Scale-up of a Luminescent Solar Concentrator-Based Photomicroreactor via Numbering-up

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Supporting Information

ABSTRACT: The use of solar energy to power chemical reactions is a long-standing dream of the chemical community. Recently, visible-light-mediated photoredox catalysis has been recognized as the ideal catalytic transformation to convert solar energy into chemical bonds. However, scaling photochemical transformations has been extremely challenging due to Bouguer–Lambert–Beer law. Recently, we have pioneered the development of luminescent solar concentrator photomicroreactors (LSC-PMs), which display an excellent energy efficiency. These devices harvest solar energy, convert the broad solar energy spectrum to a narrow-wavelength region, and subsequently waveguide the re-emitted photons to the reaction channels. Herein, we report on the scalability of such LSC-PMs via a numbering-up strategy. Paramount in our work was the use of molds that were fabricated via 3D printing. This allowed us to rapidly produce many different prototypes and to optimize experimentally key design aspects in a time-efficient fashion. Reactors up to 32 parallel channels have been fabricated that display an excellent flow distribution using a bifurcated flow distributor (standard deviations below 10%). This excellent flow distribution was crucial to scale up a model reaction efficiently, displaying yields comparable to those obtained in a single-channel device. We also found that interchannel spacing is an important and unique design parameter for numbered-up LSC-PMs, which influences greatly the photon flux experienced within the reaction channels.

KEYWORDS: Photomicroreactor, Luminescent solar concentrator, Solar energy, Numbering-up, Photochemistry

INTRODUCTION

Sunlight is the most abundant source of renewable energy on our planet. In 1 h, more solar energy strikes the Earth than we currently consume on a yearly basis. It is envisioned that solar energy will become the primary energy source in the future. Efficient use of solar energy will allow us to meet the increasing energy demand while stabilizing the atmospheric CO$_2$ concentration at an acceptable level.$^{1,2}$

An enormous number of studies have been performed to capture, convert, and store solar energy. Throughout the years, researchers have unraveled the mechanism of light absorption and the subsequent energy transfer in the natural photosynthetic process.$^{3-5}$ These insights have inspired the scientific community to create ingenious and “Nature-style” solutions to harvest solar energy.$^{5,6}$ One particular field of research focuses on the conversion of solar energy into electrical energy. This field has benefitted from insights into the natural light-harvesting system to produce improved solar cells. For example, dye-sensitized solar cells, which separate the charge-generation and charge-transport processes by mimicking photosynthesis, have achieved AM 1.5G (Air Mass 1.5-Global Illumination) power conversion efficiencies up to 13%,$^{7}$ becoming a promising alternative to the conventional P−N junction devices.$^{8}$ Another discipline has devoted its efforts toward the conversion of solar energy into chemical bond energy: many ingenious photocatalysts have been developed to produce solar fuels by imitating either the morphology or the mechanism of Nature’s tree leaf.$^{9,10}$ These “artificial leaves” are composed of a light harvester and water splitter consisting of an anode for oxygen evolution and a cathode for hydrogen evolution.$^{11-13}$ Solar energy can also be utilized to enable the synthesis of complex molecules, e.g., via visible-light photocatalysis.$^{14-17}$ Here, so-called solar reactors, such as parabolic troughs, parabolic dishes, solar furnaces, and flatbed reactors, can be used to increase the efficiency of the photochemical process.$^{18}$ However, these reactors suffer from a number of...
disadvantages, including outdoor use of large amounts of hazardous solvents, need for sun trackers and reflective mirrors, high cost, low efficiency, and difficulty in scaling up. Moreover, such solutions are less cost-efficient in sun-poor regions.\textsuperscript{19,20}

