Supporting Information

Stabilization of TiO_2-based Photocatalytic Coating on Polymer Substrates with Complex Geometry Using Laser Annealing

Hong T. Duong, Bastien O. Burek, Jonathan Z. Bloh

DECHEMA-Forschungsinstitut, Theodor-Heuss- Allee 25, 60486 Frankfurt am Main, Germany, jonathan.bloh@dechema.de

1. Wireless Light Emitter

The reactions took place in a cylindrical double-jacketed reactor with a volume of 100 mL, a diameter of 56 mm and a height of 105 mm. Wireless light emitters (WLE) consisting of a ferrite core coil (WE-PD2 4532 10 µH from Würth), an 82 nF capacitor and a UV LED (365 nm) were used for internal illumination. These components were connected in parallel and integrated in a cylindrical hollow body made of cyclic olefin polymer with a diameter of 10 mm and coated with SiO_2. The reactor was surrounded by three copper wire coils connected in series and mounted on a PMMA tube (diameter 75 mm, height 105 mm). These coils were connected to a capacitor to create a series resonant circuit with the appropriate resonant frequency. The reaction mixture was continuously mixed using a PEEK stirrer equipped with a 4-blade PTFE impeller.

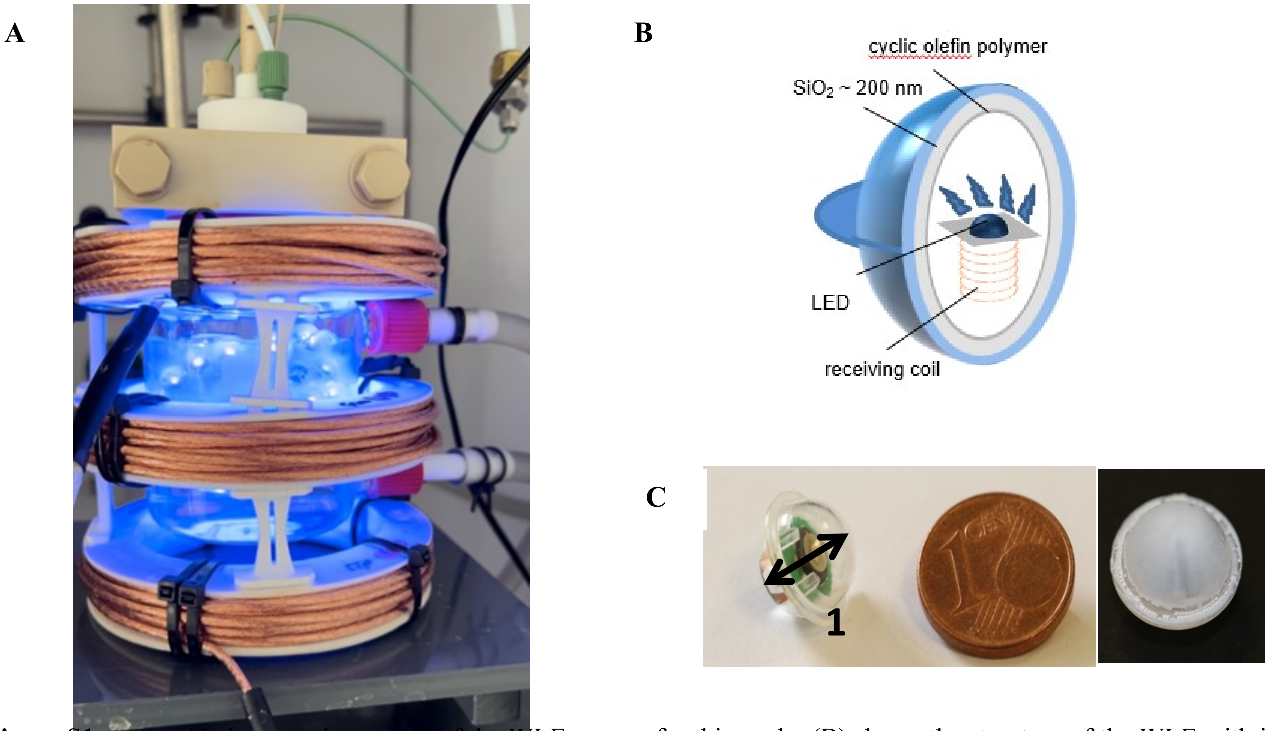


Figure S1.: (A) shows s photograph of the WLE reactor for this study. (B) shows the structure of the WLE with its components. (C) shows the size of a WLE sphere and a WLE sphere coated with TIO_2.

2. Laser-annealed WLE spheres

As described in the paper, the coated COP plates were annealed with the laser (Epilog Zing 24, 30 W CO_2 laser).

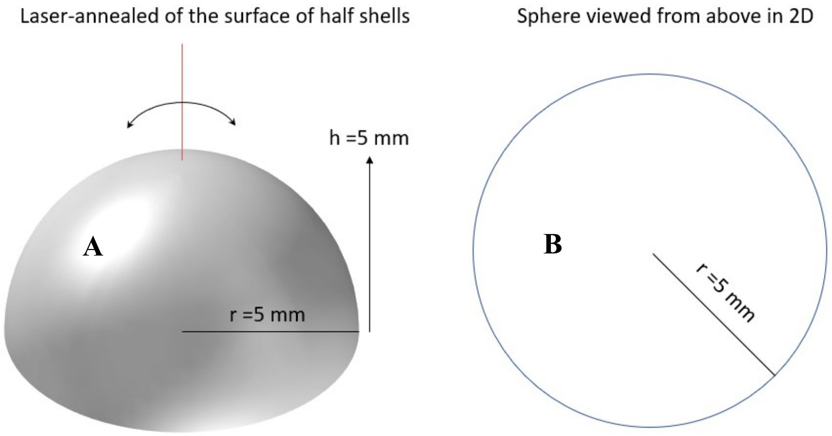


Figure S2.: Illustration of the WLE envelope in 3D (A) and 2D (B).

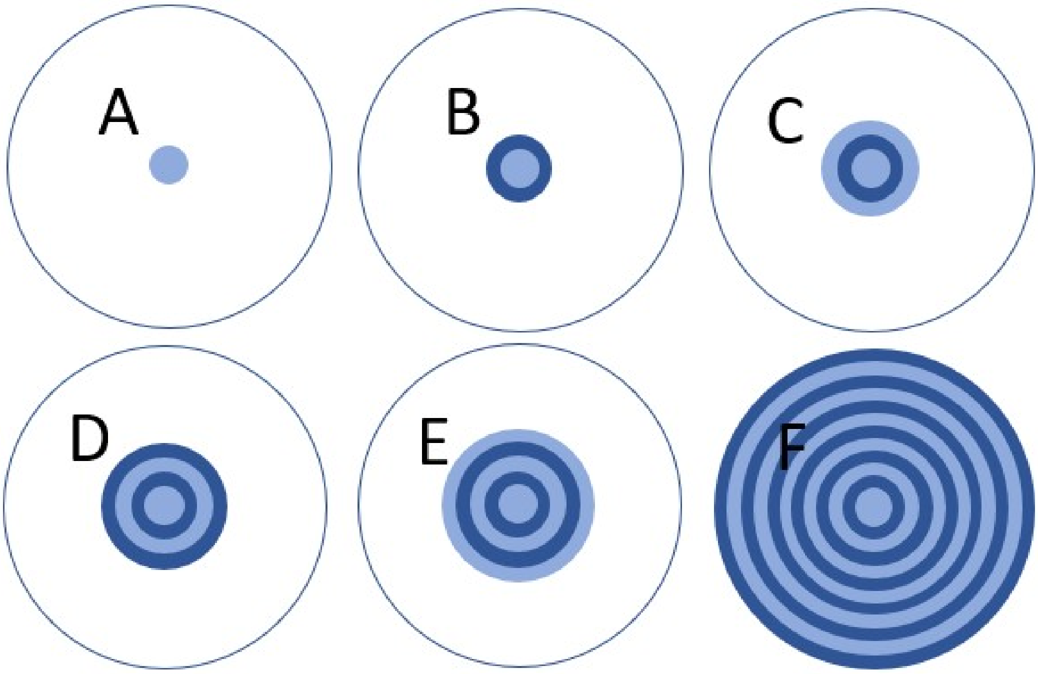


Figure S3.: Schematic representation of the laser annealed WLE sphere (2D view). (A) One line was scanned. (B) Two lines were scanned. (C) Three lines were scanned. (D) Four lines were scanned. (E) Five lines were scanned. (F) A total of twelve rings were needed to completely laser-annealed the entire sample.

3. Investigation of the dispersion methods

Various dispersion methods for the dispersion of photocatalyst P25 were investigated, including the ball mill, Ultrasonic bath, Ultra turrax and Ultra finger. A TiO2 paste was produced for the first tests (2g L^{-1} TiO_2 (P25) in 1mL 2M HCl (Hydrochloric acid), 19mL EtOH (Ethanol) und 85µL Tetrabutylorthotitanate - 60°C/12h/lab air). The paste was then dispersed using the dispersion methods listed. The photocatalyst was then dip coated ($v = 60$ mm s^{-1}) onto a cop plate.

