SONOCHEMICAL MICROREACTOR WITH MICROBUBBLES CREATED ON MICROMACHINED SURFACES

D. Fernandez Rivas[1*], A.G. Zijlstra[2], A. Prosperetti[2,3], D. Lohse[2] and J.G.E. Gardeniers[1]

[1]*Mesoscale Chemical Systems, MESA+ Institute for Nanotechnology, University of Twente, THE NETHERLANDS*

[2]*Physics of Fluids, MESA+ Institute for Nanotechnology, University of Twente, THE NETHERLANDS*

[3]*Department of Mechanical Engineering, The Johns Hopkins University, USA*

ABSTRACT

We present an efficient sonochemical microreactor system based on micromachined surfaces which generate microbubbles in a liquid when exposed to an ultrasonic field. Cavitation of these bubbles leads to radical formation, introducing chemical reactions in the solution. The system exhibits a high sonochemical yield at conditions which would otherwise not produce any significant chemical effect, providing higher efficiency than equivalent conventional sonochemical batch reactors. The results show an increase in total energy efficiency (expressed in the amount of radicals generated per unit power injected to the system) of one order of magnitude, compared to an experiment without the surface bubbles.

KEYWORDS: Microreactor, radicals, sonochemistry, ultrasound, microbubbles

INTRODUCTION

Sonochemistry employs cavitation, i.e. the growth and the implosion of gas bubbles in a liquid; a process which can generate extreme temperatures of thousands of Kelvin to achieve chemical conversion [1]. Applications are in the synthesis of fine chemicals, food ingredients or pharmaceuticals, or the break-down of contaminants in water [2, 3], but have been limited because of the energy inefficiency of large scale sonochemical reactors, mainly caused by the difficulty to focus energy to the microbubble.

THEORY

Bubble nucleation from crevices was described before [4]. We have used micromachined pits to generate microbubbles aiming at sonochemical effects. This new concept is based on the continuous splitting off of microbubbles from oscillating larger bubbles entrapped in micromachined pits in a silicon substrate. The ejected microbubbles continue to cavitate as well generating the desired chemical effect due to ultrasound insonication.

EXPERIMENTAL

The microfabrication process consists in one photolithographic and one deep reactive ion etching step, by which cylindrical pits of typical dimensions 30 μm diameter and depth of 10 μm were formed in a silicon substrate (Fig. 1 a)).

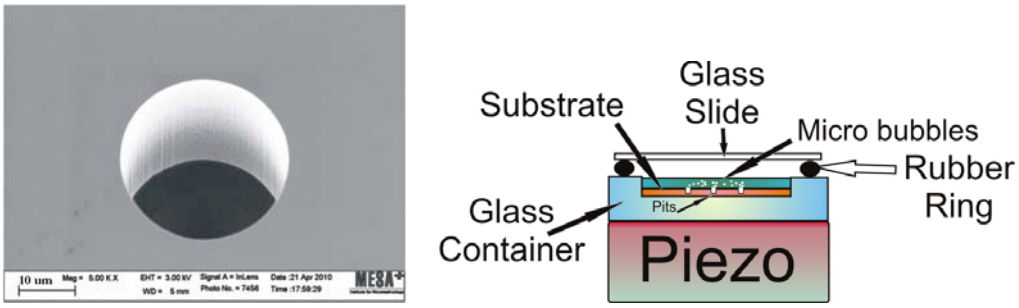

Figure 1: a) Micromachined pit (30μm diameter) in silicon substrate.

b) Experimental setup.

A piezo glued to a closed glass container with a volume of 300 μℓ served as microreaction chamber (Fig. 1 b)). The temperature was kept at 25 ^{0}C, and ultrasound frequency was 200 kHz. The power delivered was measured with an oscilloscope and current probe.

RESULTS AND DISCUSSION

A visible pattern of bubbles ejecting from a three-pit configuration substrate is seen on (Fig. 2 a and c):

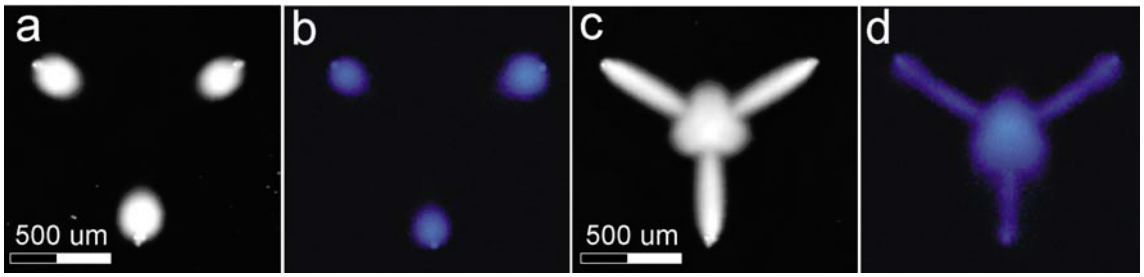

Figure 2: Normal illumination (a and c) and Luminol photograph (b and d) of three pits continuously irradiated using ultrasound at 0.2 W (a and b) and 0.6 W (c and d).

The fact that the microbubbles cavitate and lead to sonolytical reactions is proven by dissolving luminol and using this solution in the same setup. Sonochemiluminescent patterns matching with microbubble traces are clearly observed (Fig. 2 b and d).

Quantification of radical formation was performed by adding terephthalic acid, an OH^* scavenger leading to formation of the fluorescent molecule hydroxy-terephthalic acid (HTA). Fluorescence of each solution was measured with excitation at 310 nm and emission at 428 nm (Fig. 3 a)).

