Chemical Engineering Journal 160 (2010) 738–741

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Gas-phase photocatalysis in μ-reactors

Peter C.K. Vesborg [a,*], Jakob L. Olsen [a], Toke R. Henriksen [a,b], Ib Chorkendorff [a], Ole Hansen [a,b]

[a] CINF, Dept. of Physics, Building 312, Fysikvej, Technical University of Denmark, DTU, DK-2800 Kgs. Lyngby, Denmark
[b] Dept. of Micro- and Nanotechnology, Technical University of Denmark, DTU Nanotech, Building 345 East, DK-2800 Kgs. Lyngby, Denmark

ARTICLE INFO

*Article history:*
Received 22 March 2010
Accepted 30 March 2010

*Keywords:*
Microreactor
Nanoreactor
Photocatalysis
Photooxidation
Methanol oxidation
CO oxidation
$TiO_2$
P25
W 2730X

ABSTRACT

Gas-phase photocatalysis experiments may benefit from the high sensitivity and good time response in product detection offered by μ-reactors. We demonstrate this by carrying out CO oxidation and methanol oxidation over commercial $TiO_2$ photocatalysts in our recently developed high-sensitivity reactors. We demonstrate that the system exhibits great versatility in terms of photocatalyst, illumination source and target reaction.

## 1. Introduction

Photocatalysis is the conversion of chemicals to other chemicals over a semiconducting catalyst which is activated by band-gap excitation as opposed to conventional catalysis where reactions are thermally activated. Photocatalysis may be used for elimination of unwanted chemicals such as pollutants in air or waste water by mineralizing, e.g. organics down to $CO_2$ and $H_2O$ [1–3]. The second main use of photocatalysis is (solar) energy harvesting since a photocatalyst, unlike a thermal catalyst, may convert reactants to products of higher energy thereby storing some of the energy from the absorbed photons in chemical bonds [4].

The merits of μ-reactors in the study of catalysis have been broadly demonstrated [5–7], but only comparatively little work has been done to use the benefits of μ-reactors in the study of photocatalytic reactions [8–11]. We have recently reported the development of a new μ-reactor fabricated in silicon and sealed with a Pyrex lid [12]. Compared to previously published photochemical "micro"-reactors which typically are based on one or more channels of 10–1000 μm in depth and width [10] our reactors are quite different with their large frontal area combined with their *very* shallow chambers (3 μm depth) and resulting small volumes. This new design features a large frontal area of 0.78 $cm^2$ – useful for photocatalyst illumination – while keeping the total reactor volume down to ~240 nl giving very short time constants and high sensitivity due to the integrated direct quadropole mass spectrometer (QMS) interface. In this paper we demonstrate that these μ-reactors can be very useful in characterizing photocatalysts.

Focusing on the technique two commercial photocatalysts, P25 and W 2730X $TiO_2$-catalysts (both from Evonik—formerly Degussa) are used to photooxidize CO and methanol. CO oxidation has previously been established as a useful probe reaction for gas-phase photocatalysis [13,14] and methanol is a commonly used sacrificial reductant in photoelectrochemical studies [2].

## 2. Experimental

The μ-reactor system (fabrication, gas handling system, QMS detection, etc.) has been described in a previous publication [12]. Briefly, the reactors are planar (16 by 20 $mm^2$ by 0.35 mm silicon (+0.5 mm Pyrex lid)) with a circular active area of 10 mm diameter and a reactor volume of roughly 240 nl. Up to four simultaneous gas streams can be led to the reactor via two inlets (I1 and I2, Fig. 1C) and the reactor effluent is led to a quadropole mass spectrometer (QMS) for detection through a capillary (which limits the reactor flow to ~$10^{15}$ molecules/s) via O2. The bypass flow which never enters the circular reactor area exits via O1. This bypass flow is normally chosen to be on the order of 10 sccm to get good regulation using off-the-shelf mass flow controllers.

