we reported that a cyanation reac-

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tion of pyrene via a photoinduced electron transfer mechanism proceeded very efficiently along with oil/water solution-flow in polymer-based microchannel chips [19]. Lu et al. also reported photoreduction of benzophenone in glass microchannel chips, and demonstrated that the use of the microchannel chip was very advantageous in respect to the efficiency of photon transfer [20]. In a bulk system, namely, an incident light intensity for a photoreaction decreases exponentially during propagation of light in a reaction mixture (i.e., Beer's law), while incident photons are absorbed almost homogeneously in a thin reaction layer as in the case of a photoreaction in a microchannel. Such characteristics of photon transfer would be also applicable to an inhomogeneous photoreaction in a microchannel chip. In the case of photooxidation of a substrate by a solid-supported sensitizer, although it is certainly true that the diffusion rate of the substrate into the solid support is slow as compared to that in a homogeneous solution system, one-directional solution-flow in a microchannel chip is highly advantageous for forced diffusion of the substrate to the solid-support catalysis. Therefore, a combination of a solid-supported sensitizer and solution-flow in a microchannel chip will be very promising to conduct efficient photooxidation reactions of various substrates. Furthermore, such a system will provide a potential means to conduct a continuous and automated photosensitized reaction by flowing a reactant solution without separation of a solid-support sensitizer from a channel chip.

In this study, we explored a sensitized photooxidation reaction of phenol by a silica gel-supported porphyrin derivative in polymer microchannel chips. It has been reported that porphyrin derivatives are a very good photosensitizer for generating singlet molecular oxygen; the quantum yield for $^1\Delta_g$ generation is 0.63 for metal-free tetraphenylporphyrin. In this paper, we report fabrication of polystyrene microchannel chips accommodated with silica gel bead-supported monopyridyltriphenylporphyrin (PyTPP) as a photocatalyst and its application to photodecomposition of phenol, which is a typical example of an estrogen in vivo and a toxic compound in the wastewater of paper and dye manufacturing industries [9,10]. On the basis of optical trapping-absorption microspectroscopy of single PyTPP-silica gel beads before and after the photoreaction, furthermore, we discuss the photocatalytic activities of the PyTPP-silica gel beads evaluated for both the microchip and bulk suspension systems. The advantages of a photoreaction in a microchannel chip are discussed.

2. Experimental

2.1. Chemicals

Metal-free monopyridyltriphenylporphyrin was synthesized according to the literatures with some modifications [26,27]. Pyrrole (7.0 mL), benzaldehyde (7.5 mL), and 4-formylpyridine (2.5 mL) were refluxed in propionic acid (250 mL) for 1 h. After the reaction, the precipitates collected by suction filtration were washed thoroughly with methanol and dried in vacuum. The crude product was then chromatographed on a silica gel column with CH_2Cl_2. The first band eluted was tetraphenylporphyrin. PyTPP was then eluted with CH_2Cl_2 containing 5% ethanol and purified by column chromatography on silica gel (CH_2Cl_2:ethanol: 95:5 vol%). The structure and purity of PyTPP were confirmed by ^{1}H NMR and LC–MS [28].

Silica gel bead-supported PyTPP (PyTPP-SiO_2) was prepared as follows. Silica gel beads with the diameter around 10 μm (1 g, Wakosil, Wako Pure Chemicals Co., Ltd.) were treated with chloromethyltriethoxysilane (0.8 g, Aldrich) in toluene (10 mL) for 2 h at room temperature. Into the solution, PyTPP (5 mg) was added and the reaction between the pyridyl group in PyTPP and the chloromethyl group in the silane compound on the SiO_2 particle was allowed under reflux for 2 h [29]. The SiO_2 beads modified with PyTPP were collected by filtration, washed with toluene, and dried in vacuo. Other chemicals used in this study were the highest grade available from Wako Pure Chemicals Co., Ltd., which were used without further purification.

