Investigation of the reaction kinetics of photocatalytic pollutant degradation under defined conditions with inkjet-printed TiO$_2$ films – from batch to a novel continuous-flow microreactor

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S1. Investigation on the influence of pH value on the ink stability

In order to obtain a stable ink, the influence of pH value on the particle size and zeta potential of the inks was studied. To ensure a reproducible printability of the ink and the formation of homogeneous catalyst layers, 3 criteria have to be fulfilled: 1) the particle size must be lower than 1/100 of the nozzle diameter; 2) the ink suspension should have enough stability to prevent quick agglomeration and sedimentation; 3) rheology (e.g., viscosity) of the suspension should meet the requirements of the printer. In this work, the used nozzle had a diameter of 100 μm. Thus, the particle size was required to be smaller than 1 μm. It has to be noted that the particle size measurement must take particle agglomeration into account, which can be done by using DLS. To determine the suspension stability, zeta potential is usually employed. Generally, zeta potentials higher than 30 mV or less than −30 mV represent a good suspension stability, and the particles tend to repel each other and, thus, agglomeration can be prevented. The influence of the pH value on the particle size and the zeta potential was studied. As shown in Fig. S 1, higher pH value results in a drastic decrease of the mean particle size and the zeta potential. When the pH value is in the range of 8 to 10, the ink shows the smallest particle size and sufficient stability. Therefore, in this work, the optimized pH value was set to 10 (± 0.3).
S2. Inkjet-printing procedure

The printer was equipped with a piezoelectric dispenser head (MD-K-140) composed of an ink reservoir (5 ml) and a nozzle (100 µm diameter). The ink droplet was generated by an impulse induced by the piezoelectric transducer inside the dispenser head. The impulse had a specific voltage and impulse length to be tuned for droplet formation. For all the printing runs, a double-impulse mode was chosen, i.e., a positive and negative voltage were applied sequentially to improve stable droplet generation. The droplet formation, droplet size and directional stability were examined using images captured from the CCD cameras attached to the printing system.

The ceramic substrate was mounted on a computer-controlled platform and the dispensing head was programmed to move with a velocity of 19 mm/s. The droplet counts as well as the distance between two droplets in both vertical and horizontal directions can be set in the operating software program. A layer-by-layer printing was used throughout this work.

Fig. S2 Inkjet-printer used in this work.
S3. Illustration of the droplet formation and two model substrates

Fig. S3 (a) Illustration of droplet generated from the nozzle at different time interval from the pulse start and printed substrate in 2 sizes: (b) 2.5 cm × 2.5 cm and (c) 10.8 cm × 0.8 cm with 2 semicircle ends, and the rectangular printed area is 0.6 cm × 10 cm.
S4. Influence of the calcination temperature

As shown in Fig. S 4, samples calcined at 250 °C present the fastest degradation. No significant degradation due to photolysis was observed in the blank test using glass without coating. In contrast, the blank ceramic substrate shows some degradation, which indicates that the substrate surface also has some catalytic activity. This is not surprising since the surface of the ceramic substrate contains TiO\textsubscript{2} (composed of the active phase anatase, which was detected and discussed elsewhere\textsuperscript{3}) as indicated by the manufacturer. According to the TGA results (Supporting Information S5), the weight loss of the dried ink increased from 92.6% to 97.9% by increasing the calcination temperature from 150 °C to 250 °C. This can explain the enhanced degradation by increasing the calcination temperature to 250 °C, since more organic solvent can be removed (can even be observed in SEM, see Supporting Information S6). Further increasing the temperature to 300 °C did not result in a higher reactivity since the onset of particle sintering is another influencing factor which could, e.g., reduce the internal surface area of the coating. Thus, 250 °C was selected as the standard calcination temperature for further experiments in this work.

![Graph showing degradation of RhB by printed TiO\textsubscript{2} photocatalysts with 3 layers calcined at different temperatures.](image)

Fig. S 4 Degradation of RhB by printed TiO\textsubscript{2} photocatalysts with 3 layers calcined at different temperatures (symbols: mean values of n≥3 replicates; error bars: standard error of the mean).
S5. TGA result for the developed TiO$_2$ ink

![TGA result for the developed TiO$_2$ ink](image)

Fig. S5 TGA result for the developed TiO$_2$ ink

Thermogravimetric analysis (TGA, Setsys Evolution 16/18, Setaram) was conducted for the developed ink in order to investigate the removal of the inks’ additives upon calcination.
S6. SEM images of the TiO$_2$ coating before and after calcination

Fig. S6 SEM images of the TiO$_2$ printed layer (a) before and (b) after calcination at 250 °C
S7. Measuring the thickness of the coating using 3D optical profiler

Fig. S7 Illustration of the measurement of the coated layer thickness by 3D optical profiler: (a) 2D overview of the substrate and 9-layer coating, with the selected area used for thickness determination; (b) profile of the Z-value along the X axis, with Z-value being the mean along the Y axis in the selected area.

The 3D optical profiler scanned the sample in confocal mode. In the 2D overview, a rectangular area covering both catalyst coating and uncoated substrate was selected, as shown in Fig. S7 (a). The optical profiler can automatically generate the Z-value profile along the X axis from the selected area (Fig. S7 (b)). The Z-value is the mean from the Y direction of the selected area. By selecting two certain areas representing the coating and uncoated substrate in the Z-profile graph, the profiler can read the difference of the mean value originating from both areas, which is the average thickness. The same procedure was applied to 3 individually prepared samples to obtain the mean thickness.