Fig. 1A and B are cross-sections of the μ-reactor showing the two basic ways photocatalyst may be loaded into the reactor and that

---

[*] Corresponding author.
*E-mail addresses:* petervesborg@gmail.com, peter.vesborg@fysik.dtu.dk (P.C.K. Vesborg).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.03.083

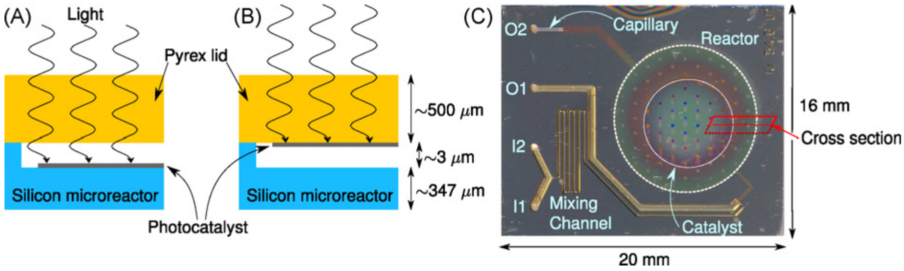

**Fig. 1.** Partial cross-sections of two different μ-reactors loaded in two different ways and a photograph of a μ-reactor. Sketch A shows that when photocatalyst is deposited on the silicon reactor the illumination is frontal – i.e. light is incident from the same side as the reactants – while sketch B shows that photocatalyst deposited on the Pyrex lid (as in the examples in this paper) is effectively illuminated from behind. Sketch C shows a top view of the reactor where main parts are indicated. Gas is let in via I1 and I2 and out via O1 and O2. O1 goes to a pressure controller and O2 leads from the reactor to the mass spectrometer. The location of the cross-sectional cut shown in A and B is also indicated in C.

they allow for both front-side and back-side illumination. The light sources available range from small, cheap LEDs directly over the reactor to a large Xe-arc broadband source (Newport model 66942 1 kW OF) which may or may not be filtered or passed through a monochromator before light is guided to the reactor with a fiber bundle terminated with a collimating optic. In the present paper we excite the photocatalysts using a small 4 W Hg lamp (UVP model UVGL-15). Regardless of the light source used the incident spectrum and intensity is recorded by replacing the reactor with the measurement head of a calibrated spectroradiometer (International Light model RPS-900R). The measured spectrum incident on the reactors in the present paper is shown in Fig. 2. Since some of the light is lost passing through the Pyrex lid due to reflection and absorption for the deeper UV we include the transmittance spectrum of the 0.5 mm Pyrex lids used to seal our reactors in Fig. 3. Even though Pyrex starts absorbing light at ~330 nm the lids are sufficiently transparent that experiments down to well below 300 nm are possible.

For the experimental examples presented in this paper the P25 and W 2730X photocatalysts are loaded onto the Pyrex lids which are subsequently bonded to the silicon reactors. This corresponds to sketch B of Fig. 1 and the photocatalyst is effectively illuminated from "behind". One advantage of depositing the photocatalyst on the glass lid is that it may be characterized by transmission UV–vis spectroscopy before measurements begin. The catalyst is deposited by spin coating. The suspension is made by sonication and the Pyrex area for deposition (circular, 8 mm diameter) is masked by "Blue Tape" (SWT20, Nitto Scandinavia AB). The thickness of the catalyst layer is controlled by the concentration of the suspension and the number of depositions in the spin coater. Once the catalyst is deposited (and possibly characterized by UV–vis or other techniques) the lid is anodically bonded to the reactor [15,12]. During anodic bonding the temperature of the catalyst is kept well below 100 °C using a special "locally-cooled anodic bonding" method [16].

Once the reactor is bonded it is mounted in the gas manifold fixture and the target gas mixture flow is started. It takes a while for the reactor and catalyst to dry (as evidenced by the $m/Z=18$ signal in the QMS) and since trace water in our experience inhibits CO oxidation over $TiO_2$ care is taken that the chip is dry before experiments are started. Sometimes cycles of illumination and/or heating to ~100 °C are used to speed up the drying process. For methanol oxidation careful drying is not relevant since the reaction itself evolves water.

In general, the experiment consists of supplying the relevant reactant gas mixture to the μ-reactor and pulsing the light on and off while monitoring the relevant masses with the QMS. This procedure is conducted for all wavelengths and intensities of interest. Generally, illumination causes only negligible (<4 K) increase in reactor temperature, since the metallic gas manifold to which the reactor is clamped acts as a massive heat sink.

