DROPLET MICROREACTOR FOR REACTION MONITORING AT ELEVATED TEMPERATURES AND PRESSURE

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ABSTRACT

Recording reaction kinetics in detail and at various reaction conditions can be a time-consuming process. Microdroplets form ideal reaction chambers, suitable for high-throughput studies [1]. We report the fabrication of a microfluidic droplet-based microreactor operating at elevated temperatures (up to 130 °C) and pressures (up to 0.7 MPa), to rapidly study reaction kinetics. As proof-of-principle, the temperature-dependent fluorescence of Rhodamine B in ethanol is monitored [2]. Time-resolved information is obtained by measuring at multiple spots in the microreactor.

KEYWORDS: Microreactor, droplets, elevated temperature and pressure, integrated heaters, reaction monitoring

INTRODUCTION

One advantage of using droplet microfluidics over continuous flow reactors is the increased reliability of information obtained on reaction kinetics, due to the fact that reaction products are not dispersed along the length of the channel [1]. Although droplet-based microreactors already exist for high-throughput chemical and biological applications [3,4], our device offers the advantage of rapid heating (within seconds) due to integrated heaters, as well as the possibility to work at pressures up to 0.7 MPa.

EXPERIMENTAL

The microreactor, shown in Figure 1, consists out of a silicon substrate containing microfluidic channels (150 µm deep and 200 µm wide) made with DRIE etching. The glass cover contains integrated platinum (with a tantalum adhesion layer) heaters with interlaced temperature sensors that are positioned above the fluidic channels. The heaters and temperature sensors are embedded into the glass wafer with a SiO_2 insulation layer on top. A heater-free zone provides an optical window for fluorescence measurements. A flow focusing geometry is used to create droplets. By treating the surface of the channels with a fluorinated silane compound, ethanol-in-oil-droplets (containing 0.1 mM of Rhodamine B) are

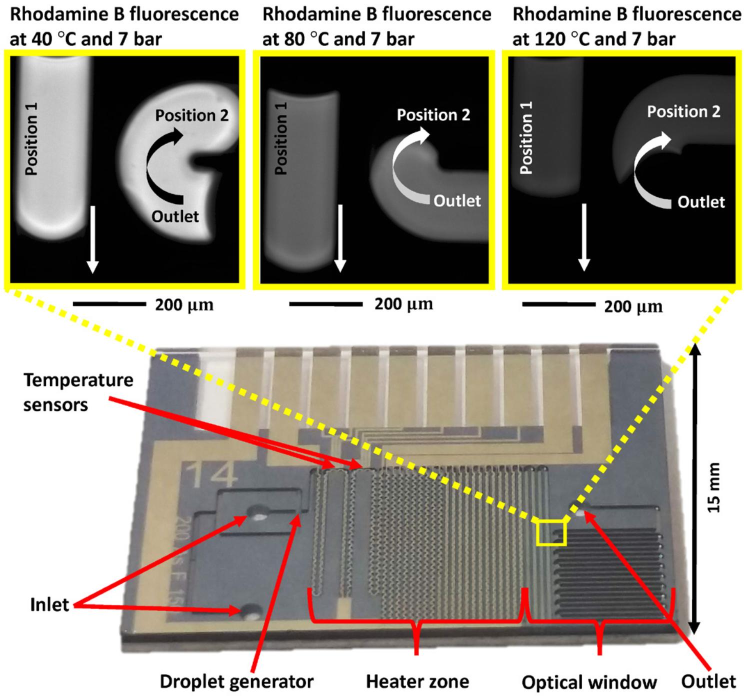

Figure 1: The lower part shows the fabrication result of the droplet microreactor with various features. Fluidic channels (150 µm deep and 200 µm wide) are etched into the silicon bottom substrate. Pt heater and temperature sensor structures are embedded into the glass top substrate. In the top an overview is shown of the fluorescence intensity of Rhodamine B at various chip temperatures(i.e. 40 °C, 80 °C, and 120 °C) measured in the optical window region (the intensity of the 3 images is enhanced using Matlab by a factor 5 for visibility purposes). Furthermore, the positions at which the fluorescence intensity is measured are indicated: a droplet arrives 8 seconds later at position 2, with respect to position 1, upon using flow rates of 2 µL/min for ethanol and 12µL/min for oil, respectively.

created with a Nemesys syringe pump at flow rates of 2 μL/min for ethanol and 12 μL/min for oil, respectively. A back-pressure regulator with a backing pressure of 0.7 MPa is placed at the outlet to raise the pressure inside the reactor. Fluorescence movies of Rhodamine B are made, with a Hamamatsu Orca-Flash4.0 V2 camera, in the optical window region within a temperature range of 30 °C to 130 °C. The flexible structure of Rhodamine B causes its quantum yield to be highly dependent on temperature [5]. Due to the elevated pressure in the microreactor, measurements in ethanol could be done up till 120 °C (boiling point ethanol at 0.7 MPa: ~130 °C).