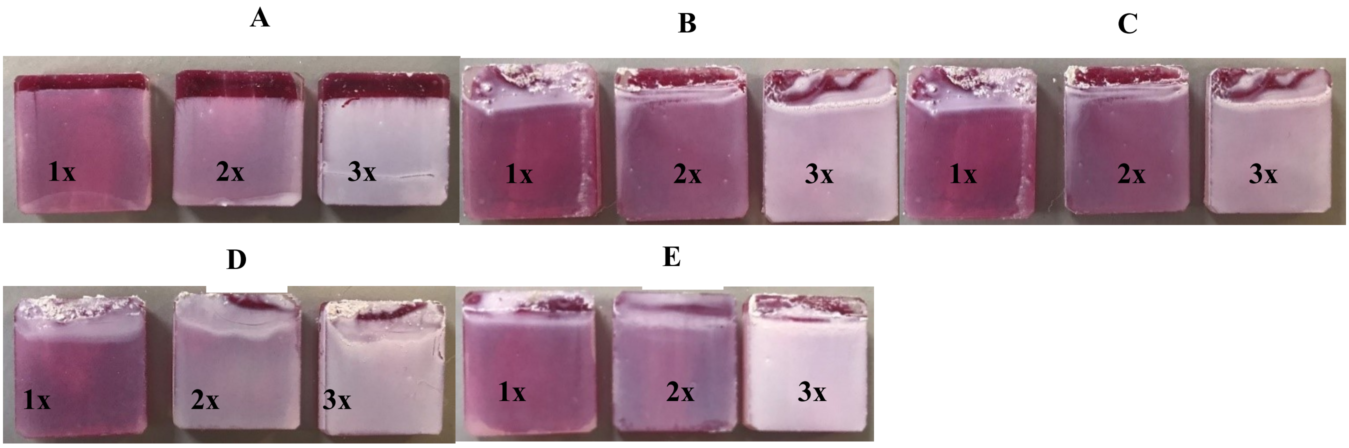


Figure S4.: Coated COP plates with TiO_2 (2g L^{-1} TiO_2 (P25) in 1mL 2M HCl, 19mL EtOH und 85µL Tetrabutylorthotitanate - 60°C/12h/lab air) as photocatalyst. **A:** TiO_2 paste was not dispersed. **B:** ball mill: dispersion for 4 hours at 400 rpm. **C:** Ultrasonic bath: dispersion for 50 min. **D:** Ultra finger: dispersion for 30 min and **E:** Ultra turrax: dispersion for 30 min. The samples were coated once to three times.

The decolorization of methylene blue in the test reactor was examined for all samples.

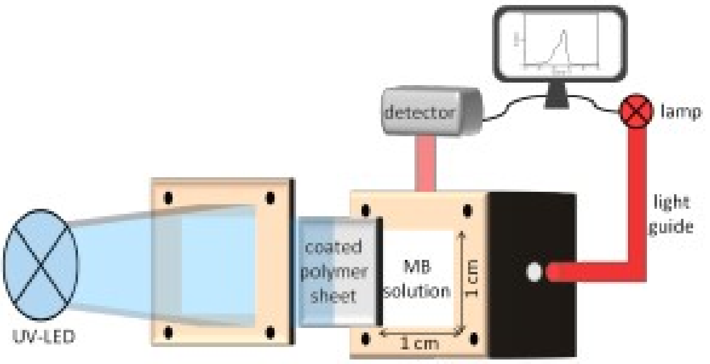


Figure S5.: Test reactor for the decolorization of methylene blue and the reduction of nitrobenzene. The COP platelets, previously coated on one side, are clamped in the illumination window (1 cm x 1 cm). The polymer platelet (1,5 cm x 1,5 cm) is illuminated from the back side by LED (LEDMOD 365.1050.V2, Omicron). During the decolorization of methylene blue, the optical density could be recorded in situ using a red LED lamp (M660L4, THORLABS).

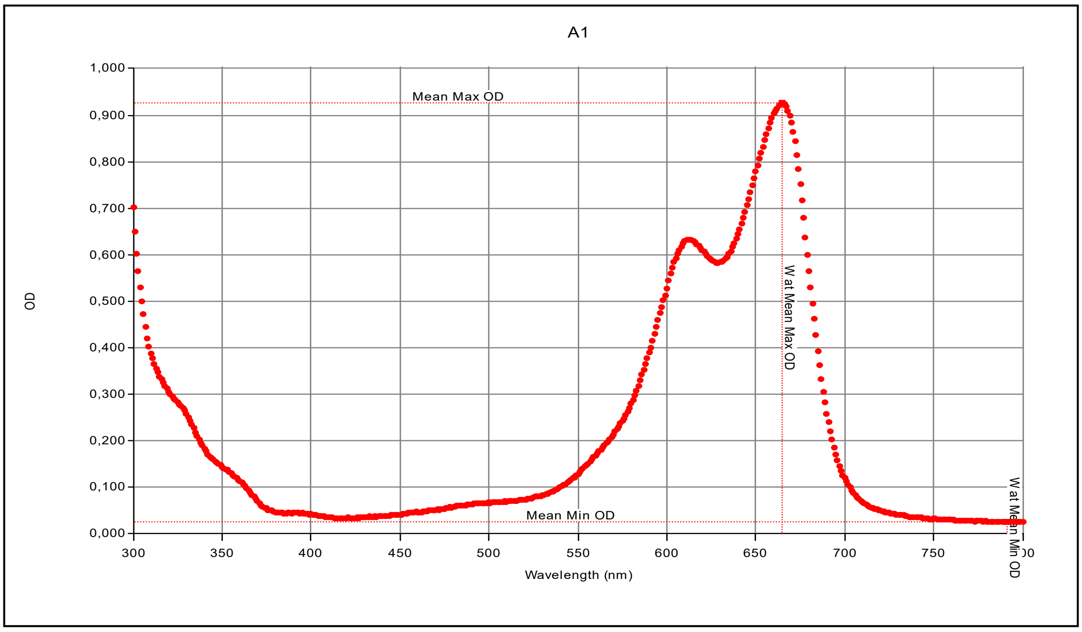


Figure S6.: Absorption spectrum of methylene blue. Absorption maximum at λ=633 nm.

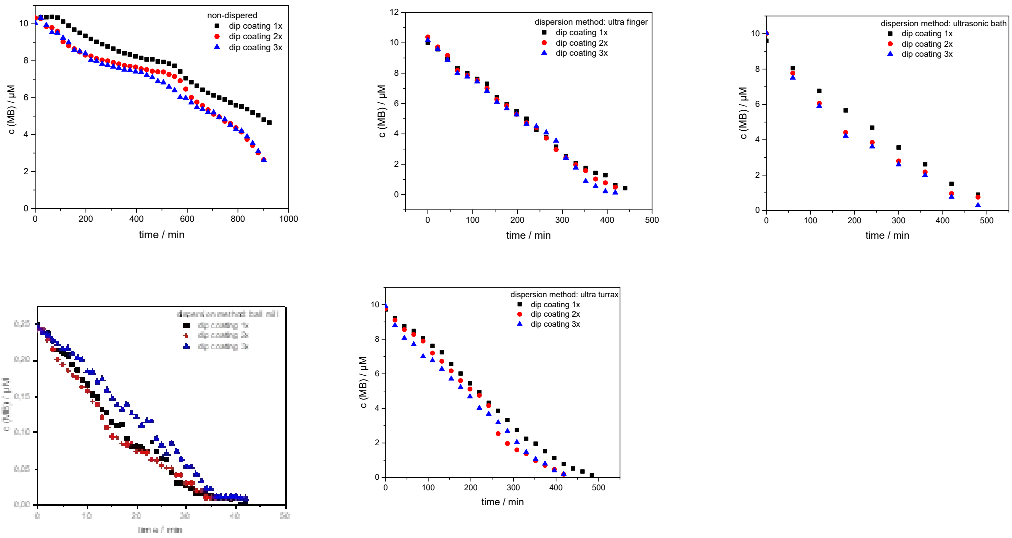
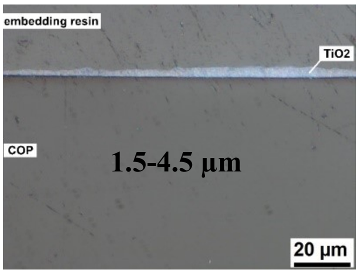
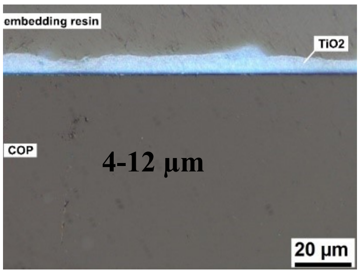


Figure S7.: Concentration-time curves for the decolorization of methylene blue. The photocatalyst was dispersed using different dispersion methods and then dip-coated onto a COP plate. The samples shown here were coated once.

For the coated COP samples, which were treated with various dispersion methods, a cross-section was prepared and the coating thickness analyzed.