To develop reactor solutions that can operate at relatively high latitudes, where light is less abundant and more diffuse (e.g., by clouds and buildings), we have recently developed so-called luminescent solar concentrator-based photomicroreactors (LSC-PMs).\textsuperscript{21} These reactors constitute a synergistic merger between luminescent solar concentrators\textsuperscript{22} and microflow chemistry.\textsuperscript{23−27} The LSC-PM is based on fluorescent doped polydimethylsiloxane (PDMS) material, and, similar to Nature’s biomachinery, it allows harvesting of solar energy and its downconversion to a narrow-wavelength window that matches with the absorption maximum of the photocatalytic reaction. The re-emitted photons are subsequently light-guided to the embedded reaction channels. LSC-PMs display all the advantages that are associated with microreactors, such as enhanced mass transfer, uniform irradiation of the reaction mixture, and increased safety.\textsuperscript{6,27} However, like microreactor technology, it suffers from its small scale, which is not sufficient to meet the productivity requirements of large-scale chemical processes. Two strategies are often employed for the scale-up of microreactors: sizing-up and numbering-up. The former involves a dimension-enlarging strategy, in which the reactor size is gradually increased while keeping the mass- and heat-transfer phenomena stable.\textsuperscript{28,29} However, due to the light-attenuation effect, this strategy is not compatible with photochemical reactions. A potential solution to scale up LSC-PMs is to use a numbering-up strategy. In analogy to a tree, which has many leaves through which water and other nutrients are pumped, several LSC-PM devices can be placed in parallel to increase the overall throughput. The challenge for efficient numbering-up is to ensure an equal distribution of the fluid flow over the different reactors. To achieve equipartitioning among the parallel microchannels, various flow distributors/collectors with different structures and geometries have been developed.\textsuperscript{30−32} Many methods have been reported to characterize the flow distribution, including experimental methods,\textsuperscript{33,34} modeling,\textsuperscript{35} computational fluid dynamics (CFD) simulations,\textsuperscript{36} micro-PIV (microparticle image velocimetry),\textsuperscript{37} and flow-visualization techniques.\textsuperscript{38} For chip- or plate-based microreactors, the most frequently used distributor/collector designs are manifold-type and bifurcation-type, as shown in parts A and B of Figure 1, respectively.

For the manifold-type design, the flow manifold (or chamber) can have different inlet/outlet positions. The design shown in Figure 1A has a right inlet and left outlet, which makes the total residence time the same for each channel. The inlet and outlet can also both be located at the center of the distributing and collecting manifolds, respectively.\textsuperscript{36} Moreover, the flow manifold can have varying cross sections to ensure a uniform pressure drop over the parallel reaction channels.\textsuperscript{39}

The bifurcation structure is a symmetrical design and typically provides an excellent distribution as shown by both simulations and experiments,\textsuperscript{30−41} with flow variations below 5% for single-phase flow.\textsuperscript{43} However, in the context of this work, there are two main disadvantages associated with the bifurcation design: the large footprint of the distributor/collector section compared to the reactor section and the relatively high pressure drop due to the splitters. This is especially true when the total number of parallel reaction channels is high. A good compromise is the combination of a bifurcation distributor design with a collecting chamber.\textsuperscript{38,44} This numbered-up design ensures a good flow distribution, while minimizing the overall footprint and the pressure drop (Figure 1C).

In this work we describe a numbered-up version of our solar-driven LSC-PM, which allows us to scale up solar photochemistry in an efficient fashion. The developed design provides high flow uniformity in devices containing up to 32 parallel channels. A crucial parameter in our LSC-PM numbered-up design is the interchannel spacing, which is equivalent to the solar energy harvesting area.

\section*{EXPERIMENTAL SECTION}

\textbf{Materials.} Ethanol (purity (V/V) ≥ 99.5%) and diethyl ether (technical) were purchased from VWR Chemicals. Acetonitrile (AR, Biosolve Chmie SARL) and methylene blue were bought from Merck KGaA. Lumogen F red 305 and 9,10-diphenylanthracene (>95.0%) were acquired from BASF and TCI, respectively. Sylgard 184 silicone elastomer (base + curing agent) was purchased from Dow Corning.

