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Enabling real-time detection of photocatalytic reactions by a re-useable micro-reactor

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Abstract

We present a highly sensitive and versatile Si-based μ -reactor for photocatalytic experiments. The μ -reactor can be operated in front side (through a borosilicate window) as well as backside (through the catalyst support) illumination. The μ -reactor is sealed by compressing the Si-based microchip, a parafilm gasket and the supported catalyst by four screws. This design allows for fast and reliable assembly of the μ -reactor and the microchip is re-usable for several independent experiments, making the presented μ -reactor ideal for catalyst screening studies. We analyze volatile reactants on-line by connecting the μ -reactor to a mass-spectrometer. The limiting capillary of the μ -reactor allows for nearly 100% collection efficiency (i.e. every produced molecule will be collected) by limiting the gas flow to the mass-spectrometerenabling highly sensitive measurements and an absolute calibration. Finally, the small height of the reactor volume results in very fast response times, which make the reactor suitable for studies of transient activity phenomena-including catalyst activation and deactivation. We demonstrate these capabilities of the μ -reactor by performing CO oxidation experiments on a TiO_2 thin film with subsequent calibration of the chip. Based on a mathematical model of the μ -reactor we additionally present a method for determining the residence time, the reaction volume and the working distance.

Keywords: photocatalysis, microreactors, microfabrication, mass transport modeling

1. Introduction

Through the application of microfabrication, it has become possible to study catalytic reactions in reactors with characteristic dimensions in the micrometer range [1–6]. Compared to conventional reactors, μ -reactors thus offer very small reaction volumes allowing for highly sensitive measurements and fast time responses. Traditionally our group has based the design of such μ -reactors on a silicon bottom part and a borosilicate top part [2, 4]. The silicon part is thereby microfabricated from a standard silicon wafer. Using deep reactive ion etching (DRIE) the desired reactor volume (240 nl), the gas channels and a capillary for direct interfacing of the reactor with a quadrupole mass spectrometer (QMS) is fabricated. For catalytic measurements the catalyst

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can then be deposited on the borosilicate lid or the microreactor itself and the system is subsequently anodically bonded in order to ensure a leak tight seal of the reactor [7]. The small reaction volume together with the limiting capillary flow to the QMS allow for very high time resolutions and high sensitivities. These characteristics enable measurements of the transient activity of thermal catalysts and photocatalysts as well as the study of very low catalyst loadings. In the field of photocatalysis this has led to investigations of oxidation reactions, overall water splitting and fundamental mechanisms in photocatalysis [8–11]. Despite the above mentioned numerous advantages, the traditional design of our microreactors for photocatalysis makes it necessary to seal the reactor with anodic bonding. While it is possible to perform in-situ spectroscopical analysis of the catalyst and open the reactor after reaction for post reaction characterization, the microreactor cannot be re-used after opening the lid [12]. This restriction makes the traditional microreactors single use, i.e. disposables. Additionally, in practice the success-rate of the anodic bonding procedure is around 75%-90%, which further increases the demand in μ -reactors, the use of potentially expensive catalysts, and time. In order to address these challenges, it is desirable to manufacture a microreactor that is reusable and easier to seal but retains the fast time response and high sensitivity of the original design. Inspiration for such a system comes from our microchip interface for electrochemical mass spectrometry [3]. The microchip for this application also consists of a reaction volume that is connected via a capillary to the mass spectrometer. Thereby, the very low detection limit and fast time response are preserved, which enable fundamental investigations in hydrogen and oxygen evolution as well as CO reduction [13–17]. However, the reaction volume is sealed in this case via an o-ring that allows for easy assembly of the reactor and the chip is re-usable for independent measurements. In this article we now report on a μ -reactor for photocatalytic experiments that allows us to adapt the sealing methodology of our electrochemical microchip. Using a parafilm gasket we demonstrate that the reactor can be assembled leak tight which enables us to use the reactor for independent experiments. The reactor geometry allows for testing of thin film samples, dropcasted samples or samples grown on a thin film substrate with front or back illumination depending on the substrate used-overcoming the transparency limitation of borosilicate sealed μ -reactors. We demonstrate the successful operation of the reactor using CO oxidation on TiO₂ as a model reaction and discuss how the microchip is manufactured and calibrated. We would also like to note that our groups recently developed a transparent microreactor based purely on borosilicate [18]. Compared to the recently published version the microreactor demonstrated in this publication offers an even smaller reaction volume and it is compatible with the commercial offering from Spectro Inlets. In the future this will allow for improved comparability of experiments performed in different laboratories and accelerate the development of the field.



