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Partial reduction of anthracene by cold field emission in liquid in a microreactor with an integrated planar microstructured electrode

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A B S T R A C T

We report a novel microreactor with a photolithographically defined integrated electrode containing micro tips that serve as emission points for solvated electrons into liquid *n*-hexane in a microfluidic channel. The implementation of sharp electrode tips permits to extract electrons from the electrode material at relatively low voltages. The electric field distribution in the gap between a planar patterned platinum microtip array and a planar rectangular counterelectrode is analyzed by a computational model. Cold field emission using these microdevices is experimentally verified, and the partial reduction of anthracene to 9,10-dihydroanthracene, via solvated electrons emitted in solutions with or without ethanol in *n*-hexane is investigated. It is found that in the current microreactor configuration, the majority of the products are products originating from coupling of ethanol fragments to, and/or oxidation of 9,10-dihydroanthracene at the platinum counterelectrode, leaving no detectable yield of the desired reduction product.

1. Introduction

Solvated electrons have been observed for the first time in 1807 by Sir Humphry Davy and are mentioned in a scientific report in 1864 by Weyl [1,2]. In more recent days, in particular the nature of the solvated electron in water, the hydrated electron, with its typical characteristics of a short lifetime (nanoseconds), exceptionally high diffusion rate and high reactivity, has been extensively studied [3]. The enormous reducing power of solvated electrons has been noted early on, e.g. in the groundbreaking work of Birch, who investigated the partial reduction of polycyclic aromatic hydrocarbons (PAH) using solvated electrons generated by dissolving an alkali metal in liquid ammonia [4]. More recent studies have focused on the development of greener Birch reduction processes that avoid the use of alkali metals or liquid ammonia, such as electrochemical or plasma techniques [5–7].

Following earlier studies on field emission into organic liquids [8,9], the possibility to generate solvated electrons by cold field emission (CFE) from nanostructured electrodes was proposed by Krivenko et al. and Agiral et al. [10,11]. The latter authors show the possibility to inject electrons directly into liquid hexane by using carbon nanofibers and a defined small interspace between these fibers and a flat counter electrode. The micrometer range electrode gap and the nanometer scale radius of curvature of the structures on the cathode surface facilitate the emission of electrons by creating a high electric field with only a relatively low voltage difference.

State of the art microfabrication technology permits the creation of integrated electrodes with well-defined geometry and dimensions. Using physical vapor deposition (PVD) of a metal film in combination with photolithography, in this report the construction of microreactors, which are suitable to perform CFE in a flow of liquid *n*-hexane, is described. Background theory of field enhancement is considered and the electrical field distribution around the electrode tips is numerically modeled. Electrical analysis of the electrode configuration is performed, and the chemical performance of the microreactor system for the reduction of anthracene is evaluated.

2. Electrical model and device design aspects

2.1. Microreactor design

The microreactors (Fig. 1) are composed of glass and silicon and have two platinum (Pt) electrodes in a planar configuration positioned at the edges of a flow channel. In order to locally increase the electric field, which enhances the emission of electrons from the metal surface, one of the two electrodes, the cathode, contains lithographically defined microtips with a triangular shape. The distance (d) between the two electrodes is varied within the range: 1, 2, 3, 5, 10 and 20 µm. The cathode consists of a series of isosceles triangles (10 µm height and 10 µm length), connected by a rectangle of 6 mm length and 100 µm width. The thickness of the electrode is 100 nm. The anode is a

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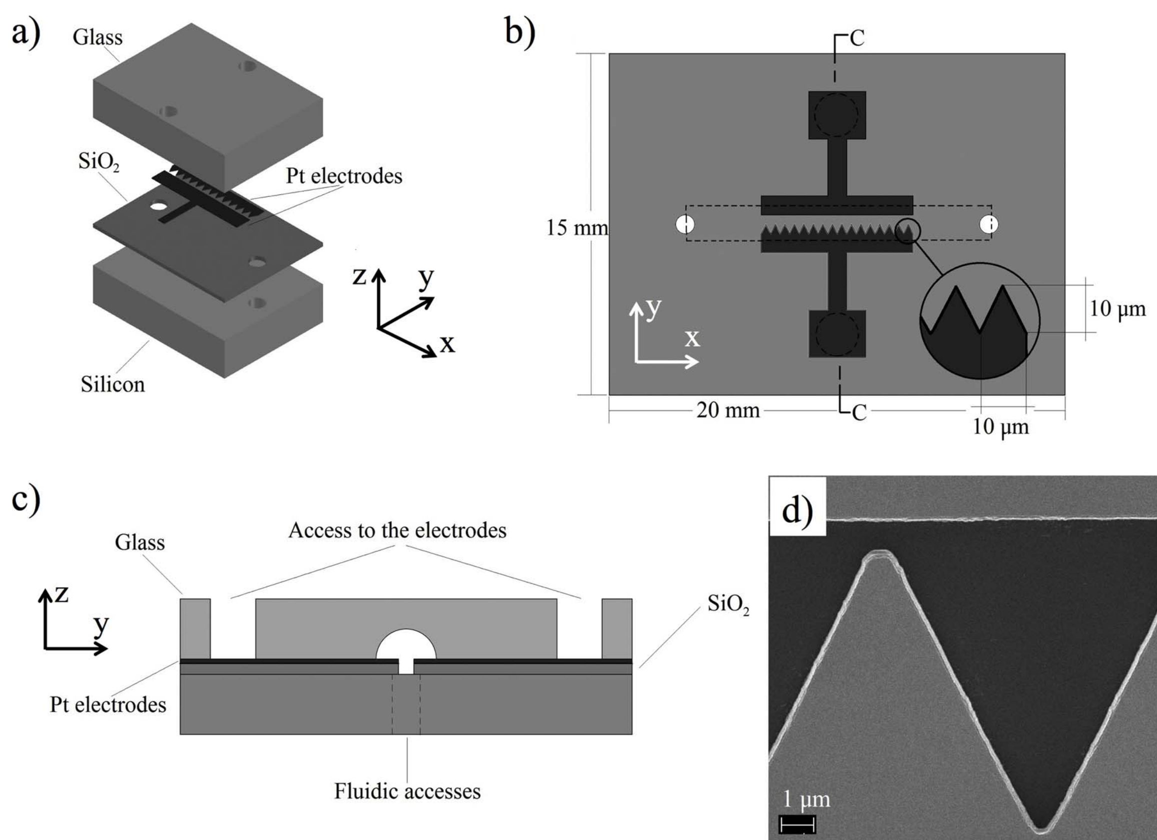