For the 3D printing of the reactor molds, high-impact polystyrene filament (ø1.75 mm, neutral, Apollo series) was obtained from webshop 123-3D.nl polystyrene plates (black, 270 length x 260 width x 3 thickness mm\textsuperscript{3}) were provided by S-POLYTEC GmbH.

\textbf{Device Design and Fabrication.} In this study, polydimethylsiloxane (PDMS) is used to construct the LSC-PM. The PDMS is doped with Lumogen F red 305 (LR305) as the fluorescent dye. The numbered-up LSC-PM can be fabricated by combining the entire design (distributor, reaction channels, and collector) in one single PDMS slab. This scaled-up device has only a single entrance and exit port; thus, only a single pumping system is required to deliver the feeds. Hence, our scaled-up device consists of five primary parts (Figure 2): inlet zone, distributing zone, reaction zone, collecting zone, and outlet zone. The microchannels of these five zones, all with a height of 1 mm, are embedded in a 3-mm-thick PDMS slab, centrally located in the vertical cross section.

In the reaction zone, identical parallel microchannels (0.35 width x 1 height x 150 length mm\textsuperscript{3}) are distributed with constant interchannel distance. The interchannel spacing is defined as the spacing between two adjacent parallel channels. To equalize the flow among the parallel channels, the bifurcation design is employed in the distributing and collecting zones (Figure 1B). For a system with a high pressure drop, or just for simplification of the device, a collecting channel can be employed as a substitute for the bifurcation structure in the collecting zone (Figure 1C).

The main process for manufacturing our LSC-PM device is presented in Figure 3. Two molds are printed on polystyrene plates.
with a 3D printer (FELIX, Pro 1): one mold is for the 2-mm-thick layer wherein the microchannels are embedded and the other mold allows one to produce the 1-mm-thick covering layer. The main advantage of this 3D-printed mold strategy is that it enables rapid prototyping, which makes it possible to screen multiple designs in a time-efficient fashion.45,46 Next, the prepolymer mixture (silicone elastomer base + curing agent) with or without the dye LR305 was subsequently treated with oxygen plasma (Plasma asher Tantec, SpotTEC), and are bonded together to form the 3-mm-thick device.

**Characterization of Flow Distribution.** The devices used to evaluate the flow distribution did not contain a collecting zone, as shown in Figure 4. Instead, ethylene tetrafluoroethylene (ETFE) capillaries (IDEX, 1.6 mm o.d. × 1 mm i.d., 2 cm length) were inserted, which allowed us to collect the effluent of individual channels in separate vials. Ethanol was used as the fluid and pumped through the device using a high-performance liquid chromatography (HPLC) pump (Shimadzu, LC-20AD). Effluents were collected individually during a given time in a 1.5 mL vial and weighed. Next, the flow rate in the reaction channel i, \( F_i \) (mL/min), was calculated based on the mass of the collected effluent.

As a measure of the uniformity of the flow distribution, the relative standard deviation, RSD (%), of the flow rates in \( N \) parallel reaction channels was used, which is given by

\[
\text{RSD} (\%) = 100 \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (F_i - \bar{F})^2}
\]

where

\[
\bar{F} = \frac{1}{N} \sum_{i=1}^{N} F_i
\]

(1)

**Characterization of Reactor Performance.** The \([4 + 2]\) cycloaddition of 9,10-diphenylnanthracene (DPA) with singlet oxygen, generated via photosensitization in the presence of methylene blue (MB), was used as the benchmark reaction to evaluate the performance of the scaled-up LSC-PMs (Figure 5).

\[
\text{Conversion} = \frac{C_t - C_0}{C_0}
\]

where \( C_0 \) is the initial DPA concentration, \( F_t \) is the total volumetric flow rate, and \( V_{LH} \) is the light-harvesting volume of the device (the total device volume exposed to the light — the total reaction volume).

The space-time yield \( Y \) defined here represents the amount of DPA converted per unit time and per unit light-harvesting volume.