2.2. Fabrication of polystyrene microchannel chips

Polystyrene microchannel chips were fabricated by an imprinting method reported previously with some modifications [30]. For the present purpose of the study, 10 μm-sized PyTPP-SiO_2 particles should be accommodated in the bottom of a microchannel without flowing out even under solution-flow conditions. Therefore, we fabricated a dam-structured microchannel as illustrated in Fig. 1a [31]. A hard-cured Teflon® substrate with the width of 450 μm, the thickness of 30–130 μm, and the length of 2.3 cm was used to fabricate the upper layer of the microchannel for solution-flow, while that with the width of 450 μm, the thickness of 130 μm, and the length of 0.6 cm was employed to fabricate the lower dam-structured channel for accommodating PyTPP-SiO_2 particles. These two Teflon® substrates attached with each other as a template for imprinting and a polystyrene substrate (2.3 cm × 1.3 cm, Tamiya Co., Ltd.) were fastened tightly between two glass plates and heated at 114 °C for 25 min to fabricate the microchannel as illustrated in Fig. 1b. The SEM image of the microchannel fabricated by such a method has been reported elsewhere [30]. An aqueous slurry of PyTPP-SiO_2 particles was then spread onto the dam-structured microchannel and dried for ∼5 min upon heating the

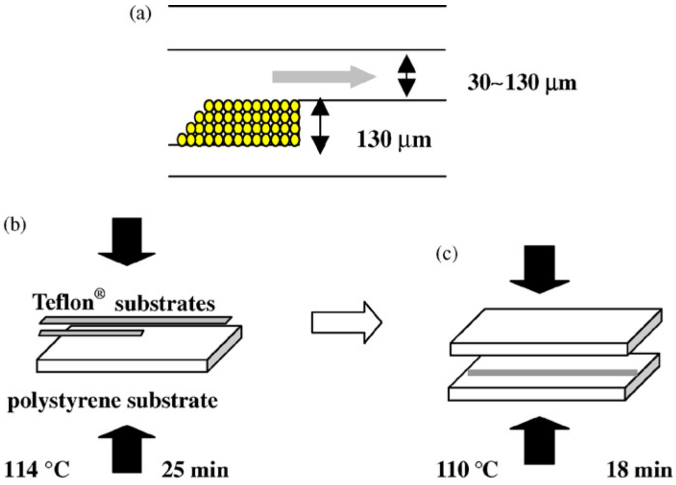

Fig. 1. Fabrication of polystyrene microchannel chips embedded with the PyTPP-SiO_2 particles. (a) Schematic illustration of the side view of the microchannel. (b) Imprinting method. (c) Bonding of the substrates.

substrate on a hot plate. The channel and other flat polystyrene substrates were then placed between two glass plates and heated at 110 °C for 18 min to bond the two substrates (Fig. 1c). The PyTPP-SiO_2 particles loaded thicker than the height of the dam-structured channel (i.e., >130 μm) were flowing out by pumping an enough amount of a reactant solution before a photoreaction. The effective photocatalysis channel length, defined by that accommodated with PyTPP-SiO_2, was ~6 mm as determined by observation under an optical microscope. The number of the PyTPP-SiO_2 particle introduced into the microchannel chip was $\sim 8 \times 10^8$ as estimated on the basis of the size of the dam-structured channel (450 μm (width) × 130 μm (depth)), the effective catalysis channel length (6 mm), and the size of the SiO_2 particle (10 μm). Two minutes holes were drilled on the cover substrate just above the entrance and exit regions of the microchannel for injection and collection of a sample solution, respectively. A programmable syringe pump (Harvard model 44) and the entrance hole of the channel chip were connected with a fused silica capillary tube. The exit hole was also connected with a capillary tube for collection of a sample solution. Connections between the tubes and the polymer chip were made by using an epoxy resin.

2.3. *Measurements*

Absorption spectra were recorded on a Hitachi U-3300 spectrophotometer. Optical trapping-absorption microspectroscopy of single PyTPP-SiO_2 particles in water was conducted by using a system reported previously [32]. GC–MS measurements were conducted by using a QP-5500 system (Shimadzu).

3. Results and discussion

3.1. *Characterization of PyTPP-SiO_2 particles and oxidative photodecomposition of phenol in a bulk suspension system*

Fig. 2 shows the optical micrographs of the SiO_2 particles before (a) and after modification with PyTPP (b). The PyTPP-SiO_2 particles after modification with PyTPP were yellow,

