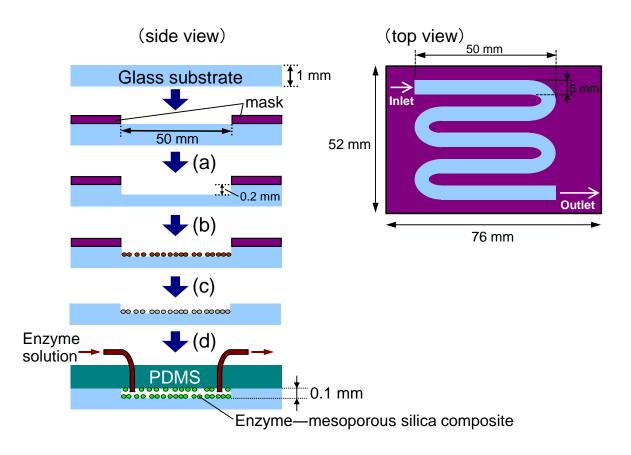
Electronic Supplementary Information (ESI)

Synthesis of amino acid using a flow-type microreactor containing enzymemesoporous silica microsphere composites

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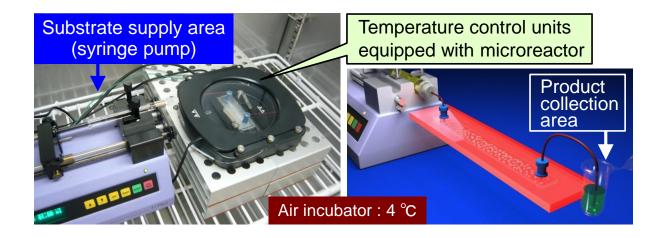


**Figure S1.** Preparation of a PDMS/glass microreactor containing an enzyme–mesoporous silica composite. (a) Etching (1 M HF, 2 M  $NH_4F$ ). (b) Deposition of calcined mesoporous silica powder via a thin layer of liquid PDMS prepolymer as adhesive. (c) Heating for 3 h at 85 °C to immobilise silica particles by polymerization of a PDMS prepolymer layer. (d)

Sealing the PDMS membrane containing the immobilised silica particles. The upper PDMS membrane could be attached to the lower glass substrate by pressing it by hand without air plasma pretreatment of the membrane because there was no liquid spill from the microreactor when the flow rate ranged from 5 to 20  $\mu$ L min<sup>-1</sup>, due to low pressure in the interior channel.

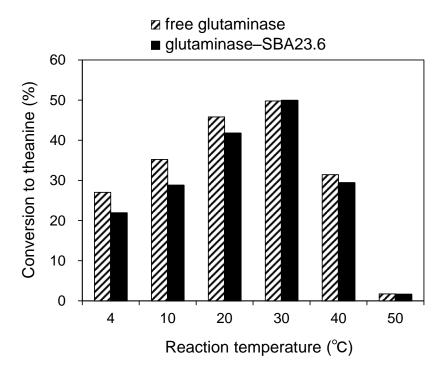
## Characterisation of the microflow channel

The thickness of the microflow channel was directly measured with a micrometre (Digimatic Micrometer, Model MDC-25MJ, Mitutoyo Corporation, Japan). The average thickness of the flow channel, as determined by measuring ten spots from the channel chosen at random, was estimated to be approximately 100  $\mu$ m. The inner volume of the microflow channel was estimated by filling the empty flow channel with the first delivery of the enzyme solution.; the inner volume of the flow channel of the microflow channel were 0.83, 1.66, and 3.33 at flow rates of 5, 10, and 20  $\mu$ L min<sup>-1</sup>, respectively.

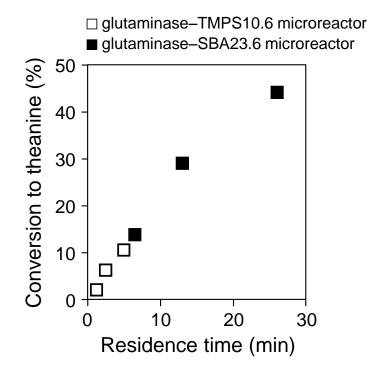


**Figure S2.** Photo and diagram of the experiment apparatus used for local heating. The photo and the diagram demonstrate the simple mechanism (flow channel: width: 5 mm, length: 50 mm) used for the local heating. The temperature in the main reactor was controlled by temperature control units (Stage top incubator, INU-ONICS; Tokai Hit Co., Ltd.) in those cases for which the main unit of the reactor within the microreactor system was locally

heated, whereas both the substrate supply and the product collection area were kept at 4 °C using an air incubator (MIR-154; SANYO Electric Co., Ltd.).



**Figure S3.** Effect of reaction temperature on conversion to L-theanine in batch reactions by free glutaminase (slash) and glutaminase–SBA23.6 composite (black). Reaction conditions for one assay: enzyme content, 50  $\mu$ g; composition of substrate, 20 mM glutamine–100 mM ethylamine (pH 10); total volume of reaction mixture, 1.1 mL; reaction time, 1 h; reaction temperature, 4, 10, 20, 30, 40, and 50 °C.



**Figure S4.** Effect of residence time on the conversion to L-theanine in microflow reactions using the glutaminase–SBA23.6 composite (black squares) or the glutaminase–TMPS10.6 composite (white squares)<sup>13</sup>. Reaction conditions: composition of substrate, 20 mM glutamine–100 mM ethylamine (pH 10); reaction temperature, 30 °C.