Figure 1. Illustration of the fabrication steps for the μ -reactor. (a) Etching of the capillary into a silicon wafer (blue), (b) etching of the gas channels, (c) application of a protective Al₂O₃ etch-stoplayer (pink), (d) etching of the transparent window for the light source, (e) removal of the Al₂O₃ etch-stoplayer and the features in the borosilicate wafer are cut using a CO₂ laser. (f) The two wafers are anodically bonded.

2. Experimental

The μ -reactor chip is made from a standard 100 mm diameter double side polished 350 µm thick silicon wafer and a 100 mm diameter borosilicate glass wafer with a thickness of 500 µm. The two wafers are patterned separately and then fused together with anodic bonding. The features of the silicon wafer are created by three UV lithography steps and subsequent DRIE as shown in figure 1. The pattern is defined in a positive AZ MiR 701 resist (Microchemicals GmbH) using a Heidelberg 150 maskless lithography system (Heidelberg Instruments Mikrotechnik GmbH). First the capillary is defined and etched to a depth of 6 µm using a Pegasus DRIE system (SPTS Technologies Ltd) (a). A new resist mask is applied to define the gas channels, and these are etched to a depth of 150 μ m using the same DRIE tool (b). Prior to the third etching step a 30 nm Al₂O₃ layer is deposited by atomic layer deposition (ALD) in a Picosun R200 system (Picosun Oy), this layer will serve as an etch stop. The Al₂O₃ layer is removed with BHF (buffered hydrofluoric acid) on the unpatterned side (c). The third resist mask defines the large 8 mm diameter opening in the chip and is applied to the unpatterned side. Using the resist as a mask, the wafer is etched in a DRIE process as earlier, using the Al_2O_3 layer as an etch stop (d). Finally the remaining Al₂O₃ is removed with BHF. The borosilicate wafer has 1 mm diameter holes cut through it with a CO_2 laser (Epilog Laser). A 5 min etch in 40% HF is used to removed residue around the holes from the laser process (e). The two wafers are aligned and bonded in an anodic bonding process using a Süss SB6 wafer bonder (Süss MicroTec SE) before it is diced into chips using a DAD 3241 automatic dicing saw (Disco Coorporation) (f).

The photocatalytic measurements are performed with a Hammamatsu UV-LED Spot Light Source LC-L1 with approx. 4 W cm⁻² at $\lambda = 365$ nm. The CO oxidation activity of 1.5 µm thick sputter deposited TiO₂ (anatase phase, deposition temperature 400 °C) was detected on-line with a Pfeiffer Prisma Pro Quadrupol Mass spectrometer.

3. Results and discussion

Figure 2(a) shows an image of our microchip with the gas inlet, gas flow channel, gas outlet, inlet to the reaction volume, outlet to the mass spectrometer, limiting capillary and borosilicate glass window.

The microchip is manufactured with standard cleanroom technologies of UV lithography, DRIE, anodic bonding, molecular vapor deposition and CO₂ laser etching (see experimental section for details). Similar to our previous versions of the μ -chip the heart of the technology is the orifice/limiting capillary (figure 2(a)), which limits the analyte flow to the mass spectrometer to a magnitude where a differential pumping is not necessary. For a reliable operation of the mass spectrometer a pressure at or below the 10^{-5} mbar range is necessary as the signal does not respond linearly with the amount of analyte at higher pressures and if the pressure is raised even more the ionization filament will be damaged. Considering the turbo molecular pump used for this study ($S_{pump} = 50 \text{ 1 s}^{-1}$) the maximum flux of analyte to the mass spectrometer $\dot{n}_v^{\text{desired}}$ can be calculated according to equation (1)