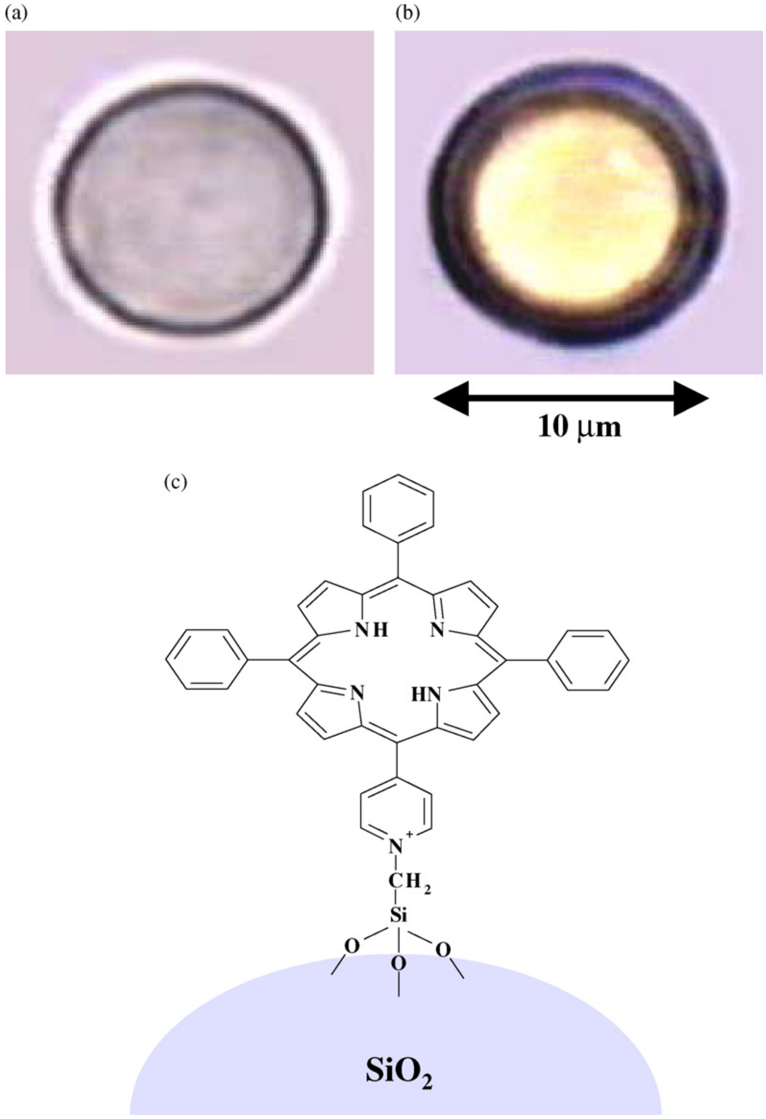

Fig. 2. Optical micrographs of the SiO_2 particles before (a) and after modification with PyTPP (b). (c) Represents schematic illustration of a PyTPP-SiO_2 particle.

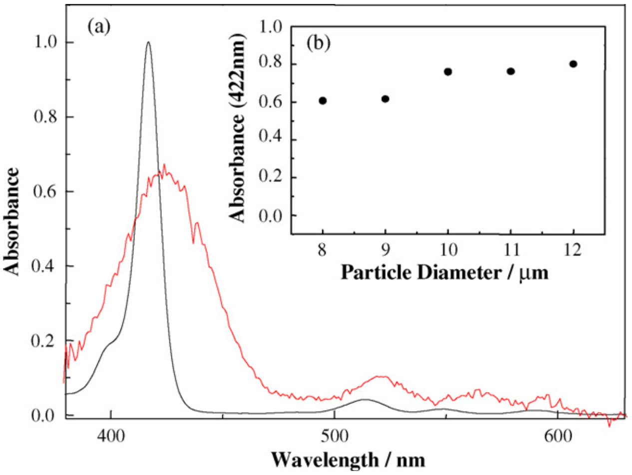

Fig. 3. Absorption spectra of a single PyTPP-SiO$_2$ particle in water (shown by the red curve) and PyTPP in dichloromethane (shown by the black curve). The inset (b) shows the SiO$_2$ particle diameter dependence of the absorbance of PyTPP at 422 nm.

suggesting an introduction of PyTPP to the silica beads (Fig. 2c). Furthermore, the ring-like structure of the particle seen in Fig. 2b indicates that the refractive index of the surface of the particle varies after the modification reaction. In order to study further the point, we conducted optical trapping-absorption microspectroscopy on single PyTPP-SiO$_2$ particles as a typical example of the spectrum was shown in Fig. 3a (shown by the red curve), together with that of PyTPP in CH$_2$Cl$_2$ (shown by the black curve). Although the absorption spectrum of a PyTPP-SiO$_2$ particle was broader than that of PyTPP in CH$_2$Cl$_2$, the spectrum showed distinct Soret-(~422 nm) and Q-bands (500–600 nm) characteristic to that of a porphyrin derivative [33]. The absorbance at 422 nm observed for the PyTPP-SiO$_2$ particles did not change before and after thorough washing the particles with toluene. Therefore, we concluded that PyTPP was introduced onto the SiO$_2$ particles with the covalent bond through the silane coupling reagent (Fig. 2c).