**RESULTS AND DISCUSSION**

**Flow Distribution Tests in Scaled-up Devices. Optimization of Bifurcation Design.** An ideal bifurcation distributor should be symmetrical, and the channel length

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**Figure 2.** Schematic representation of our scaled-up device. The dashed lines do not represent the actual flow path.

**Figure 3.** Schematic diagram describing the basic steps of the LSC-PM fabrication process.

**Figure 4.** Sketch of the numbered-up device used to investigate the flow distribution. The dark blue channels in the red waveguide represent the microchannels, and the light blue outside the red waveguide are the capillaries that are inserted in the microchannel outlets.

**Figure 5.** Singlet oxygen-mediated cycloaddition of 9,10-diphenylnanthracene using methylene blue as the photocatalyst and acetonitrile as the solvent at room temperature.

**Figure 6.** Displays the microfluidic setup, which is used to characterize the performance of the numbered-up reactor. Feed solutions of 0.2 mM DPA and 0.02 mM MB were pumped by two HPLC pumps (Shimadzu, LC-20AD). The two streams were merged in a PEEK T-micromixer (IDEX, P-714, inner diameter 1 mm), and the combined reaction mixture was introduced into the device, which was illuminated by a metal halide solar simulator (KHS Solar Constant 1200). The conversion was measured by directing the effluent through the micro flow cell (Avantes, Micro flow Z-cell-10) of an inline spectrophotometer (Avantes, AvaSpec-2048L) equipped with a balanced deuterium light source (Avantes, AvaLight-DH-S-BAL). The conversion was measured in real time by monitoring the disappearance of the DPA peak at 372 nm.

The conversion \( X \) and space-time yield \( Y \) were calculated using the obtained DPA concentration \( C \) as follows:

\[
X = \frac{C_t - C_0}{C_0}
\]

\[
Y = \frac{F_t C_0 X}{V_{LH}}
\]
After the elbow should be long enough to result in a fully developed flow profile (Figure 7). The distributor symmetry requirement can be fulfilled by using a 3D printer with a high level of accuracy. The value of $L_E$ to reach a fully developed velocity profile depends on the hydraulic diameter of the channel ($D$) and the Reynolds number ($Re$) and can be calculated by

$$L_E = 0.05 \cdot Re \cdot D$$

under laminar flow conditions. However, high values of $L_E$ would lead to a too-large distributor section and thus a larger overall footprint of the device. Consequently, $L_E$ needs to be optimized based on the hydraulic diameter of the channels at different $Re$ numbers.

For rectangular channels, the hydraulic diameter $D$ can be calculated using the following equation:

$$D = \frac{2\omega h}{\omega + h}$$

where $\omega$ and $h$ are the channel width and height, respectively.

To optimize $L_E$, three 8-channel devices were made that only differed in their $L_E$ values, as shown in Table 1. The reaction channels in these three devices have all the same dimensions, i.e., 0.35 width $\times$ 1 height $\times$ 150 length mm$^3$. In device I, $L_E$ is set to be two times the corresponding hydraulic diameter, i.e., 2D. Likewise, in devices II and III, $L_E$ is set to be, respectively, 3D and 4D. The exact $L_E$ values within these three devices are presented in Table 1, as well as the theoretical entrance length calculated by eq 5 using the corresponding largest $Re$ in each distributing level investigated in the experiment.

Next, flow-distribution tests were conducted at two extreme flow rate values, namely, 0.1 and 0.6 mL/min/channel. The unit mL/min/channel represents the flow rate in an individual reaction channel when the flow is equalized among the parallel reaction channels. In other words, 0.1 mL/min/channel represents a total flow rate of 0.8 mL/min in an 8-channel device. From Table 2, it can be seen that the flow distribution improved with increasing $L_E$ values (device I < device II < device III). Furthermore, it can be expected that if we further increase the value of $L_E$ (entrance length, as presented in Table 1), an improved flow distribution with RSD < 2% can be achieved. In general, RSD values < 5% can be regarded as excellent, and both devices II and III meet that criterion. To keep the size of the distributor section small, we selected $L_E = 3D$ (as in device II) for our further investigations.