$$\dot{n}_{\rm v}^{\rm desired} = \frac{1}{RT} p_{\rm v}^0 \, S_{\rm pump} \approx 2 \text{ nmol s}^{-1}. \tag{1}$$

where *R* is the ideal gas constant *T* is the temperature p_v^0 is the desired pressure of 10^{-6} mbar and S_{pump} is the pumping speed of the turbo pump (50 l s⁻¹). The usage of the capillary allows us to collect our analytes with almost 100% efficiency since no differential pumping is necessary. This means that every produced molecule will be collected, which results in up to two orders of magnitude higher sensitivity compared to differential pumping [3]. Additionally, the 100% collection efficiency allows us to perform absolute calibration as the integral of the calibrated signal gives directly the amount of products produced at the catalyst surface.

Figure 3 shows pictures of the assembly of the reactor in the modified stainless steel interface block, which is also sold commercially (by Spectro Inlets Aps) [19]. The μ -reactor chip is thereby placed on four O-rings that seal the connection of the reactor to the mass spectrometer as well as the gas supply and exhaust system as also shown in figure 2(b). The interface block has been additionally modified compared to the commercial version in order to host the LED light source to allow for photocatalysis with front side illumination. Alternatively, the catalyst can also be operated in backside illumination as illustrated in figure 2(b). On top of the chip interface a parafilm sealing gasket and the catalyst layer are placed, which are compressed with four screws. If a silicon wafer is used as a catalyst support an additional glassy carbon back plate is introduced in order to dissipate the pressure applied by the screws and avoid breaking of the silicon wafer.

Figure 4(a) shows a schematic illustration of the μ -reactor in operation with front side illumination in an exploded view. The catalyst (shaded yellow) is illuminated from the bottom by a light source through a borosilicate glass window. The reaction atmosphere (CO and O₂) is converted on the catalyst surface to CO₂ (shown as red spheres) and the CO₂ is transported through the outlet of the reaction volume and the limiting capillary to the mass spectrometer (path highlighted in red). The reaction volume is sealed by a parafilm gasket, and the assembly is compressed by a steel ring. The ring geometry also allows, in principle, for illumination from the backside if the catalyst support is transparent to the used illumination source.

Before each experiment the assembly is checked for leak tightness by flowing He into the reactor and monitoring the decay in the air signals (oxygen at m/z = 32 and nitrogen at m/z = 28 in figure 4(b)). Based on our experience from the electrochemical μ -reactor we would the corresponding signals to drop by two orders of magnitude (maximal 1% residual air) in case of a leak tight seal. If leak tightness is ensured, subsequently, the reaction gas mixture can be introduced into the reactor. If necessary, the amount of residual air can be further reduced by placing the reactor into a container filled with inert gas.

3.1. CO oxidation on TiO₂

In order to perform CO oxidation as a model reaction as a proof of concept for the μ -reactor, the reaction volume is filled with a mixture of CO and O2 with excess oxygen compared the stoichiometric ratio and a 1.5 μ m thick TiO₂ thin film on a silicon substrate is used as the catalyst. After the gas mixture has reached equilibrium in the reaction volume, the light source is turned on and the CO oxidation performance is monitored with the QMS at 50%, 70% and 90% of the maximum power of the light source. The illuminated area of 0.5 cm² is defined by the hole in the interface block. Figure 5(a) shows thereby the raw CO_2 signal at m/z = 44, CO at m/z = 28 and O_2 at m/z = 32. With increasing power of the light source, an increase in CO_2 production of approx. 25% (by increasing the power of the light source from 50% to 90%) is observable which demonstrates that our μ -reactor is a functioning reactor for photocatalytic measurements. To facilitate the comparability of measurements, we convert the secondary electron multiplier output signal into a flux of CO_2 (figure 5(b)) by correcting for the m/z = 44 background and dividing the signal by the calibration factor for CO₂ such as described in the next section. We stress that the possibility of performing quantitative measurements



Figure 2. (a) Top view of the μ -reactor interface chip on the wafer with the components labeled (b) side view of the μ -reactor with the components labeled.