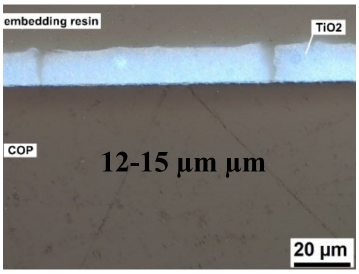


Figure S8.: Cross-section of a C 25 (2 t dispersed. Left picture: coated once, middle pict oated

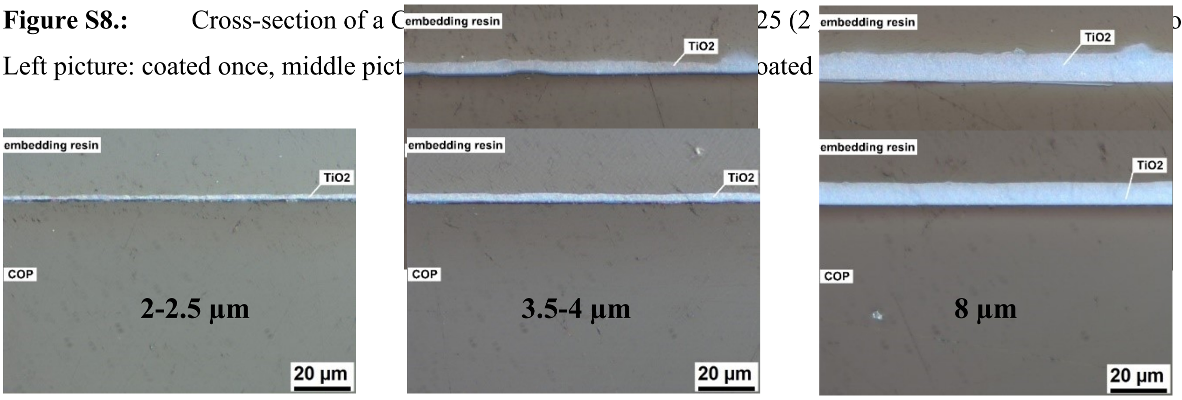


Figure S9.: Cross-section of a COP plate coated with SiO_2 and P25 (2 g L^{-1} TiO_2). The P25 paste was dispersed by ball milling for 4 h at 400 rpm. Left picture: coated once, middle picture: coated twice, right picture: coated thrice.

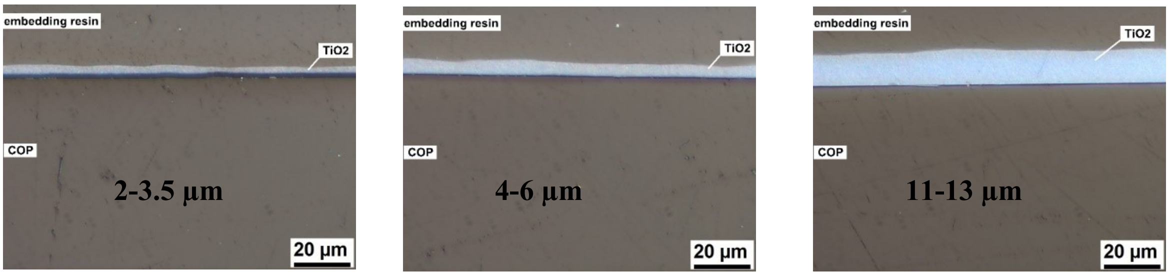


Figure S10.: Cross-section of a COP plate coated with SiO_2 and P25 (2 g L^{-1} TiO_2). The P25 paste was dispersed by ultrasonic bath. Left picture: coated once, middle picture: coated twice, right picture: coated thrice.

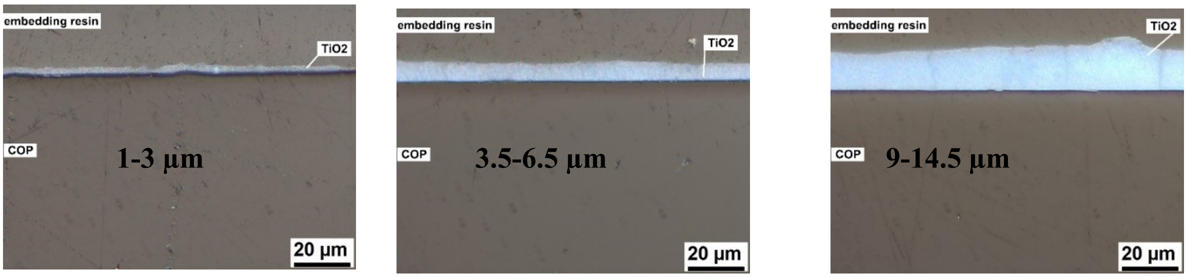
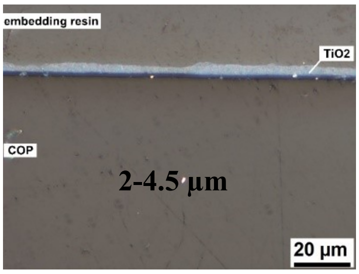


Figure S11.: Cross-section of a COP plate coated with SiO_2 and P25 (2 g L^{-1} TiO_2). The P25 paste was dispersed by ultrasonic finger. Left picture: coated once, middle picture: coated twice, right picture: coated thrice.



6.5-8 µm

12.5-19 µm

Figure S12.: Cross-section of a COP plate coated with SiO_2 and P25 (2 g L^{-1} TiO_2). The P25 paste was dispersed by ultraturrax. Left picture: coated once, middle picture: coated twice, right picture: coated thrice.

It can be clearly seen that the ball mill is the best dispersion method for producing the TiO_2 photocatalyst. As a result, the ball mill was selected as the dispersion method for the further optimization steps of the coating method.

4. Drawing speed for dip coating

In the next step, the drawing speed for the dip coating was investigated. The drawing speed during dip coating influences the coating quality and the reaction kinetics, particularly with regard to the degradation of methylene blue. A drawing speed of 60 mm/min probably offers the optimum balance between coating thickness, coating quality and reaction dynamics. If the drawing speed is too low (30 or 40 mm/min), the coating will be thicker and may be uneven. A thicker coating can hinder the access of reactants or light to the catalysts, which can affect the degradation process. As shown in the experiment, the degradation of methylene blue was actually slower at lower drawing speeds than 60 mm/min. Higher speeds lead to thinner, less homogeneous layers. This theory is also confirmed by the experiment: if the drawing speed is increased above 60 mm/min, the degradation of methylene blue slows down.

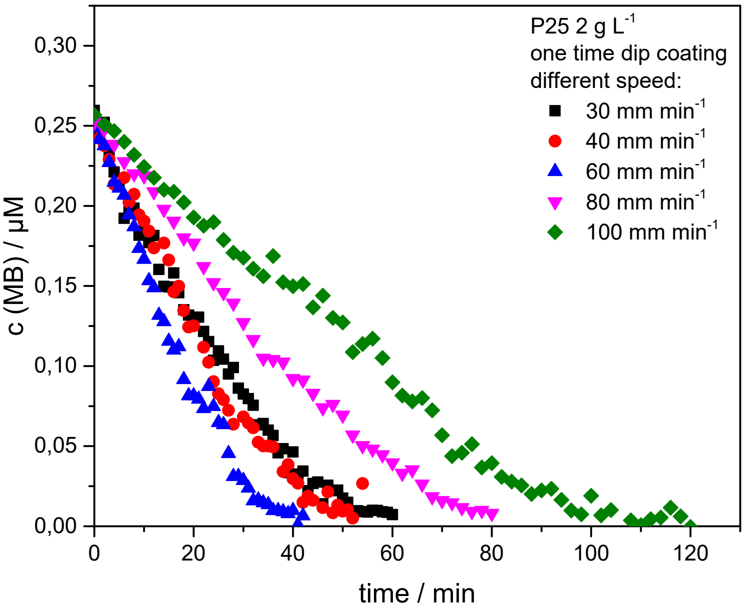


Figure S13.: Concentration-time curves for the decolorization of methylene blue. The photocatalyst was dispersed ball milling for 4 h at 400 rpm and then dip-coated onto a SiO_2 COP plate. investigation of the different drawing speeds for dip coating

5. Investigation of different dispersion times for dispersion with the ball mill

In the next step, the dispersion time was investigated. A dispersion time of 4 hours, 6 hours and 8 hours was selected.

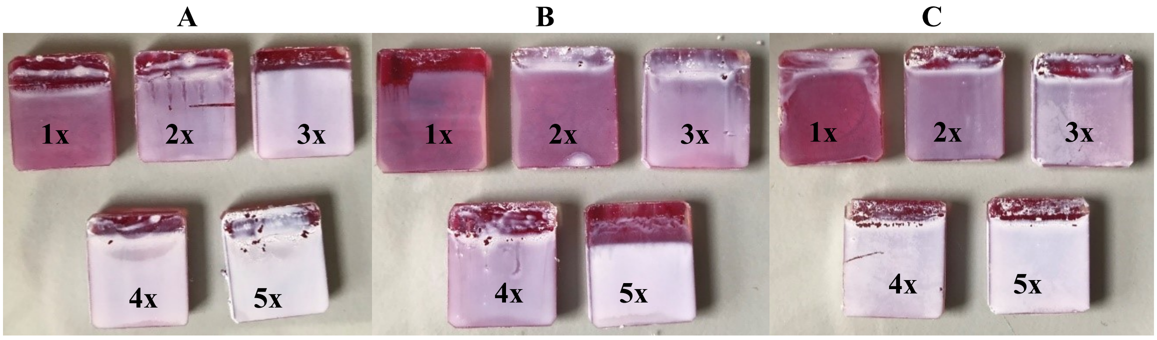


Figure S14.: SiO_2 Coated COP plates with TiO_2 (2 g L^{-1} TiO_2 (P25) in 1 mL 2M HCl, 19mL EtOH und 85 µL Tetrabutylorthotitanate - 60°C/12h/lab air) as photocatalyst. The P25 paste was dispersed by ball milling for A: 4 h, B: 6 h and C: 8 h at 400 rpm. The samples were coated once to five times.

The results of the decolorization of methylene blue are shown below. The TiO_2 paste was produced at different dispersion times.

