YIELD IMPROVEMENT BY AN EFFECTIVE MICROREACTOR FOR PHOTOREACTIONS USING A BLACK ALUMINUM OXIDE CHANNEL SUBSTRATE

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ABSTRACT
We developed an effective microreactor for photoreactions using a black aluminum oxide channel substrate with low reflectance and good heat conductance. The performance of this microreactor was verified by applying to a photoreaction of benzophenone. In the microreactor made of quartz glass, the channels got blocked at smaller flow rates, because of crystal precipitation by vaporization of liquid components. On the other hand, in the microreactor made of black aluminum oxide, the channels did not get blocked even at the same flow rates and the yield was improved by more than 30 %.

KEYWORDS
Microreactor, Photoreaction, Black aluminum oxide, Benzophenone, Yield improvement

INTRODUCTION
This paper reports yield improvement by an effective microreactor for photoreactions using a black aluminum oxide channel substrate with low reflectance and good heat conductance. We verified the performance of this microreactor by applying to a photoreaction of benzophenone in Figure 1. This reaction is known to need longer reaction time of more than 20 hours in the current batch method.

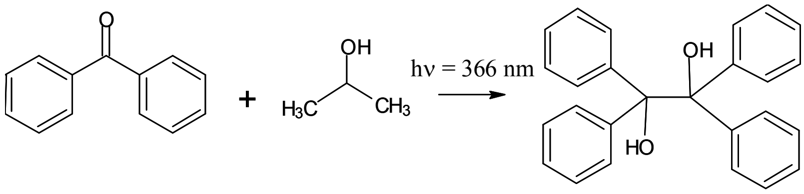

Figure 1. Photoreaction of benzophenone

Photoreactions caused by photo energies make it possible to simplify current complicated chemical synthesis processes, and have attracted attention as environment-conscious reactions. It is known that photoreactions more effectively proceed with microreactor methods using micro channels on the micrometer order, by contrast to low efficiencies with current batch methods [1, 2]. Current microreactors for photoreactions that are made of quartz glass or Pyrex® cause heating of light source based on diffuse reflection to the bottom surface of channels and vaporization of liquid components because of low heat conductance.

MICROREACTOR FOR PHOTOREACTIONS
We adopted transparent sapphire as a material for a top substrate and black aluminum oxide as that for a channel substrate based on the properties in Table 1. These materials have better heat conductance and black aluminum oxide has lower reflectance compared to quartz glass and Pyrex®. For comparison, microreactors made of quartz glass were also formed with the channel widths of 0.2 and 1 mm as shown in Table 2. Figures 2 and 3 show the exploded view and picture of the reactor 1.

Table 1. Comparison of properties

Material	Light transmittance @365 nm (%)	Reflectance (%)	Heat conductance @293 K (W/(m·K))
Quartz glass	> 90	—	1.3
Pyrex®	> 90	—	1.1
Transparent sapphire	> 80	—	41
Black aluminum oxide	—	5.1-15.3 (240-2600 nm)	31.2

Table 2. Specifications of microreactors

No.	Material		Channel width (mm)	Channel depth (mm)
	Top substrate	Channel substrate		
1	Transparent sapphire	Black aluminum oxide	1	0.2
2	Quartz glass	Quartz glass	1	0.2
3	Quartz glass	Quartz glass	1	1