Figure 3. Illustration of the assembly process of the μ -reactor (a) the interface chip with the parafilm gasket (spacer) is placed in the metal interface block and rests on 4 O-rings that seal the gas inlet, gas outlet and the channel to the mass spectrometer. (b) The catalyst layer is placed on top of the parafilm gasket. (c) The glassy carbon plate is put on the silicon wafer to protect the silicon wafer from cracking and the metal ring on top of the assembly is tightened. (d) Picture of the assembled μ -reactor.

is one of the big advantages of our developed set-up compared to other instruments.

3.2. Calibration of the μ -reactor

Quantification of mass spectrometry data relies on the determination of a sensitivity factor $(F_M{}^x)$ for each of the analytes of interest *X*, at a given m/z value *M*. $F_M{}^x$ links the molar flux of a species *X* (n^X) to the measured signal of the analyte at the respective m/z ratio (S_M) according to equation (2):

$$S_M = F_M^X \times \dot{n}^X. \tag{2}$$

For the calibration of the mass spectrometer we rely on an external calibration such as described in [11]. For this calibration method a calibration gas (in this case CO₂) is flown through the μ -reactor to the mass spectrometer at a known pressure and the respective m/z values are monitored. Since the calibration is performed right after the measurement also oxygen (m/z = 32) and CO (m/z = 28) are monitored in order to ensure a complete gas exchange in the reactor. It should be noted that m/z = 28 is thereby masked by the CO₂ cracking pattern (figure 6). In order to apply equation (2) for the determination of the calibration factors it is additionally necessary to determine the molar flow of the analyte through the capillary. For the capillary dimensions used in this study an analytical expression for the evaluation of the molecular flow to the mass spectrometer has been derived similar to our previous publications [13, 16],

$$\dot{n}_{\text{calc}} = \frac{\pi}{8} \frac{a^4 \bar{p}}{\eta RT} \frac{\Delta p}{L} \times F(\bar{K}_n)$$
(3)

where $= p_{\text{in}} - p_{\text{out}}$ is the pressure drop along the capillary, $\bar{p} \cong \frac{p_{\text{in}}}{2}$ is the average pressure in the capillary, $a = 3 \, \mu\text{m}$ the radius of the capillary, $L = 1 \, \text{mm}$ is the capillary length, η the viscosity of the gas, R the universal gas constant and T the absolute temperature. The factor $F(\bar{K}_n)$ is a correction for slip-flow and intermediate flow to the purely viscous Poiseuille flow rate; the correction factor depends on the average Knudsen number \bar{K}_n in the capillary. The average Knudsen number ($\bar{K}_n = \lambda/\alpha$ where λ is the mean free path) is defined from the viscosity to relate it to measurable quantities, i.e.

$$\bar{K}_n = \frac{\eta}{a\bar{p}} \sqrt{\frac{\pi RT}{2M}} \tag{4}$$

where M is the molar mass of the gas. The flow correction factor is reminiscent of the original expression given by Knudsen,

$$F(\bar{K}_n) = 1 + \frac{8^2}{3\pi} \bar{K}_n \frac{1 + 2\sqrt{\frac{\pi}{2}} \frac{1}{\bar{K}_n}}{1 + 2.48\sqrt{\frac{\pi}{2}} \frac{1}{\bar{K}_n}}.$$
 (5)



Figure 4. (a) Schematic illustration of the μ -reactor in operation shown as an exploded view. (b) Check for leak tightness of the reactor. The signals relating to air (N₂ at m/z = 28 and O₂ at m/z = 32) drop 2 orders of magnitude, which is the expected leak tightness in line with our electrochemical μ -reactor. He is flown into the reactor to maintain a pressure of 1.5 bar.



Figure 5. (a) Raw signal of the CO oxidation experiment in a CO/O_2 atmosphere with excess O_2 at a reactor pressure of 1.1 bar. The light source (365 nm, 4 W cm² with an illumination area of 0.5 cm²) is operated at 50%, 70% and 90% power. The illumination periods are indicated with arrows. (b) Calibrated CO_2 flux from figure 4(a). The illumination periods are indicated with arrows.



Figure 6. CO_2 calibration measurement. CO_2 is flown through the reactor to maintain a pressure of 1.1 bar until the signals equilibrate.

