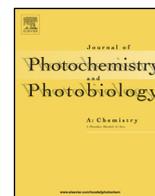




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Photocatalytic organic syntheses using a glass-milled microchip

A. Nakamura¹, K. Yoshida¹, S. Kuwahara, K. Katayama*

Department of Applied Chemistry, Chuo University, 1-13-27 Kasuga, Bunkyo, Tokyo 112-8551, Japan

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ABSTRACT

Photocatalytic reactions, typically known as difficult to control due to secondary reactions and involvement of multiple radicals, were demonstrated to be controlled well by optimizing the reaction time and the microchip design. The glass-milled microchip has a good resistivity for the organic solutions and withstands multiple usage more than 100 times. The oxidization and reduction reactions were demonstrated and the flow considerably improved the conversion and yield. Furthermore, an imine synthesis was demonstrated as a multi-step reaction by combination of photocatalytic oxidation and reduction reactions.

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1. Introduction

Photocatalytic reaction processes are classified into direct [1–3] and secondary reactions [4–7]; the former corresponds to the reaction between the adsorbed species and photoexcited electrons or holes, while the latter is the one induced by active oxygen species generated in the solvent due to the reaction between photoexcited holes and solvent or ambient molecules. Since there have been no specific methods for separating the two processes, the reactions have been usually understood on the phenomenological average, and the actual reaction mechanism is still difficult to understand for various conditions.

In most of the applications using photocatalytic reactions, only the oxidation ability, especially total oxidation from organics to carbon dioxide and water, has been paid attention to. However, photocatalyst also has the abilities such as partial or selective oxidation [8–13], and reduction [14–16] for various aromatic compounds [17,18]. Selective oxidation of the alcohol functional groups gave a high yield [19]. The reduction of nitrocompounds was investigated well on the reaction mechanism [14,20,21], and imine formation was reported after reacting with alcohols [22]. Furthermore, complicated reactions following the photocatalytically generated intermediate radical species were found, too [11,23–25].

However, in many of the organic conversions, the yields or selectivities are not high enough to be eligible for the replacement of the organic reactions [18,19]. This is probably because several

different radical species are involved and/or the direct and secondary reactions are mixed in the process. Thus, it is necessary to understand the reaction process, and to control it.

We have studied the mechanism of the photocatalytic reactions such as the formation of the active oxygen species [26], separation of the direct and secondary reactions [27], and degradation of various dyes with different main structures [28]. Furthermore, we found that photocatalytic reactions proceeded quickly with high selectivity by combining photocatalyst and microreactors, which has a high surface/volume ratio, preferable for the photocatalytic reactions [29]. There have been similar approaches on the photocatalytic microreactors, and it was reported that the reaction time became shorter, and the selectivities for specific reactions were improved [30–33]. It was also demonstrated that the microreactor is suitable for general photochemical syntheses [34,35].

In the development of the photocatalytic microreactor, we noticed that many of the photocatalytic reactions gave a high yield and selectivity within several minutes if we could appropriately stop the reaction and take out the products. However, there were several difficulties for the implementation of the combination of the photocatalytic reactions and the microreactor. We could not use the polymer microreactor, which are subject to deterioration during the photocatalytic reactions and also cannot be heated for the deposition of photocatalytic materials. This made us difficult to use a flexible microreactor, which is advantageous for the operation at high flow rate and for easy irradiation of light. Thus, we need to use a glass microreactor, which loses the above-mentioned feature of the polymer microreactors. Furthermore, it is difficult to get a large amount of products because the channel depth is typically on the order of hundreds of microns at most, by

* Corresponding author.

E-mail address: kkata@kc.chuo-u.ac.jp (K. Katayama).¹ These authors contributed equally.

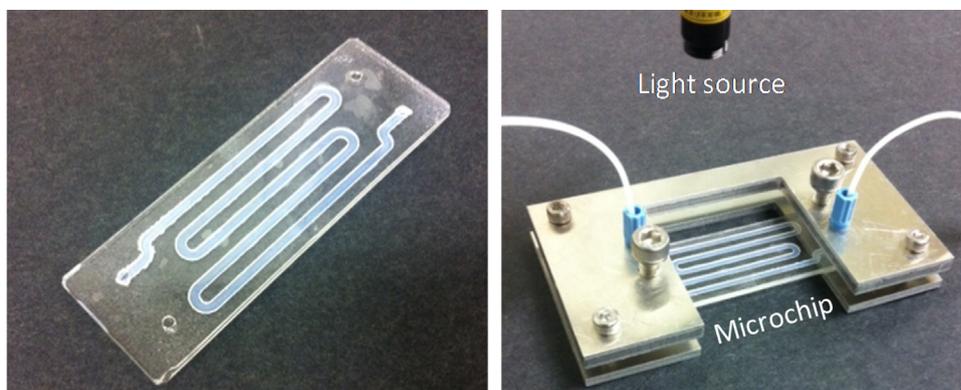


Fig. 1. A picture of a photocatalytic microchip (left) and that with an aluminium holder and the connecting tubes. A UV-LED was irradiated from the top. (right).

wet etching typically used for fabrication of a glass microchip. Also, we could not use the microchannels with heterogeneous structure for our purpose, which has a large distribution of the residence time in the reactors, and they are not favorable for the control of the reaction time.