Fig. 1. Microreactor with photolithographically defined microtips: a) 3D exploded view of the microreactor components, b) top view of electrode pattern, c) cross section of microfluidic channel, showing how the electrodes are aligned with the channel, d) SEM image of one of the microtips, for a 1 μm cathode tip to anode distance.

rectangle of 6 mm in length, 100 μm in width and 100 nm thick. Both electrodes are placed at the bottom of the flow channel which is 150 μm wide and 25 μm deep (total reactor volume: 50 nL).

2.2. Electrical field modeling

In order to study the local field enhancement at the microtips, an electrostatic model of the electric field distribution upon applying a potential between the flat anode and the microtips on the cathode surface is created. The model, that was used in the numerical calculations is based on Griffiths' work [12]. The COMSOL 4.3a Multiphysics software package was used to numerically calculate the electrostatic field between an electrode with triangular emitters and a flat counter-electrode, based on the following equations, derived from Gauss' law [13]:

$$E = \nabla V \text{ and } \nabla \varepsilon E = \rho \quad (1)$$

where ε is the absolute permittivity ($\varepsilon = \varepsilon_r{}^* \ \varepsilon_0$), E the static electric field, ρ the charge and V the electric potential. The considered dielectric constants (ε_r) in the model are 1 and 2.2 for the platinum electrode and *n*-hexane, respectively. The model considers the case of a cathode placed at 3 μm from the anode, where the volume between the electrodes is filled with *n*-hexane. The overall dimension of the model is set at 50 μm width (x-direction), 33 μm depth (y-direction) and 2 μm height (z-direction). These dimensions represent a characteristic part of the microreactor, see Fig. 2.

The mesh for the geometry was set as follows: maximum element size 128 nm, minimum element size 23 nm, maximum element growth rate 1.5, resolution of curvature 0.6 and resolution of the narrow regions 0.5. The initial values of all structures were set to a potential of 0 V, apart from the cathode potential which was set to −4 V. The temperature was set at 293.25 K. The stationary solver was set with its tolerance at 0.001 and an algebraic multigrid was selected.

3. Materials and methods

3.1. CFE microreactor fabrication

Silicon (100) substrates (p-type boron doped, resistivity 5–10 Ωcm, 100 mm diameter, 525 μm thickness, single side polished; Okmetic, Finland) were cleaned by immersion in fuming 100% nitric acid (UN2031 OM Group) for 10 min, in boiling 69% nitric acid (BASF, 51153574) for 15 min, rinsed in demineralized water, and immersed in 1% aqueous HF (D252 M Honeywell) for 1 min, followed by rinsing in demineralized water and spin drying. 1 μm of SiO_2 was deposited on the substrates in a furnace, using steam oxidation (Tempress, H_2O + N_2 bubbler, N_2 flow 2 L/min, 1150 °C). Electrode structures were photolithographically defined in photoresist (standard UV-lithography, photoresist Olin 907-17). They are centered with respect to a microreactor footprint-size of 20 × 15 mm. In the lithographically defined areas, 150 nm of SiO_2 was removed by immersion in buffered HF solution (BHF; Honeywell, 10188624), followed by rinsing in demineralized water and spin drying. A layer of 100 nm Pt with 10 nm Ta as adhesion layer was sputtered (homemade PVD machine, Ar plasma 200W, 6.66 10^{-3} mbar, 145 sccm Ar flow rate). After the lift-off process, under ultrasonication in acetone (VLSI 51150924, BASF) for 10 min, the substrates were washed with isopropanol (VLSI 51152037, BASF) followed by rinsing in demineralized water and spin drying. The flow channel of the microreactor (15 mm long with a variable width due to the various electrode spacing) was lithographically defined in photoresist (standard UV-lithography, photoresist Olin 907-17). By means of ion beam etching (15 min IBE etching Oxford i300, current 50 mA, voltage 300 V, generator power 300W) followed by 2.5 min of reactive ion etching (Adixen DE, 20/15/150 sccm flow of C_4F_8/CH_4/He,

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