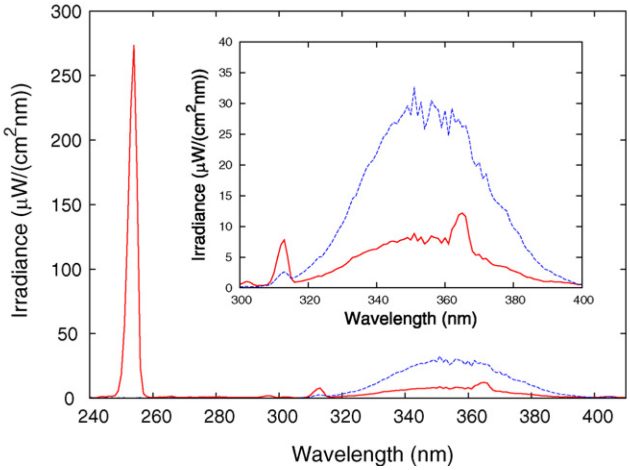

**Fig. 2.** Measured irradiation on the μ-rectors from the 4 W Hg lamp used in this paper. The lamp can be used in "short" wave mode (solid, red curve) and in "long" wave mode (dashed, blue curve). In the "short" wave mode the spectrum is dominated by the narrow Hg-line at 253.6 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

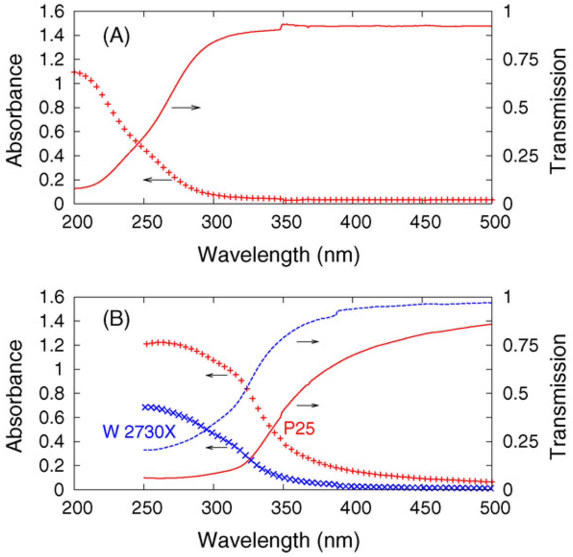

**Fig. 3.** (A) Measured absorbance and resulting transmission of a Pyrex lid. Above ~330 nm transmission is essentially flat at 0.92. (B) Absorbance and transmission of the $TiO_2$ samples studied measured against a blank Pyrex lid in the reference beam (A). The P25-based sample (red curves) has more absorption and scattering than the W 2730X-based sample (blue curves). The increased scattering of P25 is most pronounced at the higher wavelengths.

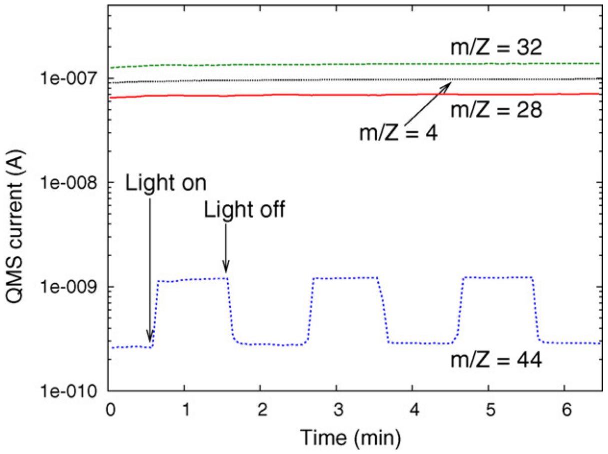

**Fig. 4.** Representative photooxidation experiment using "long" wave illumination (Fig. 2). QMS-current as a function of time. He, CO, $O_2$ and $CO_2$ (*m*/*z*: 4, 28, 32, 44) each sampled at 0.5 Hz are plotted. The $CO_2$ signal increases when the light is on and vice versa. The other channels are almost unaffected due to low turnover (<1%).

This method is also suited for long-term stability testing by leaving the light source on for prolonged periods before pulsing the light to measure photo activity. The setup is automated with LabVIEW (National Instruments) so that light sources, gas pressure and feed gas composition may be automatically scanned during longer experiments.