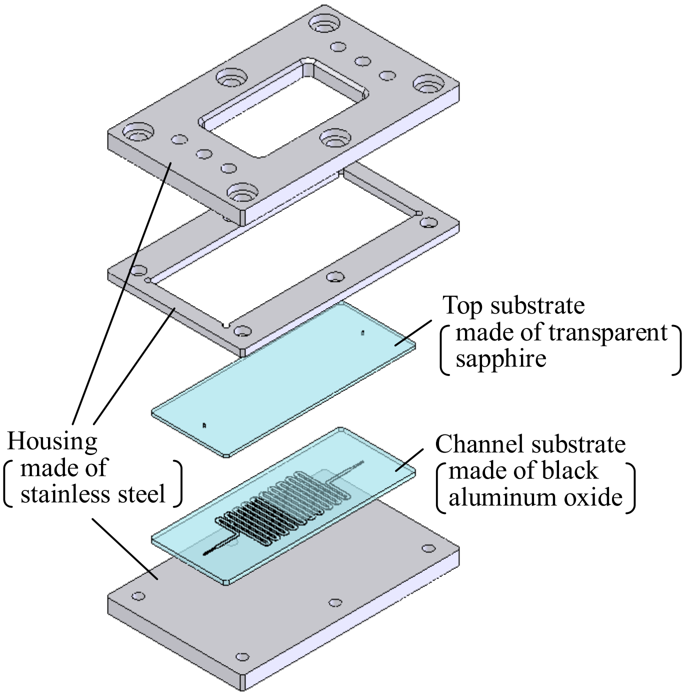

Figure 2. Exploded view of the reactor 1

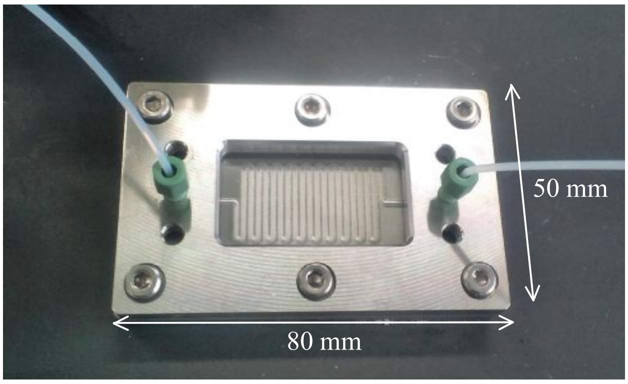

Figure 3. Picture of the reactor 1

EXPERIMENTAL METHODS

Mixing solution with the concentration of 0.5 kmol/m^3 was obtained by dissolving benzophenone in isopropanol [3]. Mixing solution was introduced into a microreactor for photoreactions exposed to ultraviolet source ($h\nu$ = 365 nm) for the process of the reaction (Figure 4). Light irradiation time was controlled by flow rates and reaction temperature was set at room temperature (296 to 297 K). Products were analyzed by HPLC (High Performance Liquid Chromatography). Micro Process Server^{TM} produced by Hitachi Plant Technologies, Ltd. (Figure 5) was used as a microreactor system.

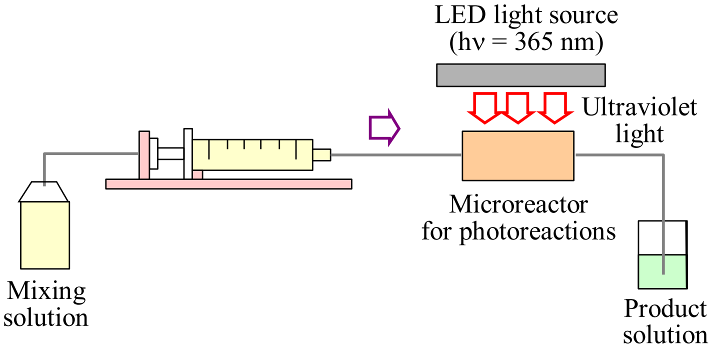

Figure 4. Microreactor system in this study

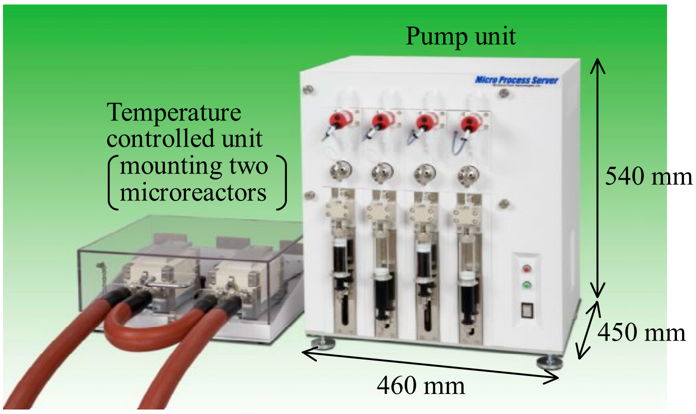

Figure 5. Micro Process Server™

RESULTS AND DISCUSSION

Figure 6 shows the yields in the photoreaction of benzophenone. The reaction more rapidly proceeded in the reactor 2 with shallower channels compared to the reactor 3. In the reactor 2, however, the channels got blocked at 187.7 s, because of crystal precipitation by vaporization of liquid components. On the other hand, in the reactor 1, the channels did not get blocked at more than 187.7 s and the yield reached 36 % at 469.2 s. Furthermore, heating of light source was depressed using black aluminum oxide as shown in Table 3. Therefore, it was considered that a microreactor using a black aluminum oxide channel substrate was effective for yield improvement of photoreactions.

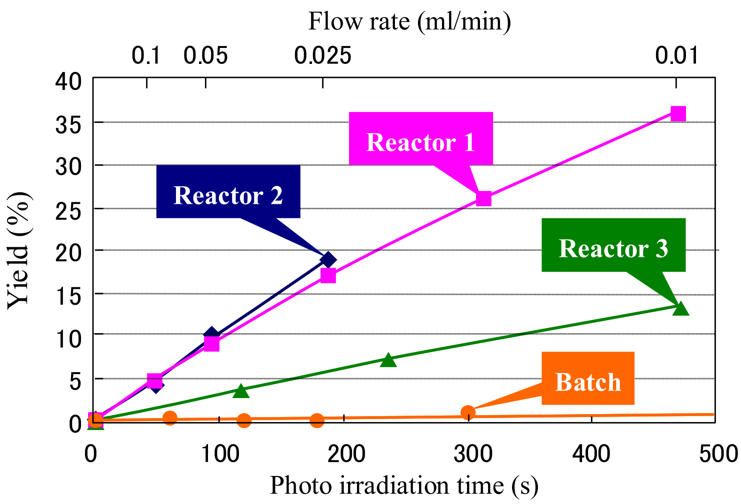

Figure 6. Yields in the photoreaction of benzophenone

Table 3. Comparison of materials to Light source temperatures

Channel substance	Light source temperature (K)
Black aluminum oxide	About 303
Quartz glass	313-323

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