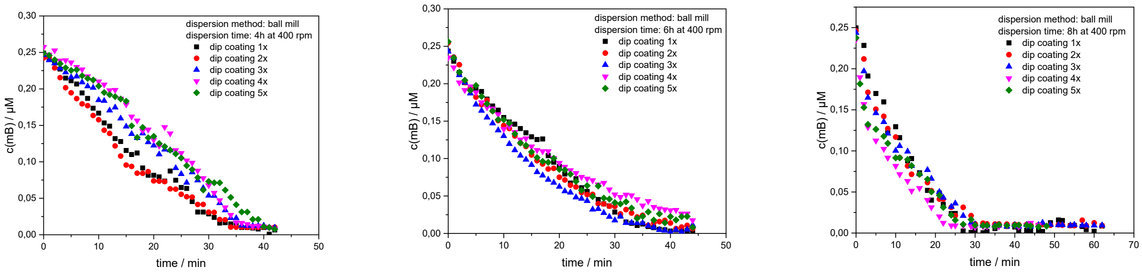


Figure S15.: Concentration-time curves for the decolorization of methylene blue. The photocatalyst was dispersed ball milling for 4 h, 6 h and 8 h at 400 rpm and then dip-coated onto a SiO_2 COP plate. The samples were coated once to five times.

A cross-section was also prepared for these samples in order to determine the layer thickness.

- 4h, 400 rpm, 2g L^{-1} TiO_2 as photocatalyst

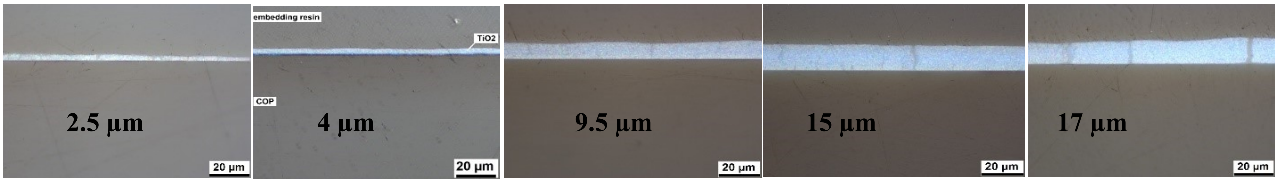


Figure S16.: Cross-section of a COP plate coated with SiO_2 and P25 (2 g L^{-1} TiO_2). The photocatalyst was dispersed ball milling for 4 hours at 400 rpm and then dip-coated onto a COP plate. The samples were coated once to five times.

- 6h, 400 rpm, 2g L^{-1} TiO_2 as photocatalyst

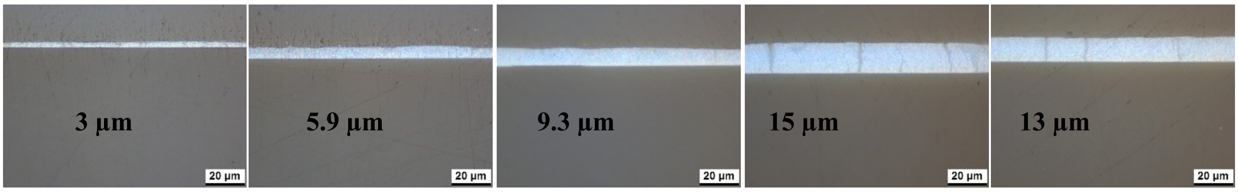


Figure S17.: Cross-section of a COP plate coated with SiO_2 and P25 (2 g L^{-1} TiO_2). The photocatalyst was dispersed ball milling for 6 hours at 400 rpm and then dip-coated onto a COP plate. The samples were coated once to five times.

- 8h, 400 rpm, 2g L^{-1} TiO_2 as photocatalyst

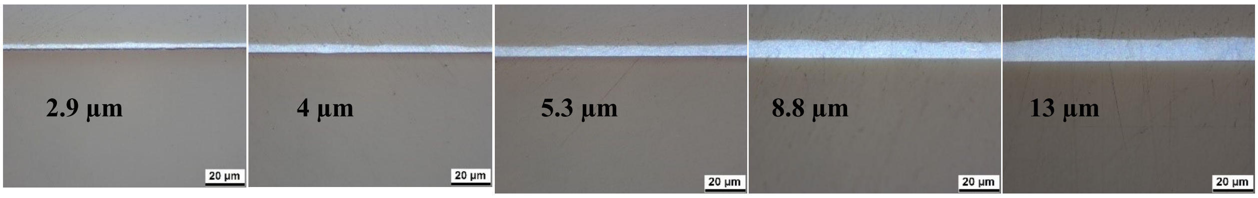


Figure S18.: **Figure S15:** Cross-section of a COP plate coated with SiO_2 and P25 (2 g L^{-1} TiO_2). The photocatalyst was dispersed ball milling for 8 hours at 400 rpm and then dip-coated onto a COP plate. The samples were coated once to five times.

6. Investigation of the different TiO2 concentrations

Next, different concentrations (1 g L^{-1} to 2.5 g L^{-1}) of the TiO_2 photocatalyst were prepared. The TiO_2 paste was tested in the ball mill for 4 hours at 400 rpm.

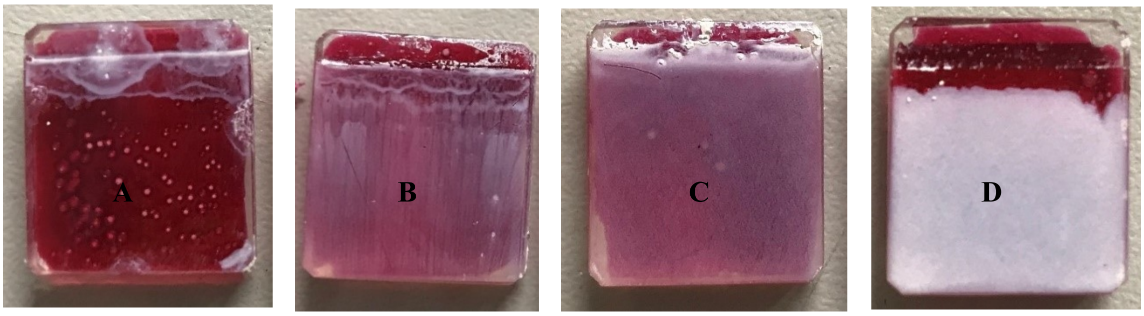


Figure S19.: SiO_2 Coated COP plates with different concentration of TiO_2 (1 g L^{-1} to 2.5 g L^{-1} TiO_2 (P25) in 1 mL 2 M HCl, 19 mL EtOH und 85 µL Tetrabutylorthotitanate - 60°C/12h/lab air) as photocatalyst. The P25 paste was dispersed by ball milling for 4 h at 400 rpm.

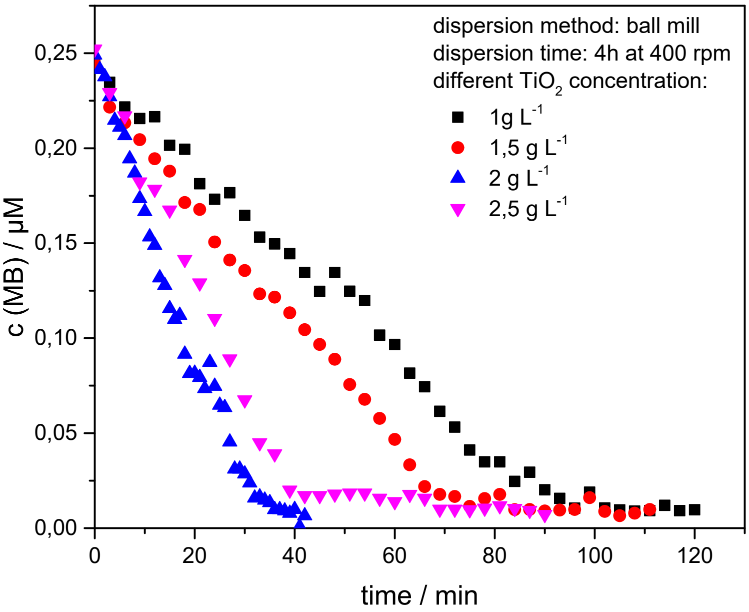


Figure S20.: Concentration-time curves for the decolorization of methylene blue. The photocatalyst was dispersed ball milling for 4 hours at 400 rpm and then dip-coated onto a SiO_2 COP plate. The samples were coated once. Different TiO_2 concentrations were examined (1 g L^{-1} to 2.5 g L^{-1} TiO_2 (P25)).

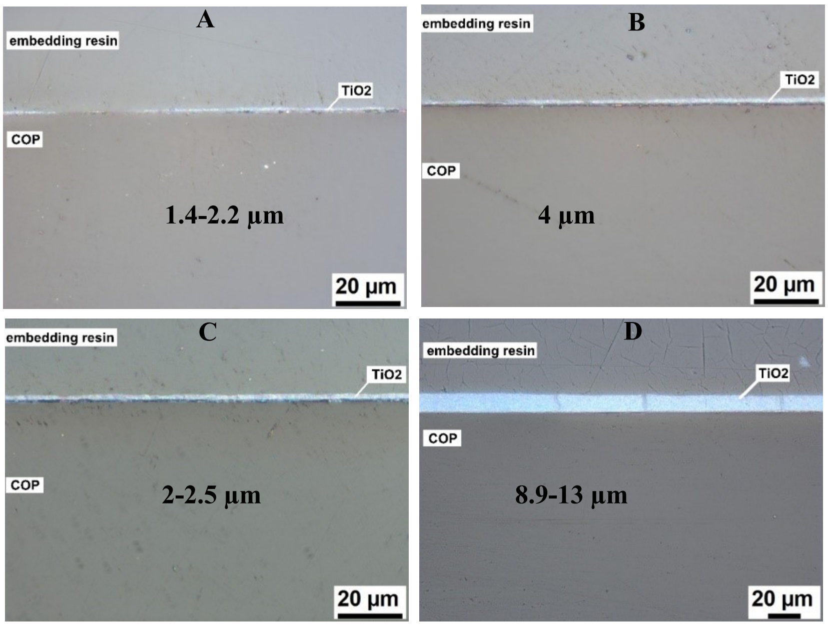


Figure S21.: SiO_2 Coated COP plates with different concentration of TiO_2: A: 1 g L^{-1}, B: 1,5 g L^{-1}, C: 2 g L^{-1} and D: 2.5 g L^{-1}. The P25 paste was dispersed by ball milling for 4 h at 400 rpm.