## 3. Photooxidation experiments

The photooxidation experiments presented in this letter serve to exemplify the method. For these experiments two reactors were prepared. Each was spin coated three times (6000 RPM, 10 s) with a $5\%_{\text{mass}}$ suspension in water (18 MΩ cm, "Millipore") of P25 and W 2730X, respectively. The resulting thickness was estimated by cross-sectional scanning electron microscopy to be approximately 400 nm on average in the case of the P25 catalyst and since the tapped density of P25 according to the data sheet is 130 g/l this corresponds to an upper limit of about $400 \times 10^{-7} \times 0.4^2 \times \pi\,\text{cm}^3 \times 0.13\,\text{g/cm}^3 = 2.6\,\mu\text{g}$ of P25 in total in the μ-reactor.

### 3.1. CO photooxidation over P25

Oxidation of CO is, in principle, a very simple reaction: $CO(g) + 1/2(O_2)(g) \rightarrow CO_2(g)$. Fig. 4 shows time traces of the main components of the CO oxidation reaction gas: $m/z = 4$ (He used as internal reference), $m/z = 28$ (CO), $m/z = 32$ ($O_2$), $m/z = 44$ ($CO_2$). The nominal feed gas composition is 6:6:2 (He, $O_2$, CO) by volume and the total pressure is fixed at 1 bar. It is obvious from the time trace in Fig. 4 when the light is switched on and off. The reason that $m/z = 44$ does not drop to zero when the light is off is background reaction on the filament of the mass spectrometer—not dark reaction in the reactor. Fig. 5 shows the another experiment where the QMS is sampling mass 44 at 10 Hz and the light is toggled every 10 s. It is seen that the system reaches 90% of steady-state level in less than 2 s after the light is toggled. This high time-resolution is a key feature inherent in our μ-reactor design and allows for e.g. very fast experiments where illumination wavelength is scanned.

In order to confirm that photooxidation is indeed responsible for the signals, an experiment of heating the loaded reactors to about 100 °C in the dark was also tried, but no measurable dark activity was seen for these catalysts. As a further check, an empty reactor (without photocatalyst) was also tested and as expected this had no activity whatsoever under illumination or under heating.

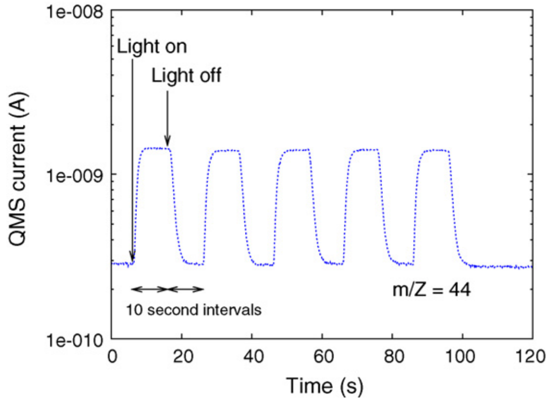

**Fig. 5.** Time trace of $CO_2$ signal sampled at 10 Hz and 10 s light on-off cycles using "short" wave illumination (Fig. 2). The very fast time response of the reactor is evident.

### 3.2. Methanol photooxidation

Methanol oxidation is slightly more complicated (and interesting) than CO oxidation. For instance it may be oxidized completely (mineralized): $CH_3OH(g) + (3/2)O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$. Or it may oxidize partially to methanal ("formaldehyde" – $CH_2O$) or to methanoic acid ("formic acid" – HCOOH). In order to carry out the methanol photooxidation experiments a bubbler made of stainless steel filled with 2 ml of HPLC-grade methanol (Sigma–Aldrich) was inserted after one of the four MFCs supplying gas to our μ-reactor. The concentration of methanol is then conveniently adjusted by the ratio of clean helium to methanol-saturated helium (at the bubbler temperature which is monitored) controlled by the two corresponding MFCs. For the measurements presented in Figs. 6 and 7 the nominal ratio of partial pressures in the feed are 6:6:0.085 (He, $O_2$, MeOH) corresponding to about $0.7\%_{\text{volume}}$ of methanol. An experiment with about five times higher methanol concentrations was also tested, but resulted in a similar turnover as estimated by the $m/z = 44$ signal and is omitted here. For all experiments the methanol signal is monitored by the strongest feature in the cracking pattern at $m/z = 31$.