### Table 1. Overview of the Dimensional Parameters of the Distributing Channels in the Three 8-Channel Devices Made for the Optimization of Distributor Design (Unit: mm)

<table>
<thead>
<tr>
<th>distributing level</th>
<th>entrance length</th>
<th>device I</th>
<th>device II</th>
<th>device III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega$</td>
<td>$h$</td>
<td>$L_E$</td>
<td>$\omega$</td>
</tr>
<tr>
<td>1</td>
<td>1.6</td>
<td>1</td>
<td>2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>1</td>
<td>1.8</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>1</td>
<td>1.1</td>
<td>0.35</td>
</tr>
</tbody>
</table>

### Table 2. RSD Results for the Three 8-Channel Devices with Different Values of $L_E$ under Low and High Flow Rates

<table>
<thead>
<tr>
<th>flow rate (mL/min/channel)</th>
<th>device I</th>
<th>device II</th>
<th>device III</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>10.9%</td>
<td>3.7%</td>
<td>2.1%</td>
</tr>
<tr>
<td>0.6</td>
<td>4.4%</td>
<td>3.6%</td>
<td>2.3%</td>
</tr>
</tbody>
</table>
Flow Distribution of Bifurcation Design with Different Reaction Channel Numbers. Having selected the optimal value of $L_n$, we set out to evaluate the flow-distribution efficiency in devices containing, respectively, 8, 16, and 32 parallel reaction channels. The dimensional parameters of the distributing channels in these three devices are listed in Table 3, and the RSD values for flow distribution are tabulated in Table 4. It can be seen that excellent flow distribution was achieved for the 8-channel device over a wide flow rate range with RSD values all <4%. When the total number of channels increased, the flow-distribution efficiency decreased slightly. However, very good RSD values below 10% can still be obtained even in devices containing 32 parallel channels. However, it should be noted that the occurrence of an increased flow maldistribution is likely caused by the insertion of capillaries at the reaction channel outlets. This was done to estimate the mass flow distribution, but in a practical device (vide infra) a flow collector is used. This means that the RSD values will be much smaller in the latter scenario. Another potential reason for flow nonuniformity is the 3D printing accuracy, which is lower for larger devices. This problem could be overcome by using classical soft lithography techniques or by using a 3D printer with higher accuracy.

Effect of Interchannel Spacing on the Device Performance. One of the crucial design aspects of our LSC-PM is that the reactor material is doped with LR305 to harvest solar light. This energy is subsequently re-emitted and light-guided toward the reaction channels via total internal reflection. Consequently, it can be simply understood that the size of the harvesting area plays a key role in the photon flux through the reaction channels. The harvesting area can be characterized by the so-called interchannel spacing, which represents the distance between two adjacent channels. The larger the interchannel spacing, the higher the photon flux will be within the channels. However, there is a limit to this distance due to the reabsorption of the luminescent photons. This reabsorption leads to energy losses caused by the possibility that the light is re-emitted within the escape cone angle and leaves the device, the nonunity fluorescence yield, and the background absorption by the polymeric matrix. The larger the interchannel spacing, the higher these losses will become.

To evaluate the effect of the interchannel spacing, we commenced our studies by investigating a set of five 8-channel devices, with varying interchannel spacings of 1.5, 2.5, 5, 10, and 20 mm, respectively. The total reaction channel volume was kept the same, and the devices were equipped with a bifurcated distributor and collector (see Figure 8A). Moreover, to demonstrate the importance of interchannel spacing for the LSC-PM device, we did the same investigations in five nondoped devices (Figure 8B) with the same reactor design as in the dye-doped ones.