7. Cross-section analysis of coatings

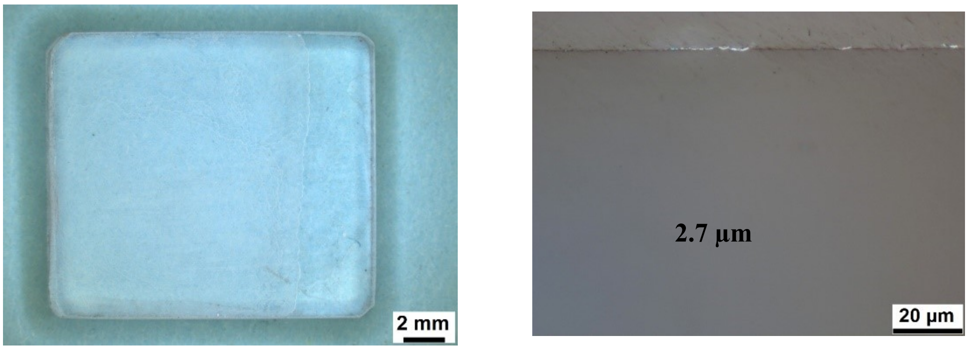


Figure S22.: Cross-section of a COP plate coated with SiO_2 and TTIP (0.5 M TTIP in H_2O and HCl). The samples were coated once and laser-annealed at 8%.

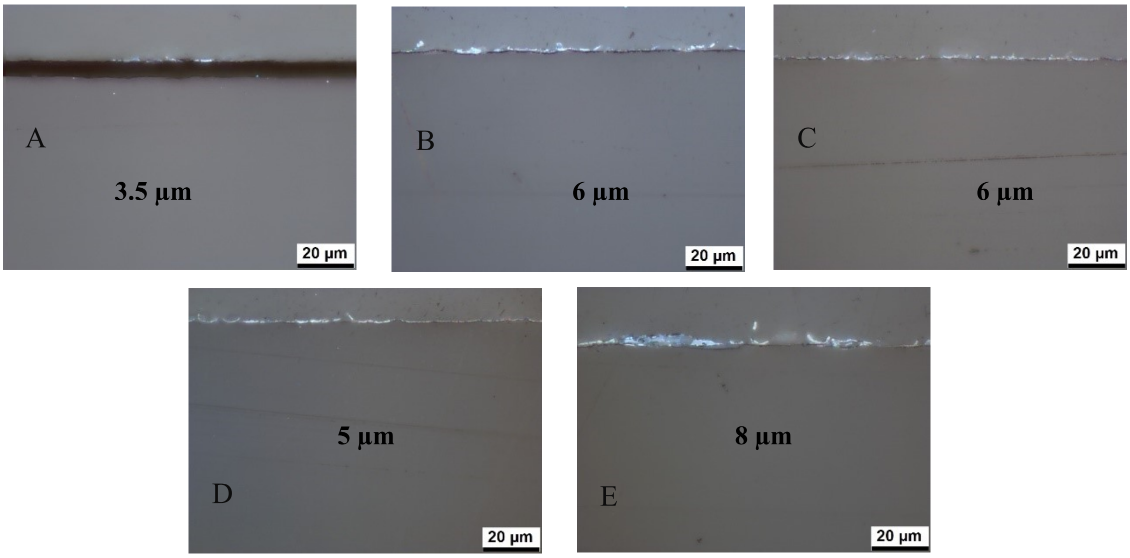
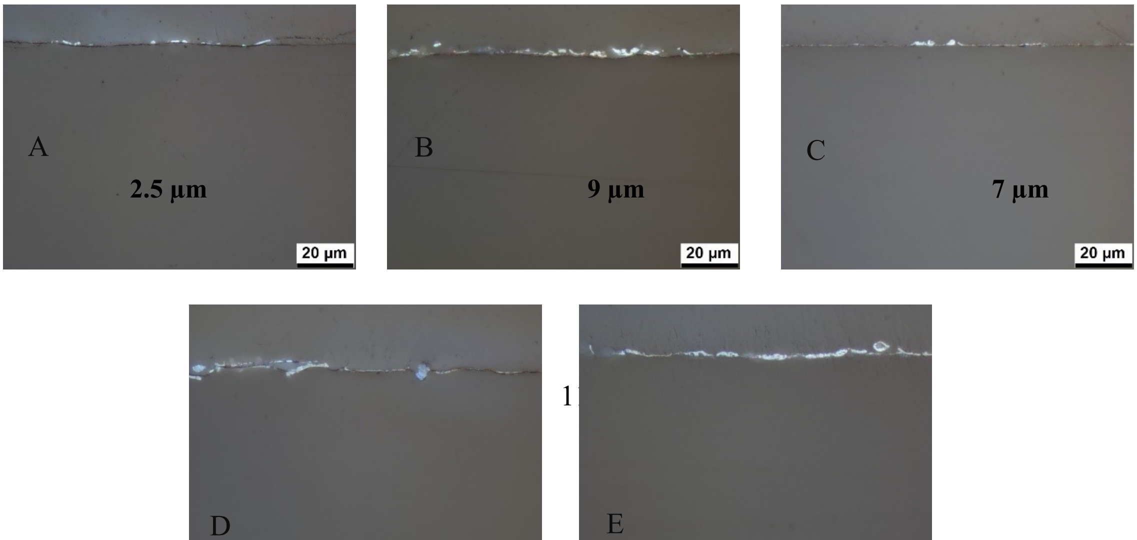


Figure S23.: Cross-section of a COP plate coated with SiO_2 and TTIP (0.5 M TTIP in H_2O and HCl). The samples were coated one to five times and laser-annealed at 9%. **A:** coated and laser annealed for once. **B:** coated and laser-annealed twice. **C:** coated and laser-annealed for three times. **D:** coated and laser-annealed for four times. **E:** coated and laser-annealed for five times.



15 µm **15 µm**

Figure S24.: Cross-section of a COP plate coated with SiO_2 and TTIP (0.5 M TTIP in H_2O and HCl). The samples were coated once to five times and laser-annealed at 10%. **A:** coated and laser-annealed once. **B:** coated and laser-annealed twice. **C:** coated and laser-annealed for three times. **D:** coated and laser-annealed for four times. **E:** coated and laser-annealed for five times.

8. Decolorization of methylene blue with coated and laser-annealed samples

2.1. P25 as photocatalyst for the Decolorization of methylene blue

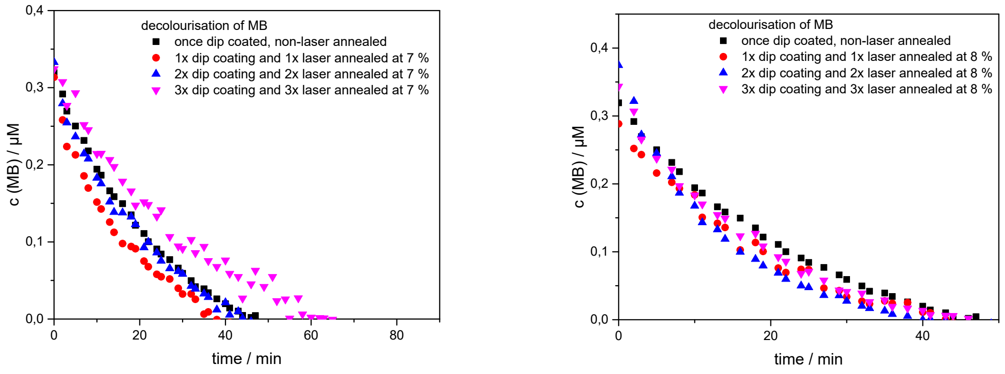


Figure S25.: Concentration-time curves for the decolorization of methylene blue. Dispersion method: ball mill. The samples were coated and laser-annealed one to three times at a laser intensity of 8 % or 9 %.

