

Photocatalytic Redox-Combined Reaction with TiO₂ Film Modified Microchannel Chip: Applied Potential Dependence of Selectivity and Enantiomeric Excess

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We have demonstrated photocatalytic redox-combined reaction with TiO₂ film modified microchannel chip (TiO₂-MC) for photocatalytic synthesis. In microchip chemistry, μm-sized channels were applied as a reaction field characterized by short diffusion length and large specific interfacial area. Photocatalysts including TiO₂ were generally used as nm-sized fine particles due to their large specific interfacial area. TiO₂-MC also has large specific interfacial area, which provide efficient reaction. In addition to that, TiO₂-MC has advantages such as reaction control by applying potential and no removal process of nm-sized particles. In this paper, we fabricated potential controllable TiO₂-MC and applied it to photocatalytic redox-combined synthesis: one-step synthesis of L-pipecolic acid (L-PCA) from L-lysine [1](Figure 1).

The picture of fabricated TiO₂-MC shows in Figure 2. On a top plate, branched microchannels (770-μm-width, 3.5-μm-depth) were fabricated by the photolithographic and wet etching techniques. On a bottom plate, TiO₂ thin films were prepared with the sol-gel method. The top and bottom plates were thermally bonded. Also, potential-controllable TiO₂-MC (PC-TiO₂-MC) was fabricated using Pt electrode integrated substrate as a bottom plate. To apply TiO₂-MC to photocatalytic redox-combined synthesis, Pt was loaded onto TiO₂ as a reduction site. SEM and XRD analysis revealed polycrystalline anatase structure (particle size: 100 nm). L-lysine aqueous solution (2 mM) is introduced into TiO₂-MC under UV irradiation (300-400 nm). Reaction products were analyzed by HPLC equipped with a chiral separation column.

Experimental results are summarized in Table 1. The results clearly show that higher efficient photocatalytic synthesis was demonstrated in TiO₂-MC with keeping almost the same selectivity and enantiomeric excess (ee) of the bulk scale reaction with 25-nm particles. Applied potential dependence of the reaction is shown in Figure 3, which clearly shows the applied potential affects both selectivity and ee. Higher selectivity at negative potential can be explained by efficient reduction of the intermediates (CSB) at the reduction site. On the other hand, the change in ee indicates the reaction path changed. As a conclusion, for the first time, we succeeded in constructing efficient and potential controllable photocatalytic system. Further details including reaction mechanism and quantum yields will be discussed at the presentation.

Reference:

[1] B. Ohtani et al., *J. Org. Chem.*, **55** (1990) 5551

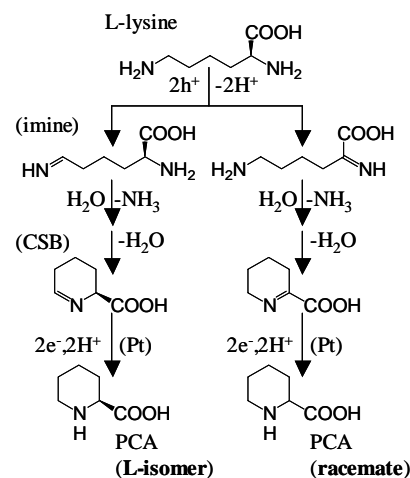


Figure 1. Mechanism of one-step synthesis of L-PCA from L-lysine

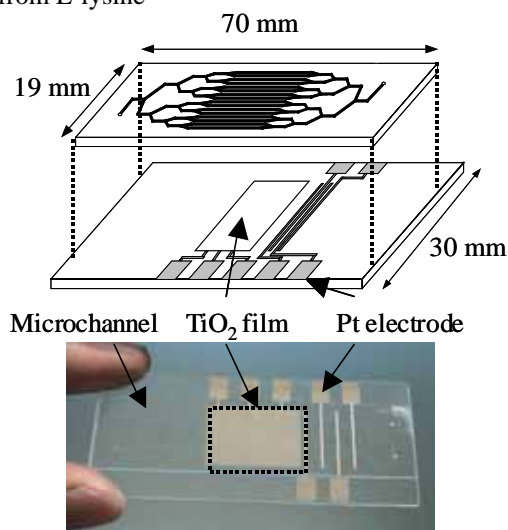


Figure 2. Photograph of TiO₂-MC and PC-TiO₂-MC

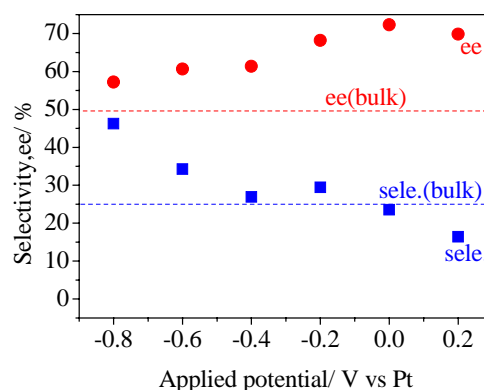


Figure 3. Applied potential dependence of selectivity and ee. Broken line describes the results on the bulk scale reaction. Selectivity = (amounts of PCA production) / (amounts of L-lysine

Table 1. Comparison among TiO₂-MC, bulk scale reaction and PC-TiO₂-MC

Reaction system	Conversion ^b / %	Reaction time / min	Selectivity / %	ee / %
TiO ₂ -MC	86	0.86 ^c	22	50
Bulk scale (25 nm ^a)	89	60	26	46
PC-TiO ₂ -MC (-0.8 V)	72	0.48 ^c	47	58

^a The bulk scale reaction is performed using powder suspension (particle size is 25 nm). ^b Conversion is defined amounts of L-lysine consumption based on the initial amounts of L-lysine. ^c Reaction time of chip reaction is defined as residential time (flow rate = 1 μL/min).