RESULTS AND DISCUSSION

In the lower part of Figure 1 the fabricated microreactor is shown. The various features such as the droplet generator, heater zone, temperature sensors, optical window, and in- and outlets are indicated. In the top part of Figure 1 three examples of fluorescence images of Rhodamine B droplets at temperatures of 40 °C, 80 °C, and 120 °C are shown (all at a backing pressure of 0.7 MPa). The droplet images are at the same spot in the optical window region indicated with the yellow square in the image. At this spot in the optical window, the fluorescence intensity at 2 positions can be determined in a single frame. The measurement positions are indicated in the droplets, where the arrows indicate the flow direction. There is a time delay of 8 seconds between the two positions. A decrease in fluorescence intensity as function of the temperature is observed, which is shown in Figure 2 for the fluorescence intensity at position 2. The measured data can be fitted with a 3rd order polynomial with an R^2 value of 0.9997. This fit is in accordance with data from [2]. Figure 3 shows a bar graph in which the fluorescence intensities at the two measurement positions (as indicated in Figure 1) are plotted with respect to temperature. It can be seen that for all temperatures the fluorescence intensity at position 2 is lower than at position 1, due to the longer retention time for position 2. The difference becomes smaller at higher temperature, because the quenching of the fluorescence occurs faster.

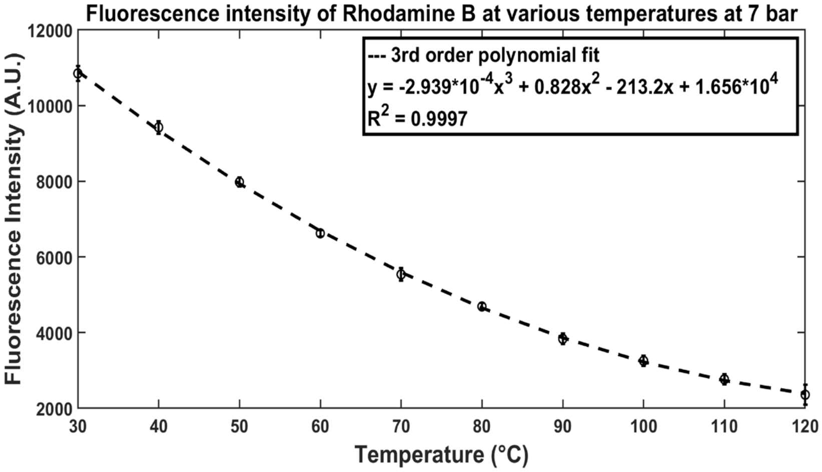

Figure 2: The decreasing fluorescence intensity as function of the temperature at position 2. The dashed line is a 3rd order polynomial fit (fitting coefficients are given in the box), with an R^2 value of 0.9997. The error bars represent the 3σ standard deviation of the average fluorescence intensity for 26 droplets per temperature point.

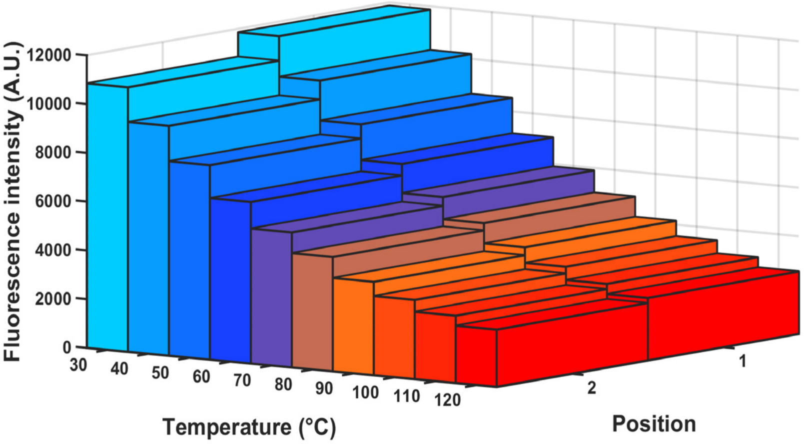

Figure 3: A bar plot showing the time-resolved difference in fluorescence intensity between the measured positions 1 and 2 (as indicated in Figure 1) as function of temperature.

CONCLUSION

In conclusion, we succeeded in fabricating a droplet microreactor, with integrated heater and temperature sensor structures. By measuring the temperature dependent fluorescence intensity of Rhodamine B, we show that a time-resolved study of kinetics with tunable temperature and pressure can be performed inside the microreactor. A possible field of application could be the screening of reaction conditions for hot-injection synthesis of quantum dots, which is now done in capillary reactors, as reported in [6]. In the future we expect to be able to work at higher values of temperature (~400 °C) and pressure (400 bar) [7,8].

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