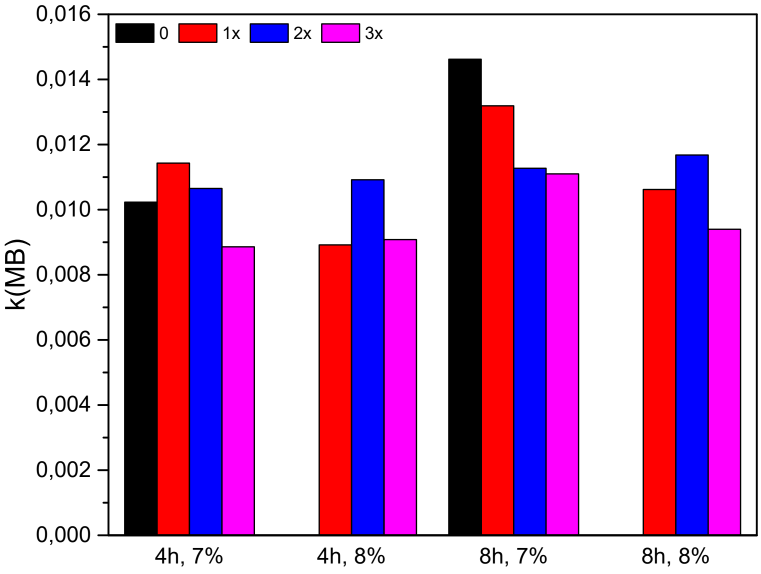


Figure S26.: Summary of the *k*-values for the decolorization of methylene blue. P25 was dispersed in the ball mill for different lengths of time (4 h and 8 h). The coated samples were then treated at different laser intensities (7 % and 8 %). For both samples, which were dispersed for 4 h and 8 h respectively, the coating and laser treatment were carried out 0 to 3 times.

2.2. Samples produced with TTIP for Decolorization of methylene blue

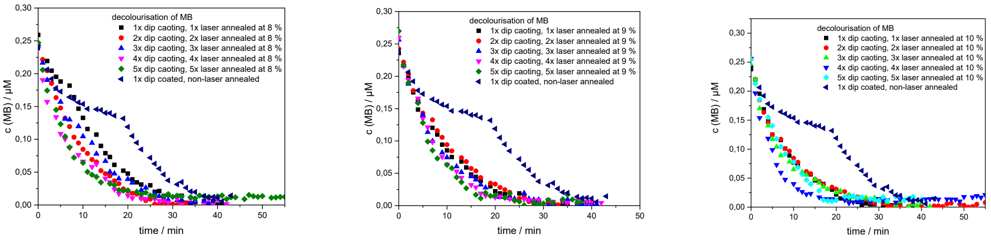


Figure S27.: Concentration-time curves for the decolorization of methylene blue with samples produced with TTIP. The samples were coated and laser-annealed one to five times at a laser intensity of 8 %, 9 % or 10 %.

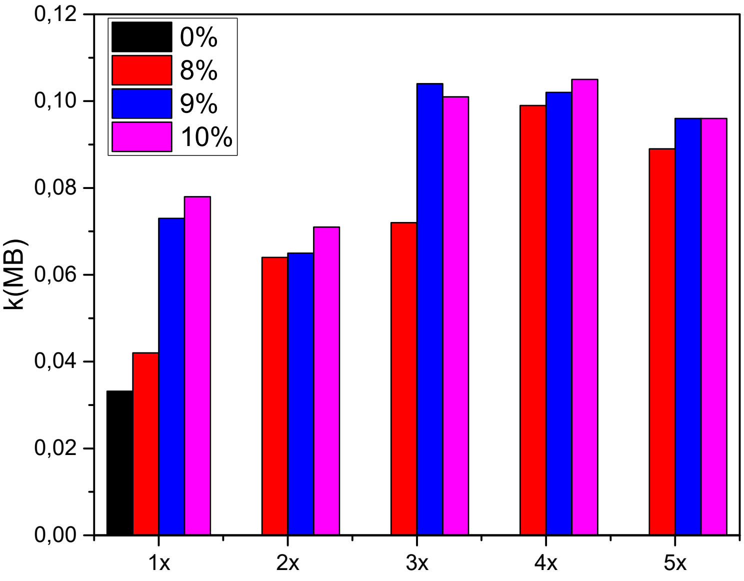


Figure S28.: Summary of the *k*-values for the decolorization of methylene blue with samples produced with TTIP. The coated samples were then treated at different laser intensities (8 %, 9% and 10 %). The coating and laser treatment were carried out 0 to five times.

9. Reduction of nitrobenzene to aniline with coated and laser-annealed samples

3.1. Raman spectra

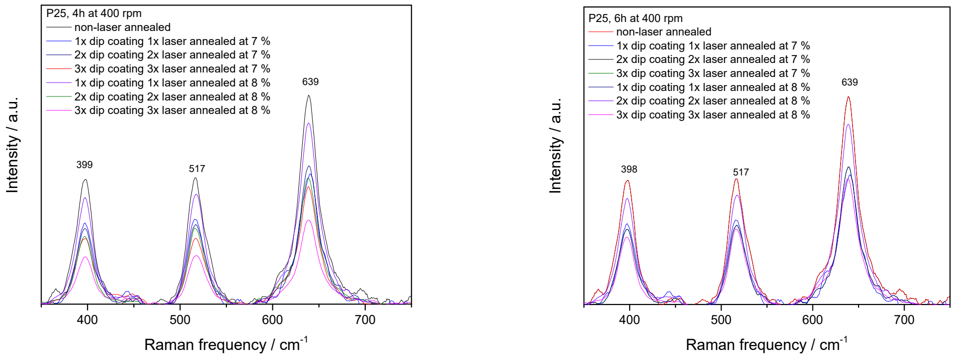


Figure S29.: Raman spectra of a COP plate coated with P25. The plates were coated one to three times and laser-annealed one to three times with either 7 % or 8 %. Left: dispersion time 4 hours. Right: dispersion time 6 hours. The plate that was not lasered was coated once.

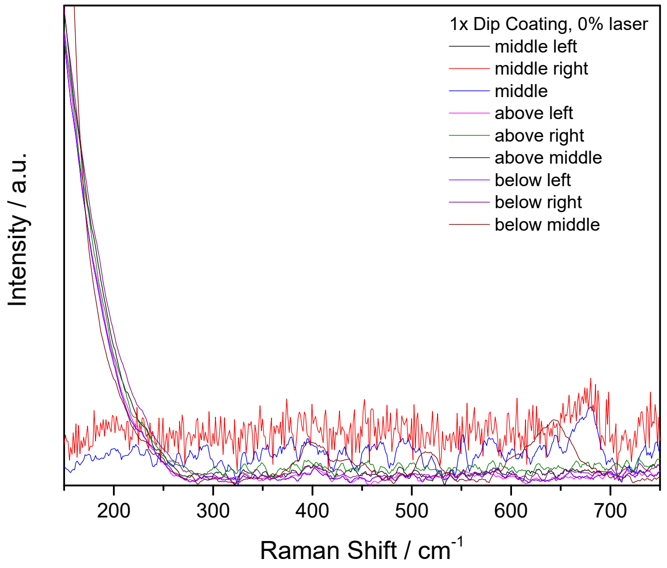


Figure S30.: Raman spectra of a COP plate coated with titanium tetraisopropoxide.

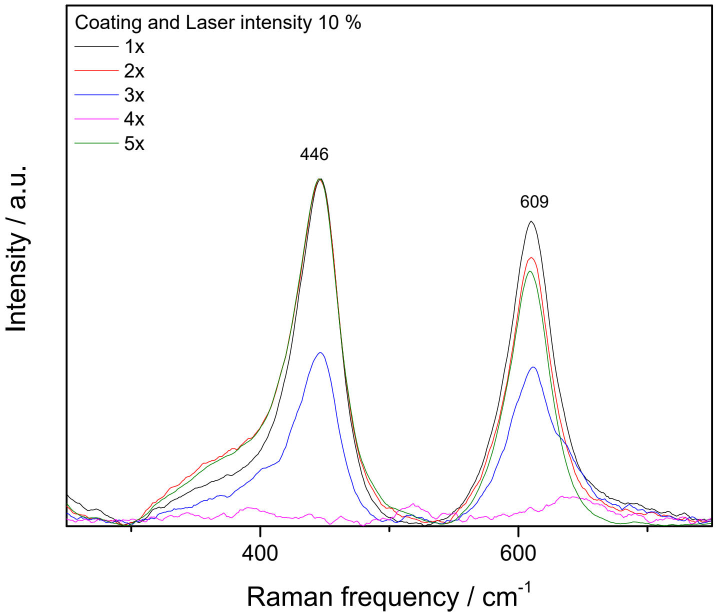


Figure S31.: Raman spectra of a COP plate coated with titanium tetraisopropoxide. Here, the plate was coated one to five times and lasered one to five times with a laser intensity of 10 %.

3.2. P25 as photocatalyst for the reduction of nitrobenzene

In this section, the concentration-time curves for the reduction of nitrobenzene to aniline are shown. The samples are shown in which the photocatalyst was dispersed in the ball mill at a speed of 400 rpm for 4 hours.