Fig. 3b shows the particle diameter (*d*) dependence of the absorbance of PyTPP-SiO$_2$ at 422 nm. Although the particle size distribution of SiO$_2$ used in the present study was narrow ($d = 8$–$12\ \mu$m), the present experiments demonstrated that the absorbance was weakly dependent on *d* and the value interpolated from the slope of the plot did not bisect the original point. If PyTPP is introduced homogeneously in the SiO$_2$ particle, the absorbance should increase linearly with *d* since the particle diameter corresponds to the optical path length for absorption spectroscopy. Therefore, the results in Fig. 3b indicate that PyTPP is not introduced homogeneously in the entire volume of the SiO$_2$ particle, but in the surface layer of the particle. It is worth noting that this agrees with the observation of the ring-like structure of the PyTPP-SiO$_2$ particle in Fig. 2b as described above. On the other hand, the number of the PyTPP molecule loaded on a single PyTPP-SiO$_2$ particle was evaluated roughly to be 10^{10} on the basis of elemental analysis of the particles. When PyTPP is introduced to the particle surface alone, the value corresponds to the surface coverage of PyTPP on the particle ($d = 10\ \mu$m) to be $\sim 3 \times 10^{16}$ molecule/cm^2. It is worth noting that Van Galen and Majda have predicted that the surface concentration of a tetrapyridylporphyrin derivative, self-assembled on a gold substrate, is $(20–4.2) \times 10^{13}$ molecule/cm^2: the values for the perpendicular and parallel arrangements of the porphyrin ring on the substrate [34]. Since the present value is much larger than those reported by Van Galen and Majda, PyTPP could be introduced to the several surface layers of a SiO$_2$ particle, which might not contradict with the optical micrograph in Fig. 2b. Dense introduction of PyTPP in the surface layers of the particle would be the primary reason for the relatively broad absorption spectrum of PyTPP-SiO$_2$ as compared to that of PyTPP in CH$_2$Cl$_2$.

Since an introduction of PyTPP on SiO$_2$ particles was confirmed, we studied photodecomposition of phenol by PyTPP-SiO$_2$ in a bulk aqueous suspension to reveal the photochemical activity of the particles. An aerated carbonate buffer solution of phenol (6.5×10^{-5} M, pH 10, 25 mL) containing 7 mg of PyTPP-SiO$_2$ was irradiated by a 150 W Xe lamp through an L-39 glass filter (Toshiba Co., Ltd., wavelength $\lambda > 390$ nm) for 1 h under vigorous stirring. The absorption spectrum of the supernatant solution after the photoreaction demonstrated the decrease in the absorbance of phenol at around 230 nm (data are not shown here). It is worth noting that photodecomposition of phenol does not proceed under an Ar-gas stream, while that proceeds more efficiently under an oxygen-gas atmosphere as compared to that under aerated conditions. In the present experiments, furthermore, PyTPP on SiO$_2$ alone absorbs incident light ($\lambda > 390$ nm) and porphyrin derivatives are known as an efficient photosensitizer toward generation of singlet molecular oxygen [3]. Although we have not detected directly singlet oxygen in the present experiments, these results indicate that photodecomposition of phenol proceeds via a singlet oxygen mechanism as reported by several research groups as discussed below [9,10].

The absorption spectral changes of the solution during photoirradiation were in good accordance with those for photosensitized oxidation of an aqueous phenol solution by polymer-supported rose bengal reported by Nowakowska and Kępczyński [9]. In an aqueous alkaline solution, they have reported that phenol is oxidized to *p*-benzoquinone by singlet oxygen, and *p*-benzoquinone is decomposed further to carbon dioxide and maleic or fumaric acid by oxygen (i.e., $^3\Sigma_g$) [10]. In practice, we confirmed an appearance of the absorption band ascribed to *p*-benzoquinone (~250 nm) during the photoreaction. Since the present experiments are conducted at pH 10, we consider that *p*-benzoquinone produced by the photoreaction is decomposed further to such species. On the basis of the present experimental observations and the discussions described above, we conclude that PyTPP-SiO$_2$ can act as a sensitizer toward photooxidation of phenol, probably via a singlet oxygen mechanism.