As expected, in nondoped numbered-up devices, the conversion remained almost constant despite the increase of interchannel spacing (Figure 8C). These nondoped devices are able to use only the direct irradiation, which depends on the illumination area of the reaction channels and does not change with the interchannel spacing. In contrast, as shown in Figure 8C, in dye-doped devices the reaction conversion increased with increasing interchannel spacing due to an augmented photon flux through the reaction channels. As can be observed in Figure 8C, for interchannel spacing up to 5 mm the observed increase in conversion is quite significant, while a further increase to 10 or 20 mm has a reduced impact on conversion. This effect, due to the lower efficiency in the light-guiding over longer distances, is even more significant when the corresponding space-time yields (Figure 8D) are taken into account.

Furthermore, due to the device geometry, the percentage of photons reaching the nonreaction zones, as calculated via Monte Carlo ray-tracing modeling, also increases with the increased interchannel spacing (Figure 8E). Further in this work, an interchannel spacing of 5 mm was chosen as >90% of the photon flux received by the reaction mixture was localized in the reaction zone.

Several aspects influence the optimal interchannel spacing in LSC-PM-based devices including the device material (transparency and refractive index), the luminophore optical properties (fluorescent quantum yield and Stoke shift), the reaction system (reaction kinetics and quantum yield), and the overall process operation (e.g., operational cost for upstream/downstream processes). For solar-based chemical-production applications, the interchannel spacing of scaled-up LSC-PMs should be determined on a case-by-case scenario by balancing various parameters as mentioned above, based on the needs of the application. The approach we followed coupling experimental investigation and ray-tracing modeling can serve as a guideline to make a judicious choice in this matter.

Reaction Performance in Numbered-up Devices with Bifurcation/Bifurcation Design and Bifurcation/Chamber Design. During our previous experiments with the reactors possessing a bifurcation/bifurcation design (Figure 8A), we observed in some situations leakage at the in- or outlet. Especially, the 32-channel device was prone to failure at higher flow rates. Due to the high pressure drop in such cases, the channels suffered also from expansion or deformation.

Feasibility of Employment of a Collecting Chamber. To address the above-mentioned undesired phenomena, we also prepared a set of reactors that contained a collecting chamber. This design could effectively decrease the footprint of collecting zone and lower the pressure drop over the entire device (see Table S1 in the Supporting Information).

Table 3. Overview of Dimensional Parameters of the Distributing Channels in Scaled-up Devices with 8, 16, and 32 Channels (Unit: mm)

<table>
<thead>
<tr>
<th>distributing level</th>
<th>8-channel device</th>
<th>16-channel device</th>
<th>32-channel device</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$</td>
<td>$h$</td>
<td>$L_n$</td>
<td>$\omega$</td>
</tr>
<tr>
<td>1</td>
<td>1.6</td>
<td>1.37</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>2.7</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>1</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>0.35</td>
<td>1</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table 4. RSD Results for Scaled-up Devices with 8, 16, and 32 Channels under Different Flow Rates

<table>
<thead>
<tr>
<th>flow rate (mL/min/channel)</th>
<th>8-channel device</th>
<th>16-channel device</th>
<th>32-channel device</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.6%</td>
<td>6.0%</td>
<td>8.5%</td>
</tr>
<tr>
<td>0.2</td>
<td>3.7%</td>
<td>4.9%</td>
<td>7.9%</td>
</tr>
<tr>
<td>0.3</td>
<td>3.6%</td>
<td>4.4%</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>3.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>2.8%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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It is easily understood that in such a design the fluid elements from the outer channels have to travel a larger distance to leave the device than those in the inner channels. To ensure flow equalization in the device, the pressure drop in the collecting chamber should be much lower than the total pressure drop so that it will not affect the flow distribution significantly. The flow resistance in the collecting chamber is mainly dependent on its width (Figure 9B). To evaluate the effect of the chamber width on the flow distribution, several devices as shown in Figure 9 were prepared to help us identify qualitatively the flow resistance in the fluid chamber. The flow distribution was evaluated for these devices, and the results are presented in Table 5.