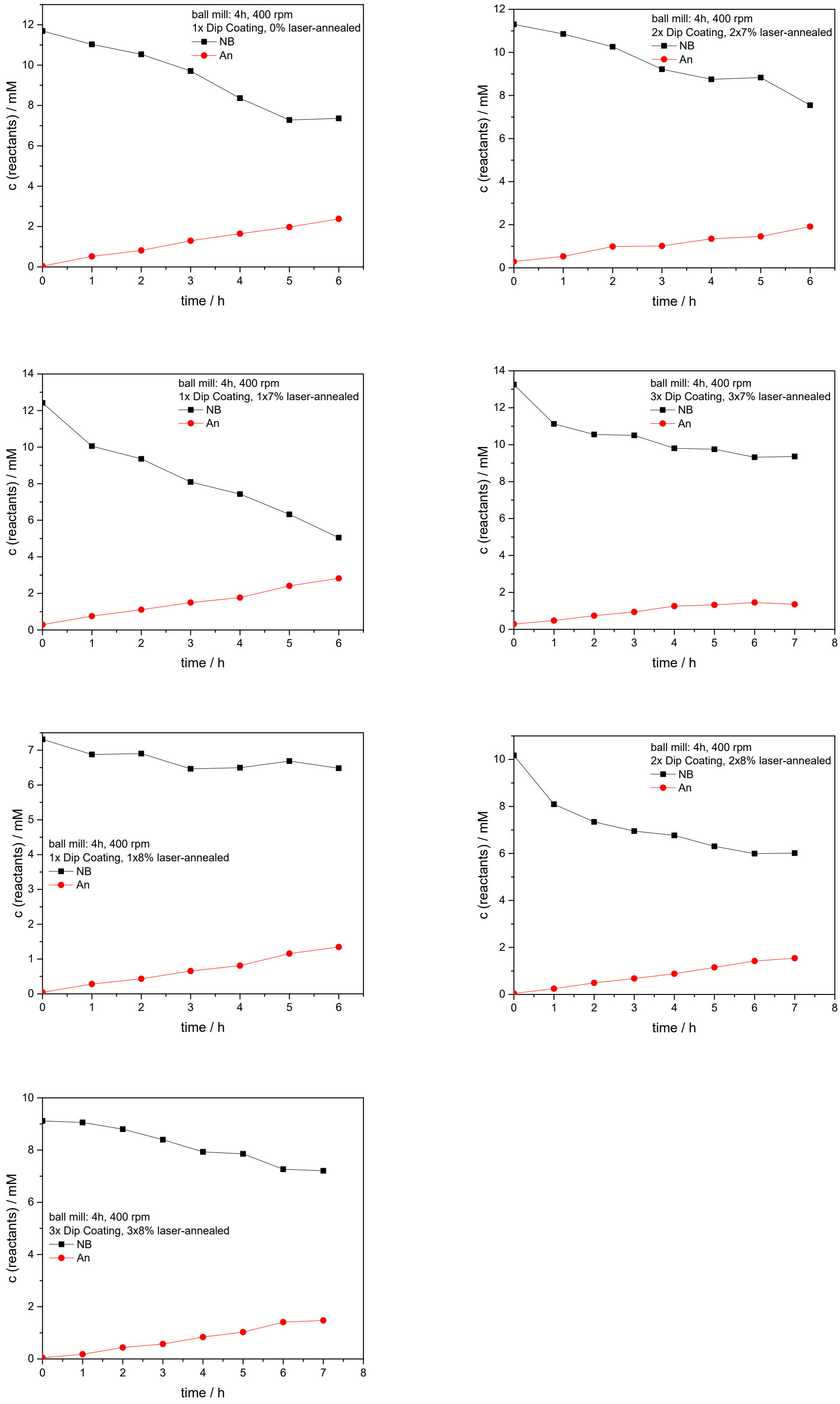


Figure S32.: Concentration-time curves for the reduction of nitrobenzene to aniline. 10 mM NB in IPA was used. P25 was dispersed for 4 hours in the ball mill at 400 rpm. The photocatalyst was coated one to three times on a SiO_2 COP plate and zero to three times laser-annealed at 7% or 8 %.

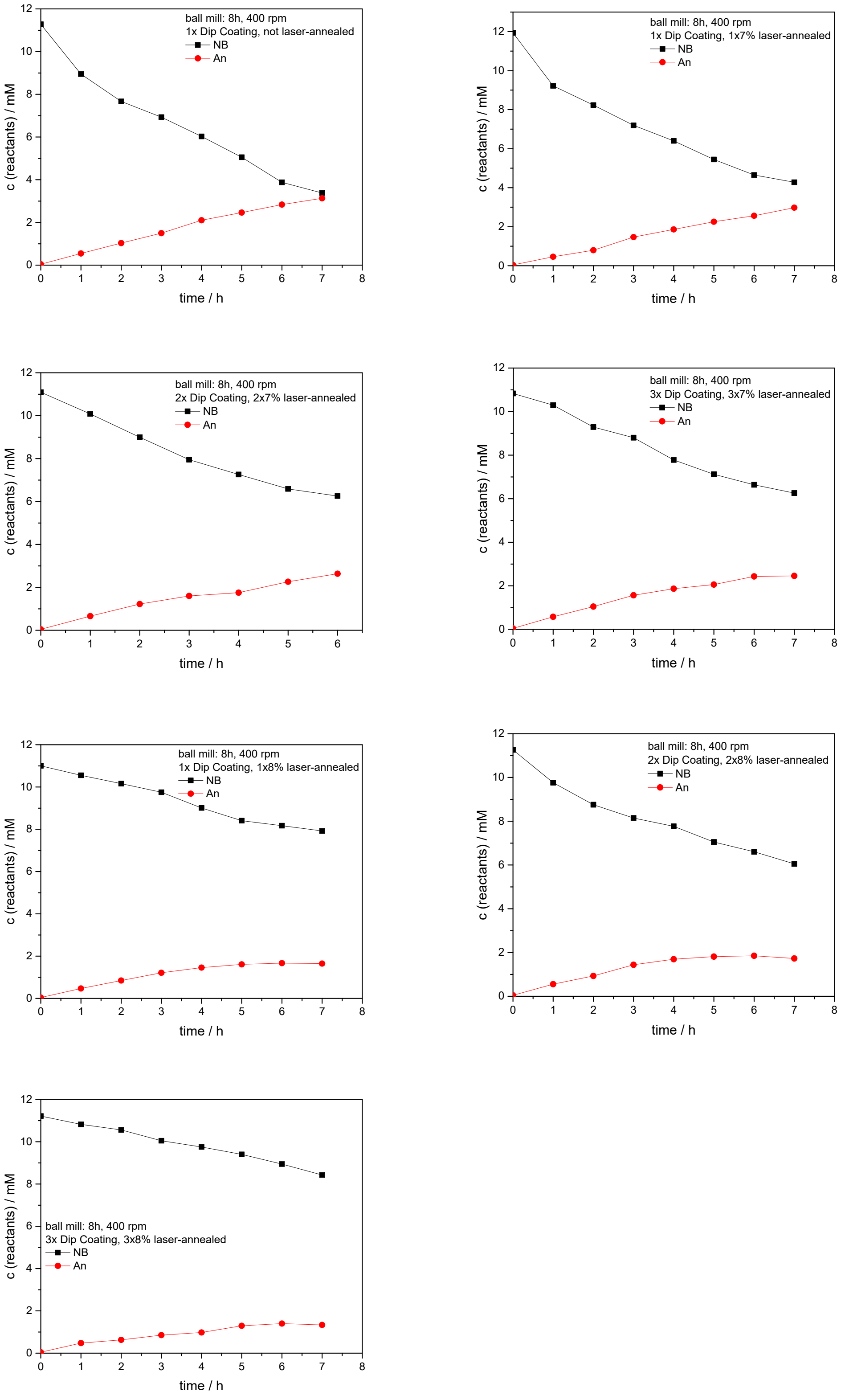


Figure S33.: Concentration-time curves for the reduction of nitrobenzene to aniline. 10 mM NB in IPA was used. P25 was dispersed for 8 hours in the ball mill at 400 rpm. The photocatalyst was coated one to three times on a SiO_2 COP plate and zero to three times laser-annealed at 7% or 8 %.

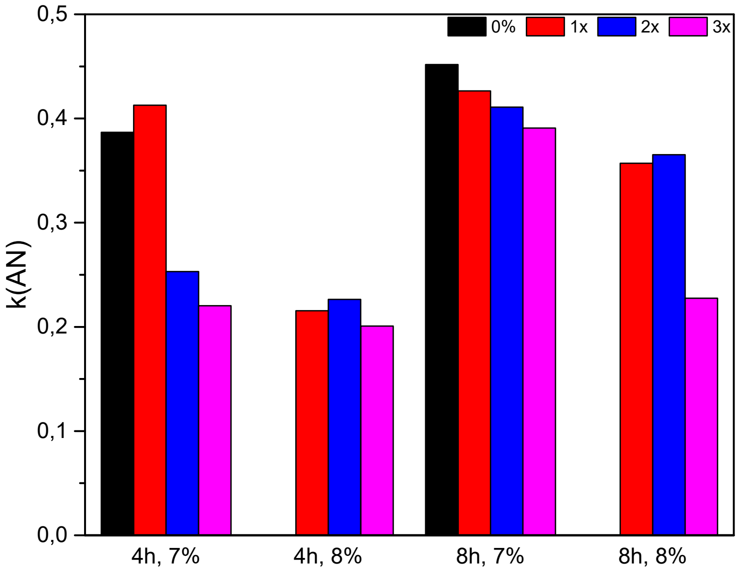
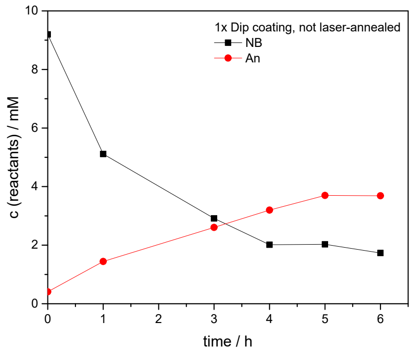
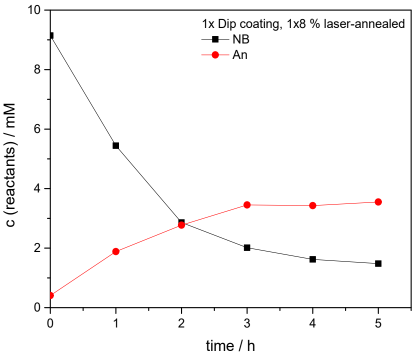


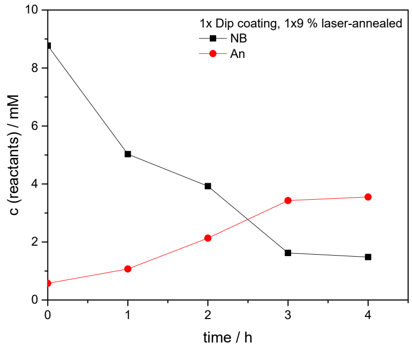
Figure S34.: Summary of the *k*-values for the reduction of nitrobenzene to aniline. P25 was dispersed in the ball mill for different lengths of time (4 h and 8 h). The coated samples were then treated at different laser intensities (7 % and 8 %). For both samples, which were dispersed for 4 h and 8 h respectively, the coating and laser treatment were carried out 0 to 3 times.