This method allows to measure the mean thickness of the coating in a certain area, which is advantageous when the coating surface is rough.
S8. Illustration of the layer transmission measurement

To measure the transmission of the TiO$_2$ coating of different layer numbers, UV-Vis spectrometer was used to obtain the data at 365 nm wavelength, which equals the wavelength used for the degradation test described in the main manuscript. The sample was prepared by printing the TiO$_2$ layer on quartz glass of 0.5 cm $\times$ 2 cm in size. During the measurement the sample was immersed into the model pollutant (RhB) solution (15 mg/L) contained in a quartz glass cuvette. The reason for not directly measuring the sample in air is that the actual environment in the degradation experiment is RhB aqueous solution. If the sample would be measured in air, the phase boundary (solid-liquid compared to solid-gas) is different, which can affect the light transmission as well as the absorbance because of the difference in reflective index. To prove this hypothesis, a comparative study was performed by measuring the transmission of the printed samples of 7 and 9 layers first in air and then in deionized water, respectively (Fig. S8). The transmission is normalized to the value obtained from the sample without any coating (transmission 100%). The result shows that if the measurement was done with the sample immersed in water, the transmission is higher, which means that more light can penetrate through the printed layers in water.

| Table S1 Results of the transmission at 365 nm of the samples in 7 layers and 9 layers |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | 7 layers | 9 layers | 7 layers | 9 layers |
| | Sample 1 | Sample 2 | Sample 3 | Sample 1 | Sample 2 | Sample 3 | Average |
| Transmission in water (%)     |     |     |     |     |     |     |     |
| 2.77                          | 2.98 | 3.61 | 3.12 | 0.91 | 1.63 | 1.07 | 1.2 |
| Transmission in air (%)        |     |     |     |     |     |     |     |
| 1.72                          | 1.63 | 2.31 | 1.88 | 0.67 | 1.19 | 0.95 | 0.94 |

Supporting Information

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Fig. S8 Illustration of the transmission measurement in two cases

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S9. Illustration of the continuous-flow microreactor (side view)
S10. Optical part of the reactor

![Optical part of the reactor: (a) overview of the optical part; (b) optical fiber with one light inlet leg and three light outlet legs.](image)

Fig. S 10 Optical part of the reactor: (a) overview of the optical part; (b) optical fiber with one light inlet leg and three light outlet legs.
S11. Experimental setup of the continuous-flow microreactor system

Fig. S11 Experimental setup of the continuous-flow microreactor for degradation of pollutant.
S12. Microreactor in operation

Fig. S12 Microreactor in operation: (a) overview; (b) view from the top without the optical part.
S13. XPS analysis for the inkjet-printed TiO$_2$ coating

![XPS survey graph](image)

Fig. S 13 XPS survey for the inkjet-printed TiO$_2$ thin film on a metal substrate (in order to conduct the XPS analysis)

It can be seen that sodium is present in the coating according to the XPS survey result. Binding energy of P$_{2p}$ is indicated in the graph. However, no distinguishable peak for phosphorus can be detected in that region.
S14. Ellipse plot illustrating the correlation between the determined kinetic parameters

Fig. S14 Ellipse plot illustrating the correlation between the determined kinetic parameters $a$, $b$ and $K_L$ (unit not shown)
S15. Calculation of mass transfer coefficient for the microreactor experiment

$\beta_m$ is the mass transfer coefficient (m s$^{-1}$), which can be calculated according to empirical correlations using the Sherwood number $Sh$, Reynolds number $Re$ and Schmidt number $Sc$. For the experimental parameters used in this work, $Re$ is in the typical regime for microreactors (1.25 for flow rate of 0.2 ml min$^{-1}$, laminar flow). Accordingly, correlations for laminar flow were taken from literature to determine $Sh^4$:

$$Sh = 7.54 \left( 1 + 0.095 \cdot \frac{d_h}{l_{MR}} Re Sc \right)^{0.45} \quad (S1)$$

The three non-dimensional parameters $Sh$, $Re$ and $Sc$ are defined as:

$$Sh = \frac{\beta_m d_h}{D_{RhB}} \quad (S2)$$

$$Re = \frac{\bar{u} d_h}{v} = \frac{v d_h}{v A_r} \quad (S3)$$

$$Sc = \frac{v}{D_{RhB}} \quad (S4)$$

Based on the equations (S1-S4), and the data given in Table S 2, the mass transfer coefficient can be calculated. For flow rate of 0.05, 0.1 and 0.2 ml min$^{-1}$, $\beta_m$ is calculated to be 6.61E-6, 7.40E-6, 8.72E-6 m s$^{-1}$, respectively.

<table>
<thead>
<tr>
<th>Table S 2 Parameter used for calculate the $\beta_m$</th>
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</thead>
<tbody>
<tr>
<td><strong>Density of water $\rho$</strong></td>
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<tr>
<td><strong>Viscosity of water $\mu$</strong></td>
</tr>
<tr>
<td><strong>Volumetric flow rate $\dot{V}$</strong></td>
</tr>
<tr>
<td><strong>Cross-sectional area of the channel $A_r$</strong></td>
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<tr>
<td><strong>Microchannel height $H$</strong></td>
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<tr>
<td><strong>Perimeter of the channel $P_c$</strong></td>
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<tr>
<td><strong>Hydrodynamic diameter $d_h=4A/P_c$</strong></td>
</tr>
</tbody>
</table>
Reference


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