At 25 °C, $p_{in} = 1.1$ bar and $p_{out} \approx 0$ the calculated molar flow rate of CO₂ in the capillary is 5.9(8) nmol s⁻¹ (the parenthesis around the last digit indicates the limited accuracy), which in equation (3) results in a SEM calibration factor of 10.(3) nmol s⁻¹ A⁻¹. At these flow conditions the average Knudsen number is 0.027 for CO₂, which results in a flow correction factor $F(\bar{K}_n) = 1.15$, thus we see that correction is necessary for accuracy.

As an alternative to evaluating the capillary flow of the chip mathematically, we developed a methodology, inspired by John Yates, to evaluate the capillary flow experimentally with a Capacitance Manometer (MKS 220d, 1 mbar pressure, measurement 4–20 mA) [20]. The experimental setup is shown schematically in figure 7 and consists of the microreactor, valves, a known volume and the capacitance manometer.

For a flow calibration measurement, the volume connecting the microreactor and the capacitance manometer is evacuated using a turbo pump, and afterwards the known volume (26 ml) is closed with valve 3. The calibration gas is flown through the microreactor at a defined pressure and the connection to the turbopump is closed (valve 1). The flow of the calibration gas through the microreactor leads to a pressure increase in the volume connecting the chip and the Capacitance Manometer, which is monitored by the Capacitance Manometer. Since this



Figure 7. Schematic illustration of the capillary flow calibration set-up.



Figure 8. Measurement of the capillary flow of CO_2 via measuring the pressure increase over time in the unknown volume V_0 (red line is the linear fit of the pressure increase) and the pressure increase over time in the unknown volume V_0 + the known volume (26 ml) V_{ref} (green line is the fit of the pressure increase).

volume is not well defined, the set-up is additionally connected to a known volume. When the pressure increases to approx. 0.4 mbar valve 3 is opened and the pressure drops due to the volume expansion. Subsequently the pressure increase is monitored again by the Capacitance Manometer as shown in figure 8.

The above stated experimental procedure allows us to calculate the molar flow rate as following: the pressure rate is measured when the microreactor molar flow rate \dot{n}_{exp} is collected in an unknown, evacuated volume V_0 (pressure rate \dot{p}_1) and with a known evacuated volume V_{ref} (pressure rate \dot{p}_2). The ideal gas law yields:

$$\dot{p}_1 V_0 = \dot{n}_{\rm exp} R T \tag{6}$$

$$\dot{p}_2\left(V_0 + V_{\text{ref}}\right) = \dot{n}_{\text{exp}}RT.$$
(7)

Table 1. Summary of mathematically calculated and experimentally determined capillary flows for CO_2 , CO and O_2 at 1.2 bar.

Gas	Mathematical \dot{n}_{calc} in nmol s ⁻¹	Experimental \dot{n}_{exp} in nmol s ⁻¹
CO ₂	7.0(4)	6.8(3)
CO	6.2(4)	6.2(7)
O ₂	5.4(6)	5.2(9)

Elimination the unknown volume V_0 results in the experimental molar flow rate:

$$\dot{n}_{\rm exp} = \frac{V_{\rm ref}}{RT} \frac{\dot{p}_1 \dot{p}_2}{\dot{p}_1 - \dot{p}_2}.$$
 (8)

Based on these calculations a capillary flow of 6.8(3) nmol s^{-1} for CO₂ has been determined for a measurement performed at 1.2 bar, which is in good agreement with our calculations based on the above described formulas (equations (3)-(5)), which result in a flow rate of 7.0(4) nmol s^{-1} for CO₂ at 1.2 bar pressure. To demonstrate the general applicability of our methodology we performed additional measurements with CO and O2 and compared the obtained results to the values obtained from solving equation (2) and the results are summarized in table 1. The viscosities of CO2, O2 and CO at 25 °C were estimated using a Sutherland's law fit to data from CRC Handbook of Physics and Chemistry online resulting in $\eta_{CO2} = 14.9(0) \ \mu$ Pa s, $\eta_{O2} = 20.6(4) \ \mu$ Pa s, and $\eta_{CO} = 17.7(9) \ \mu$ Pa s, respectively. The parenthesis around the last digit is indicative of the limited accuracy of this approach [21]. The calculations result in average Knudsen numbers of 0.025, 0.040, and 0.037 for CO₂, O₂ and CO, respectively, and correction factors $F(\bar{K}_n)$ of 1.14, 1.22, and 1.20, respectively. We find a remarkable agreement between corresponding values of the experimentally determined and mathematically calculated capillary flow; see table 1. The difference is at most 3%!