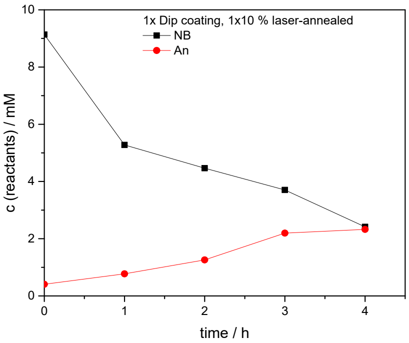
3.3. TTIP as photocatalyst

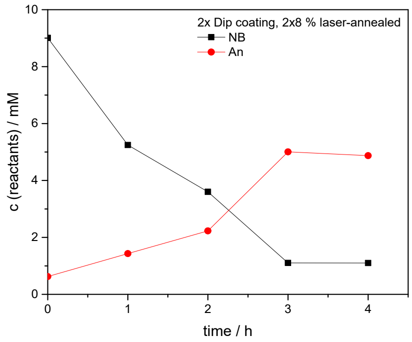
This section shows the concentration-time curves for the reduction of nitrobenzene to aniline using the photocatalyst TTIP.

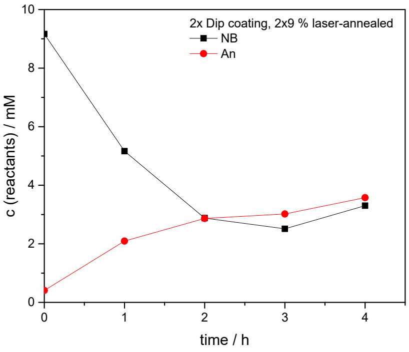

1x Dip coating, not laser-annealed
NB
An
c (reactants) / mM
time / h
0
2
4
6
8
10
0
1
2
3
4
5
6


1x Dip coating, 1x8 % laser-annealed
NB
An
c (reactants) / mM
time / h
0
2
4
6
8
10
0
1
2
3
4
5


1x Dip coating, 1x9 % laser-annealed
NB
An
c (reactants) / mM
time / h
0
2
4
6
8
10
0
1
2
3
4


1x Dip coating, 1x10 % laser-annealed
NB
An
c (reactants) / mM
time / h
0
2
4
6
8
10
0
1
2
3
4


2x Dip coating, 2x8 % laser-annealed
NB
An
c (reactants) / mM
time / h
0
2
4
6
8
10
0
1
2
3
4


2x Dip coating, 2x9 % laser-annealed
NB
An
c (reactants) / mM
time / h
0
2
4
6
8
10
0
1
2
3
4

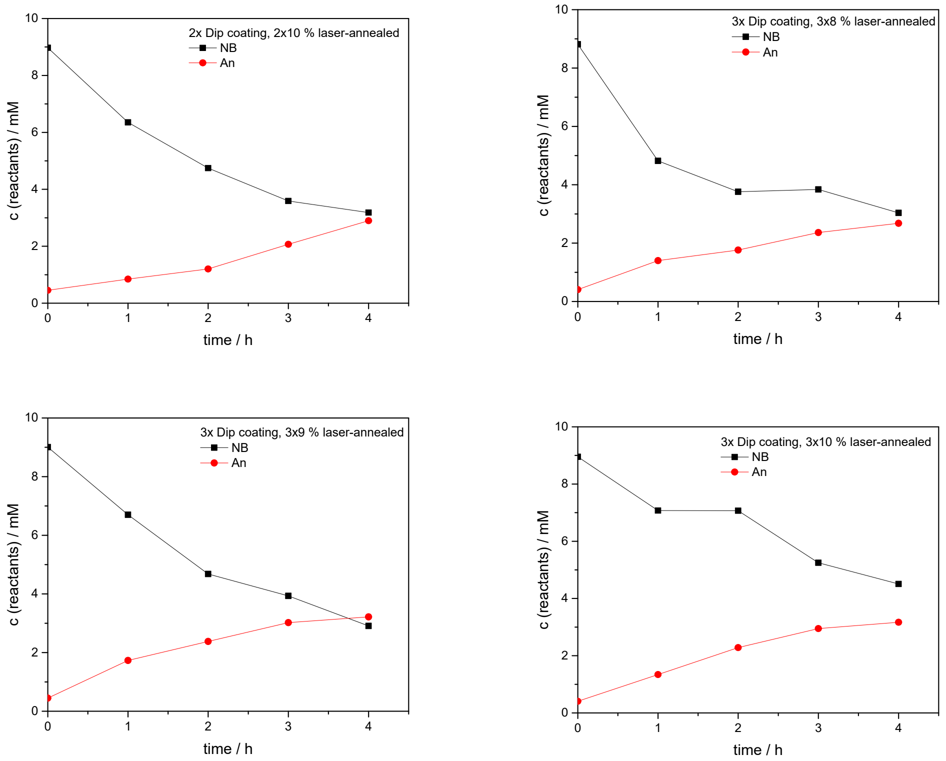


Figure S35.: Concentration-time curves for the reduction of nitrobenzene to aniline. 10 mM NB in IPA was used. The TTIP photocatalyst was coated one to three times on a SiO_2 COP plate and zero to three times laser-annealed at 8 %, 9 % or 10 %.

Transmission

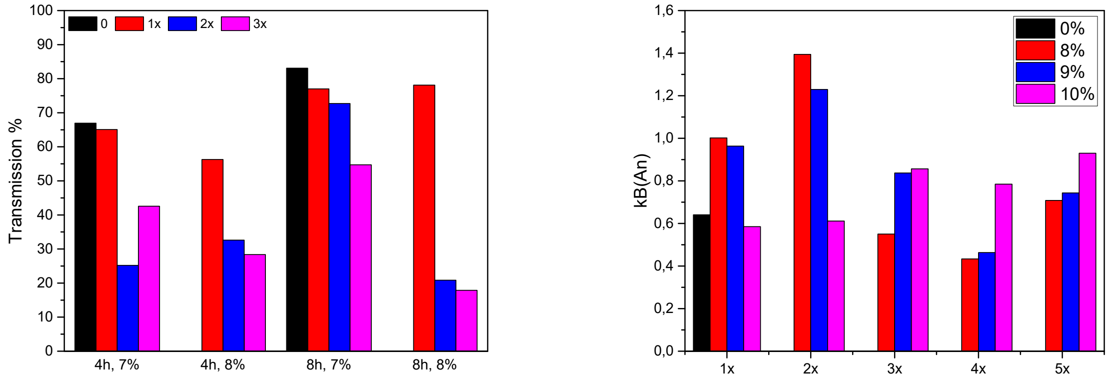


Figure S36.: Transmission measurements for all coated (once till three times) and laser-annealed (not annealed up to 1-3 times at 7 % to 10 %) till samples with the photocatalysts P25 (left) and TTIP (right).

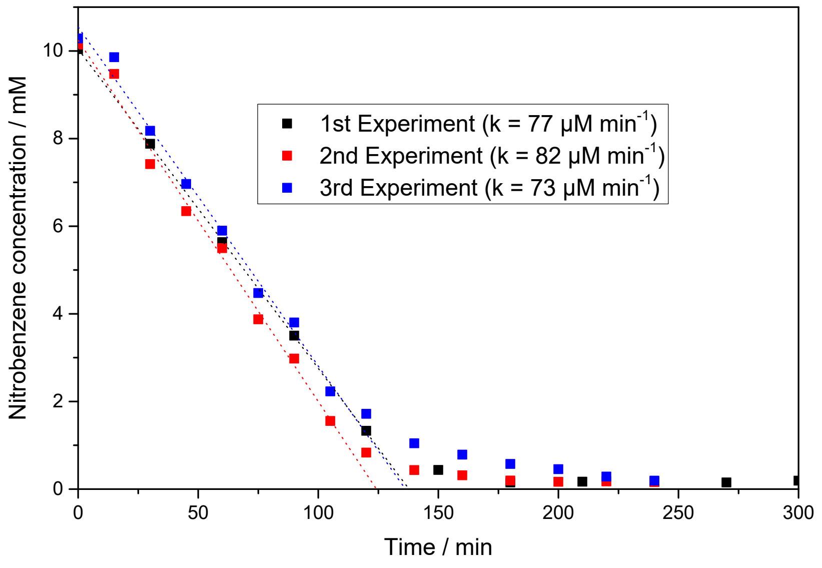


Figure S37.: The concentration-time profiles of photocatalytic nitrobenzene reduction in benzaldehyde using photocatalyst-coated WLE in repeated experiments. Reaction conditions were as follows: q_p: 322 µM s^{-1}, 50 mL 2-propanol, 10 mM nitrobenzene, N_2 bubbling.