To solve these problems, we fabricated the photocatalytic microchip by milling the glass slide, which is preferable for making a microchannel with larger width and depth with high flexibility. We demonstrated several organic reactions with high yield and selectivity by optimizing the reaction time and flow condition, which could be roughly estimated by the in-situ reaction monitoring [28]. Surprisingly, in most of the reactions, the product yields were improved under the continuous-flow condition, compared with the same residence time under the stop-flow condition.

Furthermore, we applied this microchip for more complicated reaction, imine synthesis, which is a useful chemical for agrichemical and pharmaceutical purposes [36]. In recent years, several groups demonstrated the imine synthesis by using photocatalysis [22,37–39]. In this reaction, both the oxidation and reduction reactions were utilized at the same time, which is favorable for photocatalytic reactions. Since this reaction is a multi-step reaction; photocatalytic and condensation reaction, we accomplished this reaction by separating the photocatalytic microchip and a vial.

2. Experimental

A normal glass slide (S1112, Matsunami) with the dimension of $75 \times 25 \times 1$ mm was rinsed before fabrication with acetone in a ultrasonic bath for 30 min and flowing water for 5 min and was machined by a miller (RD300, Original Mind) with a diamond mill

with a diameter of 2 mm. The channel width, and length were 2, and 250 mm, respectively, which corresponds to the inside volume of 250 μ L. The milled glass was thermally bonded with another slide glass in a furnace for 9 h at 650 $^{\circ}$ C. The top glass was drilled to have inlet holes. The microchannel was filled with a TiO₂ paste three times and furnace at 450 $^{\circ}$ C for 1 h after it was washed 3 times with an alkaline solution (5 M NaOH) and water. TiO₂ powder (P25), average diameter (D : 21 nm) was used for the paste. It was mixed with water (3.33 mL) and acetylacetone (0.33 mL) and mixed in a mortar for 30 min. The TiO₂ amount deposited for a microchip was estimated to 4–8 mg. As shown in Fig. 1, the microchip was sandwiched with an aluminium holder and the inlet was connected to a syringe pump (YSP-202, YMC), and the outlet was tubed into a vial for the analysis by gas chromatography (GC). To start the photocatalytic reactions, a UV LED with a center wavelength of 365 nm (EXECURE-LH-1 V, HOYA) was irradiated over the whole area of the channel with an intensity of 16 mW/cm², and the transmittance was >90% for the glass slide. The experiments were made after checking no reactions proceeded without TiO₂ coating in microchannels. Unless otherwise stated, the concentrations of reactants were 5 mM.

For the estimation of the reaction time, each reaction was monitored with the in-situ spectroscopic monitoring device developed recently [29] (Fig. S1). Briefly, a photocatalytic reaction inside a fused silica capillary (I.D. 500 μ m) was monitored, in which TiO₂ was coated with the same procedure as for the microchip. The photocatalytic reaction was initiated by the light irradiation from the top side with a UV-LED at 365 nm (45 mW/cm²). Perpendicularly with it, the UV spectral range in 220–400 nm was monitored. In any reactions we performed here, the necessary time was estimated less than 20 min. A typical analysis made for nitrobenzene (NB) is shown in Fig. S1.

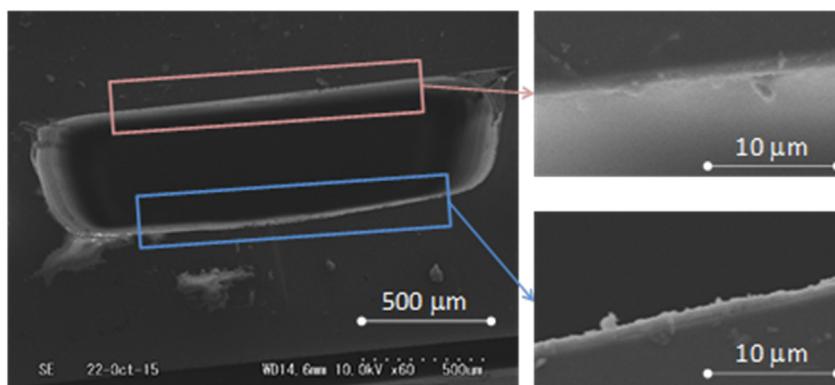


Fig. 2. A section image of the microchannel measured by SEM (left) and the expanded images at the top and bottom layer are shown on the right.

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