3.2. Photodecomposition of phenol in polymer microchannel chips immobilized with PyTPP-SiO$_2$ particles

An aerated carbonate buffer solution of phenol (1.0×10^{-3} M, pH 10) was introduced to the microchannel accommodated with PyTPP-SiO$_2$ particles at a solution-flow rate (ν) of 3.0 μL/min, and the photoreaction was allowed by irradiating

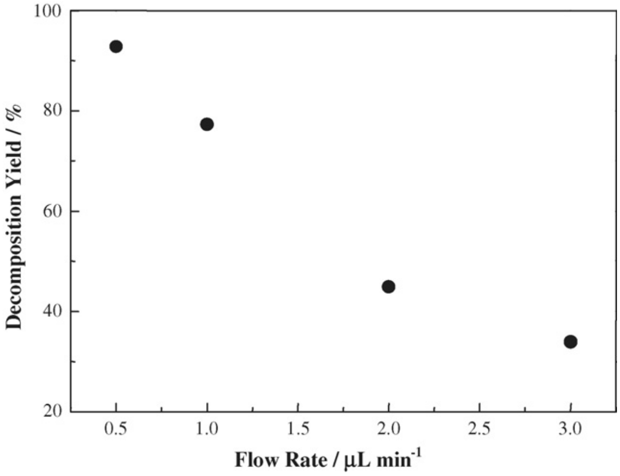

Fig. 4. Flow-rate dependence of the photodecomposition yield of phenol in a microchannel chip. For experimental details, see the main text.

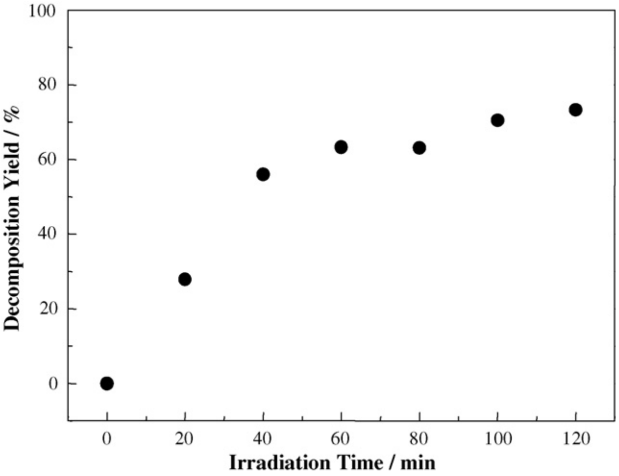

Fig. 5. Time conversion profile of the photodecomposition yield of phenol in a bulk carbonate buffer solution. For the experimental details, see the main text.

the whole of the microchannel chip through a 300 W high-pressure Hg lamp (1.0 M $CuSO_4$ solution filter, $\lambda > 330$ nm). In the experiments, the thickness of the solution-flow layer above the PyTPP-SiO_2 particles in the microchannel was set 130 µm (see also Fig. 1a). The reaction mixture being passed through the channel under illumination was collected from the channel exit and analyzed by GC to determine the photodecomposition yield of phenol [35]. At $\nu = 3.0$ µL/min, the decomposition yield was ∼35%, while the yield increased with decreasing ν as shown in Fig. 4. Since the decrease in ν gives rise to the increase in the residence time of the reactant solution above PyTPP-SiO_2 in the channel, the increase in the yield with a decrease in ν is the reasonable consequence. The residence time (i.e., actual reaction time), thus, calculated on the basis of the effective channel length (6 mm) and $\nu = 0.5$ µL/min is 42 s (Fig. 4). In the microchannel under solution-flow, therefore, phenol is photodecomposed in 93% yield with the reaction time of 42 s.