Figs. 6 and 7 both show methanol oxidation data, but with P25 and W 2730X and long and short wave illumination, respectively. The data clearly demonstrates that the photooxidation of methanol under these conditions takes *much* more time to reach

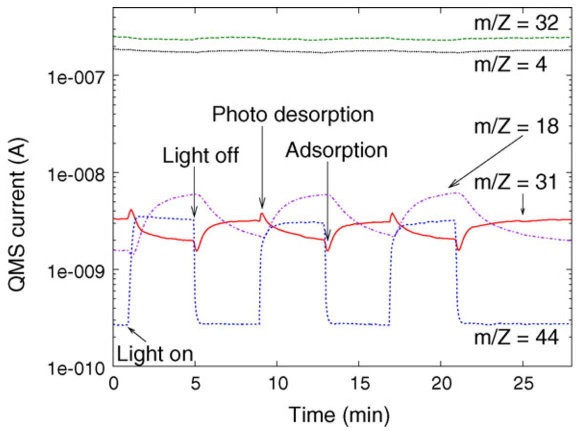

**Fig. 6.** Photooxidation of methanol over P25 photocatalyst using "long" wave illumination (Fig. 2). $m/z = 31$ is the main signal from methanol and $m/z = 18$ is the main peak from water. It is clear, that while the $CO_2$ signal responds quickly to illumination the metanol signal (and the water signal in particular) takes much longer to respond. Notable photo-desorption (and re-adsorption upon switching off the light) of methanol is observed.

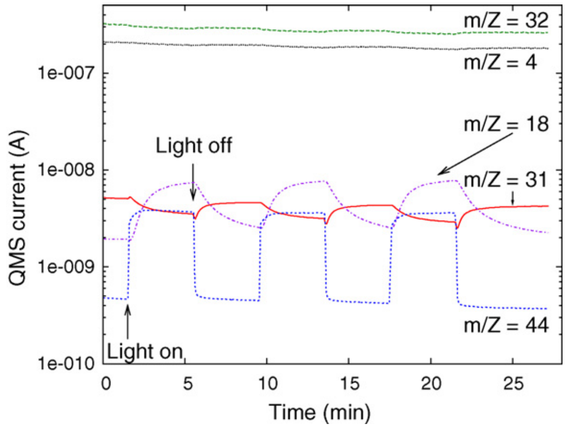

**Fig. 7.** Photooxidation of methanol over W 2730X photocatalyst using "short" wave illumination (Fig. 2). The overall picture is very similar to the P25 data (Fig. 4). However, the phenomenon of photo-desorption and re-adsorption is much less pronounced.

steady state when the light is toggled than it does with CO oxidation. The methanol signal and particularly the water signal both take many minutes to fully respond when the light is toggled. Another clear feature of the data is the apparent photo-desorption (and re-adsorption) of methanol when the light is toggled although it is less pronounced with the W 2730X reactor (Fig. 7). This phenomenon can only be resolved thanks to the fast time-resolution of the μ-reactor so even for this (somewhat slow to reach steady state) reaction the time-resolution is a useful feature.

A mass scan from *m*/*z* of 1–50 was also carried out to look for other (by)products and intermediates of methanol oxidation (such as formic acid), but nothing (that could not be assigned to cracking of water, methanol or $CO_2$) was detected in noteworthy concentrations so methanol seems to mineralize fully under these conditions.

## 4. Discussion

As illustrated by the examples of the previous section, the μ-reactor presented here is a versatile tool for characterization of photocatalytic performance. We show data for CO oxidation and methanol oxidation, but other reactions such as methane oxidation and ethanol oxidation have also been performed successfully. At present, experiments must be carried out in the gas-phase, but we are working on a liquid-capable version of the μ-reactor which would be suited for e.g. water-splitting experiments.

Compared to conventional, macroscopic batch reactors (generally hundreds of milliliters in volume and employing gas-chromatographic product detection) the μ-reactors are fundamentally different. The internal volume is smaller by about $10^6$ times and this enables *flow* measurements instead of batch experiments. This gives a tremendous advantage in terms of time-resolution compared to batch reactors. Time-resolution is useful for studying transient phenomena (such as photoadsorption/desorption (see Fig. 6)) or recording temperature programmed desorption (TPD) spectra, but it also means that a series of measurements (e.g. the performance of a sample over a range of wavelengths—"action spectrum") can be recorded very fast (future publication).

The freedom to deposit the photocatalyst on either the Pyrex lid or the silicon reactor itself enables easy comparison between performance under frontal or back-illumination (Fig. 1). It is expected that for thin films of photocatalyst the performance should be the same regardless of illumination orientation, but for thick films, frontal illumination should give higher turnover (future publication).