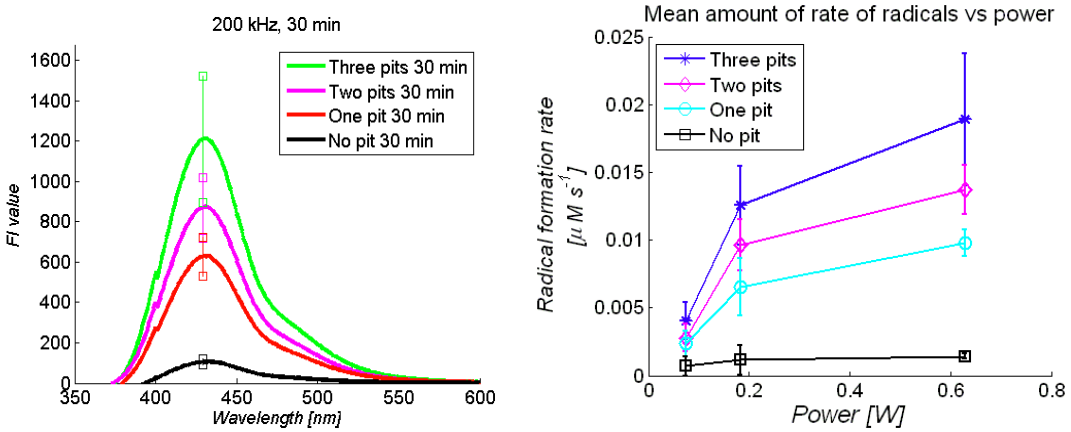

Figure 3: a) HTA fluorescence spectra for High Power value, 30 min and 3,2,1 and no pit. b) Rate of radical production at different powers for different pit configurations

From these measured values the radical formation rate as a function of power and micropit arrangement (1 pit, 2 pits, 3 pits in triangle, no pits for comparison) was determined (Fig. 3 b)).

Efficiencies were calculated as the following equation:

$$X_{US} = \frac{\Delta H \, dn_{rad}/dt}{P_{US}} \qquad (1)$$

where dn_{rad}/dt is the radical formation rate in moles per second, ΔH is the energy required for the formation of OH^* radicals, which is equal to the enthalpy of formation of a water molecule (8.17×10^{-19} J), and P_{US} is the electrical power absorbed by the transducer. The efficiencies calculated for different experimental conditions are summarized in Table 1.

Table 1. Efficiency $\times 10^6$ as defined in Eq 1.

High Power 0.629 W	**3 pits**	**2 pits**	**1 pit**	**0 pit**
15 min	4.5	3.3	2.3	0.3
30 min	4.4	3.1	2.3	0.4
Medium Power 0.182 W	**3 pits**	**2 pits**	**1 pit**	**0 pit**
15 min	9.7	7.6	4.7	0.8
30 min	11	8.0	5.9	0.1
Low Power 0.074 W	**3 pits**	**2 pits**	**1 pit**	**0 pit**
15 min	9.1	5.9	4.8	1.6
30 min	7.1	5.2	4.6	1.1

It is clear that efficiency scales with the number of pits, which indicates a possible route for further improvements.

CONCLUSION

When comparing the efficiency values of the chips with several pits with those of the chip with no pits there is an efficiency increase by an order of magnitude. This demonstrates that the introduction of pits on the reactor wall gives a considerable increase in sonochemical efficiency. Another important advantage of this new concept: the position where sonochemistry occurs, can be controlled by accurately positioning the micromachined pits.

The efficiency obtained in this experiment, $2 \times 10^{-6} \div 10 \times 10^{-6}$, is close to the highest efficiencies reported in the literature with conventional sonochemical reactors [5-7].

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support from the Dutch Technology Foundation STW through Project 07391. The participation of Bunova, Intelligent Laser Applications, KWR, and Micronit is gratefully acknowledged

Thanks to D. R. Dekker from TNW-BPE Group at University of Twente for assistance in the operation of TECAN equipment.

REFERENCES

[1] K.S. Suslick and D.J. Flannigan. Inside a collapsing bubble: sonoluminescence and the conditions during cavitation. 2008.

[2] P.R. Gogate. Application of cavitational reactors for water disinfection: Current status and path forward. Journal of environmental management, 85(4):801–815, 2007.

[3] M. Ashokkumar, D. Sunartio, S. Kentish, R. Mawson, L. Simons, K. Vilkhu, and C.K. Versteeg. Modification of food ingredients by ultrasound to improve functionality: A preliminary study on a model system. Innovative Food Science & Emerging Technologies, 9(2):155–160, 2008.

[4] A.A. Atchley and A. Prosperetti. The crevice model of bubble nucleation. The Journal of the Acoustical Society of America, 86:1065, 1989.

[5] Y.T. Didenko and KS Suslick. The energy efficiency of formation of photons, radicals and ions during single-bubble cavitation. NATURE, 418(6896):394–397, JUL 25 2002.

[6] M.W.A. Kuijpers, M.F. Kemmere, and J.T.F. Keurentjes. Calorimetric study of the energy efficiency for ultrasound-induced radical formation. Ultrasonics, 40(1-8):675–678, 2002.

[7] Y. Iida, K. Yasui, T. Tuziuti, and M. Sivakumar. Sonochemistry and its dosimetry. Microchemical Journal, 80(2):159–164, 2005.

CONTACT

* d.fernandezrivas@utwente.nl