In order to compare the results in Fig. 4 with those in a bulk solution system, we studied photodecomposition of phenol (1.0×10^{-3} M, $\lambda > 330$ nm) by PyTPP-SiO_2 (0.09 g) suspended in an aerated carbonate buffer solution (pH 10, 25 mL) under vigorous stirring. In the experiments, the ratio of the number of the PyTPP-SiO_2 particle to the mole number of phenol per unit volume was set analogous to that in the chip experiments. The time course of the photodecomposition yield of phenol determined by GC is shown in Fig. 5. The data demonstrated that photodecomposition of phenol proceeded gradually with the irradiation time (t) and the yield leveled-off at around 70% ($t = 2$ h), which was worse as compared to the results in the microchannel chip: 93% with $t = 42$ s. These results demonstrate high potentials of the present microchannel chip accommodated with PyTPP-SiO_2 particles toward photosensitized oxidative decomposition of phenol.

3.3. Channel-depth dependence of the photodecomposition yield

In order to reveal the primary reason for the higher photodecomposition yield of phenol in the microchip as compared to that in the bulk solution system, we studied a channel-depth dependence of the decomposition yield. With the depth and length of the lower dam-structured channel accommodated with PyTPP-SiO_2 being set constant at 130 µm and ∼6 mm, respectively, photodecomposition of phenol was studied by varying the depth of the upper solution-flow channel: 130–30 µm (see also Fig. 1a). As the data were shown in Fig. 6, the decomposition yield at $\nu = 3.0$ µL/min increased from ∼35 to ∼65% with decreasing the depth of the upper solution-flow channel from 130 to 30 µm. Photodecomposition of phenol could be induced by generation of singlet molecular oxygen through energy transfer from the excited triplet-state of PyTPP attached to the SiO_2 particles to O_2 in the immobilized layer as discussed before. Thus, photodecomposition of phenol should proceed more efficiently with higher concentrations of both singlet oxygen and phenol in or near the PyTPP-SiO_2 phase in the microchannel. Therefore, the thinner is the solution phase above the PyTPP-SiO_2 layer, more efficient is the reaction between singlet oxygen and phenol owing to shorter diffusion lengths of these species. Furthermore, phenol molecules in the solution phase are provided

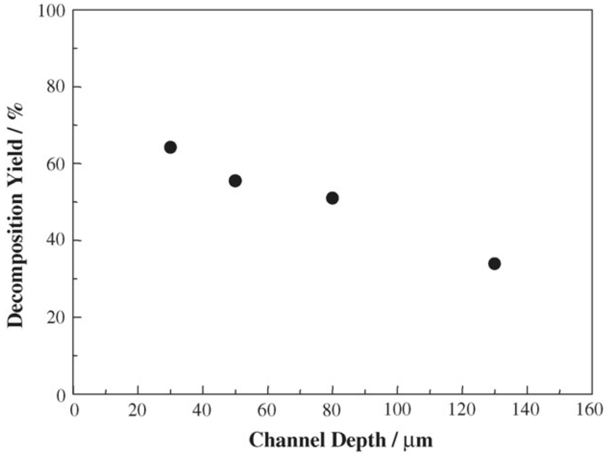

Fig. 6. Channel-depth dependence of the photodecomposition yield of phenol. For the experimental details, see the main text.

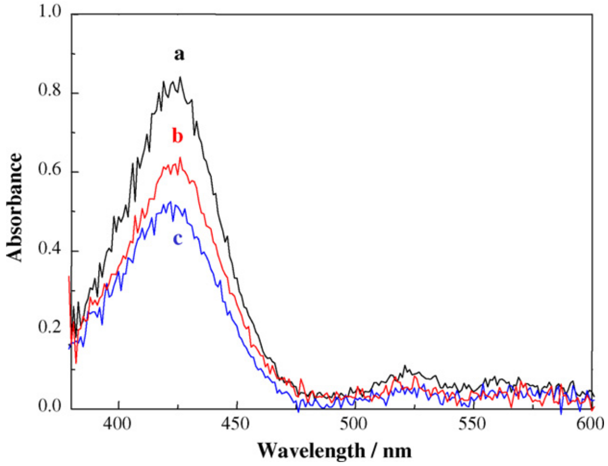

Fig. 7. Absorption spectra of the PyTPP-SiO$_2$ particles before (a) and after the photoreaction in the microchannel chip (b) or in the bulk suspension system (c). For the experimental details, see the main text.

to the PyTPP-SiO$_2$ phase by both self-diffusion and pressure-driven flow, giving rise to a higher decomposition yield in a thinner microchannel through a characteristic solution-flow profile in a microchannel as discussed elsewhere: laminar flow [36]. The channel-depth dependence of the reaction yield is very characteristic to the photoreaction in the microchip.