Finally, the lower limit on illumination wavelength imposed by the transmission of the Pyrex lid is not really a hard limit. The optical absorbtion shown in Fig. 3 is for our standard lids which are 0.5 mm thick, but we have successfully "thinned" them to less than 100 μm in thickness by etching one side in dilute HF. This procedure results in significantly increased transmission in the 200–250 nm range making measurements on photocatalysts with a band-gap up to 6 eV practical.

## 5. Conclusion

We have shown that gas-phase photochemistry may be conveniently investigated using our silicon μ-reactors due to the transparency of the Pyrex lids in the relevant wavelength range. We carried out mineralization of methanol as a general representative of such reactions, but in principle anything of interest that has a practical vapor pressure could be substituted for methanol in the bubbler. The photocatalytic oxidation of CO has become the "standard" test reaction in our group since it is convenient to do and has near-instant response to illumination which allows for mass-transport studies in thick, mesoporous systems.

To our knowledge, the combination of excellent time-resolution (which gives mechanistic information on absorption/desorption and mass transport) and versatile high-sensitivity detection offered by on-line QMS is far better than anything achievable with more conventional "macro" reactors with ~$10^6$ larger reactor volumes and gas chromatograph product detection.

## Acknowledgements

CINF is funded by the Danish National Research Foundation.

## References

[1] U. Diebold, The surface science of titanium dioxide, Surface Science Reports 48 (5–8) (2003) 53–229.
[2] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, Progress in Solid State Chemistry 32 (1–2) (2004) 33–177.
[3] A. Fujishima, X. Zhang, D.A. Tryk, $TiO_2$ photocatalysis and related surface phenomena, Surface Science Reports 63 (12) (2008) 515–582.
[4] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (5358) (1972) 37–38.
[5] K.F. Jensen, Microreaction engineering—is small better? Chemical Engineering Science 56 (2) (2001) 293–303.
[6] S.K. Ajmera, C. Delattre, M.A. Schmidt, K.F. Jensen, Microfabricated cross-flow chemical reactor for catalyst testing, Sensors and Actuators B-Chemical 82 (2–3) (2002) 297–306.
[7] P. Mao, J.Y. Han, Fabrication and characterization of 20 nm planar nanofluidic channels by glass–glass and glass–silicon bonding, Lab on a Chip 5 (8) (2005) 837–844.
[8] R. Gorges, S. Meyer, G. Kreisel, Photocatalysis in microreactors, Journal of Photochemistry and Photobiology A: Chemistry 167 (2–3) (2004) 95–99.
[9] Y. Matsushita, T. Ichimura, N. Ohba, S. Kumada, K. Sakeda, T. Suzuki, H. Tanibata, T. Murata, Recent progress on photoreactions in microreactors, Pure and Applied Chemistry 79 (11) (2007) 1959–1968.
[10] E.E. Coyle, M. Oelgemoeller, Micro-photochemistry: photochemistry in microstructured reactors. The new photochemistry of the future? Photochemical & Photobiological Sciences 7 (11) (2008) 1313–1322.
[11] Y. Matsushita, N. Ohba, S. Kumada, K. Sakeda, T. Suzuki, T. Ichimura, Photocatalytic reactions in microreactors, Chemical Engineering Journal 135 (Suppl. 1) (2008) S303–S308.
[12] T.R. Henriksen, J.L. Olsen, P.C.K. Vesborg, I. Chorkendorff, O. Hansen, Highly sensitive silicon microreactor for catalyst testing, Review of Scientific Instruments 80 (2009) 124101.
[13] A. Linsebigler, G. Lu, J. Yates, Photocatalysis on $TiO_2$ surfaces—principles, mechanisms, and selected results, Chemical Reviews 95 (3) (1995) 735–758.
[14] J.T. Yates Jr., Photochemistry on $TiO_2$: mechanisms behind the surface chemistry, surface science 603 (10–12) (2009) 1605–1612, special Issue of Surface Science dedicated to Prof. Dr. Dr. h.c. mult. Gerhard Ertl, Nobel-Laureate in Chemistry 2007.
[15] G. Wallis, D. Pomerantz, Field assisted glass–metal sealing, Journal of Applied Physics 40 (10) (1969) 3946–3949.
[16] P.C.K. Vesborg, J.L. Olsen, T.R. Henriksen, I. Chorkendorff, O. Hansen, Anodic bonding with cooling of heat-sensitive areas, Review of Scientific Instruments 81 (2010) 016111.