Table 5. RSD Results for the Flow-Rate Distribution among the Parallel Channels (Interchannel Spacing 5 Mm) Connected with a Fluid Chamber under Different Configuration Conditions

<table>
<thead>
<tr>
<th>flow rate (mL/min/channel)</th>
<th>2-mm-wide chamber, 8 channels</th>
<th>3-mm-wide chamber, 8 channels</th>
<th>3-mm-wide chamber, 16 channels</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>6.4%</td>
<td>7.1%</td>
<td>8.4%</td>
</tr>
<tr>
<td>0.3</td>
<td>7.6%</td>
<td>4.2%</td>
<td>7.1%</td>
</tr>
<tr>
<td>0.6</td>
<td>4.7%</td>
<td>4.2%</td>
<td>8.7%</td>
</tr>
</tbody>
</table>

It can be seen that the RSD values are acceptable in all cases (RSD values < 10%). An improved result was obtained with the 3 mm wide chamber. Furthermore, higher RSD values were observed for the 16-channel device, indicating that this design is less efficient as a distributor than the bifurcated one. Performance Comparison between Bifurcation/Bifurcation Design and the Bifurcation/Chamber Design. Lastly, devices containing bifurcated collectors (Figure 10A) and chamber collectors (Figure 10B), both with 8, 16, and 32 reaction channels, respectively, were prepared all with an interchannel spacing of 5 mm. Because the pressure drop was

Figure 8. Scaled-up devices with different interchannel spacings and their reactor performance. (A, B) Five dye-doped devices (A) and five nondoped devices (B) with interchannel spacings of 1.5, 2.5, 5, 10, and 20 mm, respectively. (C, D) Plots of conversion (C) and space-time yield (D) versus the interchannel spacing under different times in the nondoped and dye-doped devices. (E) Correlation between interchannel spacing and photon distribution between reaction and nonreaction (distributor, collector, inlet, and outlet) zones, calculated by ray-tracing simulations.

Figure 9. Schematic diagram of the device for the investigation on a fluid chamber. (A) Device configuration. The dark blue in the red waveguide represents the microchannels, and the light blue outside the red waveguide represents the ETFE tubes inserted at the microchannel outlet. (B) Schema for the chamber width.
overcome high pressure drops within the largest devices, we developed a numbered-up LSC-PM design with a bifurcated flow distributor and collection chamber.

The use of solar energy to produce pharmaceuticals, agrochemicals, and other fine chemicals is a dream that has been expressed by many chemists over the last century. We believe that the LSC-PM is one such strategy for meeting this vision. While the productivity of a single device is not sufficient to meet the current demand, several numbered-up devices as described in this work might overcome this particular challenge. Further scaling can be achieved by placing several of these devices in parallel, leading to solar chemical plants similar to the existing solar parks (i.e., photovoltaic power stations).

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b02687.

Comparison between bifurcation/bifurcation design and bifurcation/chamber design; light distribution among the reaction channels; influence of different fluid paths in the chamber design (PDF)

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**Notes**

The authors declare no competing financial interest.

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■ REFERENCES


lower, no leakages were observed with the bifurcation/chamber design in the experiments. Figure 10C displays the conversion as a function of the total residence time for devices with the bifurcation/bifurcation design (hollow blocks) and the bifurcation/chamber design (solid blocks) containing different number of reaction channels. Gratifyingly, excellent scalability is demonstrated for both designs, as shown by the overlapping kinetic curves.

■ CONCLUSIONS

We have described for the first time a fast scaling-up strategy of luminescent solar concentrator-based photomicroreactors (LSC-PMs), a reactor concept recently developed in our group that enables energy-efficient solar photochemistry. The use of 3D-printed molds was of paramount importance to rapidly prototype different reactors and to investigate the relative importance of several design aspects. A unique parameter for LSC-PM constitutes the interchannel spacing, which determines the photon flux experienced by the reaction medium. We validated experimentally that a symmetrical bifurcated flow distributor resulted in excellent flow partitioning in devices with up to 32 parallel reaction channels (standard deviations below 10%). Furthermore, a photosensitized benchmark reaction proved to be scalable, resulting in conversions similar to those obtained in a monochannel device. To