3.4. Evaluation of photocatalytic activity of PyTPP-SiO$_2$ particles in microchannel and bulk systems

It was shown that the photodecomposition yield in the microchannel chip was superior to that in a bulk system. However, this is not necessarily indicates a higher photocatalytic activity of PyTPP-SiO$_2$ in the microchip as compared to that in a bulk suspension system, since the reaction conditions of the two experiments are totally different. Furthermore, a determination of a reaction quantum yield in an inhomogeneous system is in general very difficult and, thus, we cannot make a discussion based on the reaction quantum yield at the present stage of the investigation. In order to discuss the photocatalytic activity of PyTPP-SiO$_2$, therefore, we evaluated the photooxidation reaction rate per particle. For this purpose, we conducted optical trapping-absorption microspectroscopy for single PyTPP-SiO$_2$ particles before and after the photoreaction as the data were shown in Fig. 7. The reaction conditions for the experiments in the microchip and bulk systems were the same with those in Figs. 4 and 5, respectively. Before the photoreaction, the absorbance of PyTPP at 422 nm loaded on a single SiO$_2$ particle was 0.83 (molar absorptivity = 4.5×10^5 M^{-1} cm^{-1}) [21], while that after 2 h photoreaction in the bulk system (solution volume of 25 mL) was 0.51 with the decomposed amount of phenol being 8.8×10^{-4} M. On the other hand, the absorbance at 422 nm of the single PyTPP-SiO$_2$ particle after the photoreaction in the microchannel chip was 0.62 ($t = 50$ min and $\nu = 0.5$ μL/min). At this solution-flow rate, 25 μL of the reaction mixture was eluted from the channel and the GC analysis of the mixture demonstrated that 1.1×10^{-3} M of phenol was decomposed by the photoreaction.

In the chip experiments, 1.1×10^{-3} M of phenol in the reaction mixture (25 μL) was decomposed by 8×10^8 PyTPP-SiO$_2$ particles with the total reaction time of $t = 50$ min, so that the photodecomposition rate was evaluated to be 0.1 fM/s per particle.

Furthermore, since PyTPP on the SiO$_2$ particle was decomposed by 27% during the photoreaction as revealed by absorption microspectroscopy, the average photodecomposition rate of phenol is calculated to be 0.08 fM/s per particle. In the bulk experiments, the system involves 8×10^7 PyTPP-SiO$_2$ particles. Analogous calculation for the data in the bulk system with that for the chip resulted in the average decomposition rate of 0.03 fM/s per particle. These estimations demonstrate that the photocatalytic activity of the PyTPP-SiO$_2$ particle is higher for the chip system by a factor of 2–3 as compared to that in the bulk system. In the microchannel, the reactants are confined in a very minute volume and the photon transfer efficiency is higher than that in the bulk system, as demonstrated by the channel-depth dependence of the photodecomposition yield. A photoreaction in a microchannel is thus very advantageous even for an inhomogeneous system.

4. Conclusions

We fabricated polymer microchannel chips accommodated with PyTPP-SiO$_2$ particles and the chip was applied to photosensitized oxidation of phenol under solution-flow conditions. The photodecomposition yield as high as 93% was achieved at the solution-flow rate of 0.5 μL/min with the reaction time of 42 s, while that in a bulk PyTPP-SiO$_2$ suspension was 73% with the reaction time of 2 h, demonstrating a high potential of the present microchannel chip integrated with the PyTPP-SiO$_2$ particles as a solid-supported photosensizer. Furthermore, it was demonstrated that the reaction efficiency was higher in a thinner microchannel, which was one of the characteristics of the chemical reaction in a microchannel. The present study also proved that the photocatalytic activity of PyTPP-SiO$_2$ was higher in a microchannel as compared to that in a PyTPP-SiO$_2$ suspension as demonstrated by optical trapping-absorption microspectroscopy of single PyTPP-SiO$_2$ particles before and after the photoreaction. Therefore, the use of a mirochannel chip combining with regulated solution-flow and an immobilized solid-supported photosensitizer or catalyst is one possible approach to conduct efficient inhomogeneous photoreactions.

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