3.3. Modeling of the μ -reactor

In order to obtain insights on the mass transport properties and residence time distributions of analytes, we build a mathematical model of our reactor. For the theoretical model we rely on the assumptions of a continuously stirred tank reactor since the diffusion length of the molecules per second is comparable to the dimensions of our reactor and shorter than the residence time. This allows us to calculate a residence time of the analyte in our reactor based on the volume (equation (9)) of the reactor and the volume flow through the capillary (equation (10)),

$$V_{\text{reactor}} = d_{\text{working}} r^2 \pi \tag{9}$$

$$\tau = \frac{V_{\text{reactor}}}{v_{\text{cap}}}.$$
 (10)



Figure 9. Impulse response of CO₂ at 90% power of the light source for 5 s. Fit of the data with the stated decay function and determined residence time τ from the fit. The arrow indicates when the light source is switched off.

Thereby, V_{reactor} is the volume of the reactor d_{working} is the distance between the catalyst surface and the chip (height of the reaction volume), *r* is the radius of the reaction volume, τ is the residence time of an analyte in the reaction volume and v_{cap} is the volume flow of an analyte through the capillary, converted from the capillary flow via the ideal gas law. To measure the mass transport properties and residence time distribution of our system, we perform an impulse response measurement at 90% power of the light source for 5 s similar to our previous study (figure 9) [15]. Subsequently, the decay of the impulse response (*t*) is fitted with an exponential function (the expected system impulse response function):

$$h(t) = \frac{1}{\tau} e^{\frac{-t}{\tau}}.$$
 (11)

Based on equations (9) and (10) the working volume and respectively also the working distance (based on a reactor radius of 0.6 cm which is defined by the spacer) can be obtained. This allows for a calibration of the reactor volume after each reaction. The reactor volume has thereby been determined to be 2.6 µl which results in a reactor height of 23 µm. Remarkably, the reactor volume is thereby only one order of magnitude higher compared to the anodically bonded version of our μ -reactor. Therefore, the fast mass transport properties of μ -reactors anodically bonded lids is preserved in our current design. Combined with the ease of changing catalysts quickly, which allows for rapid testing of different catalysts in independent experiments on the same chip, our reactor design can facilitate the discovery of new photo catalysts through high throughput screening studies. Additionally, we believe that the same reactor design can also be used for thermal catalysis measurements with an IR-laser heating through the borosilicate glass window. For such measurements the parafilm gasket should be replaced with a more temperature resistant gasket.

4. Conclusions

In this work we present a Si based μ -reactor for photocatalytic measurements, which is fabricated with standard microfabrication techniques in the cleanroom. The reactor volume is enclosed by the microfabricated interface chip, a parafilm gasket and the catalyst layer. We demonstrate that the reactor is leak-tight (1% residual air) in this configuration and perform CO oxidation over TiO₂ with front side illumination with a 365 nm light source as a proof of concept. The 100% collection efficiency of the reactor additionally allows for quantitative measurements by external calibration with a calibration gas, which is demonstrated on the basis of the CO oxidation experiment. Additionally, we provide an experimental method for determining the capillary flow through the μ -reactor based on a capacitance manometer measurement. Finally, we perform an impulse response to determine the mass transport characteristics of our reactor and calibrate the reaction volume and working distance. Our measurements show that our presented set-up has a very fast time resolution, allowing for dynamic reactivity studies. Additionally, the catalyst is rapidly exchangeable, which will aid in the discovery of new photocatalysts through rapid screening studies. The measurements can thereby be performed in front and backside illumination geometry which further stresses the versatility of the presented set-up.

Data availability statement

The data cannot be made publicly available upon publication because the cost of preparing, depositing and hosting the data would be prohibitive within the terms of this research project. The data that support the findings of this study are available upon reasonable request from the authors.

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Conflict of interest

The authors declare no conflict of interest.

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