MICROREACTOR ARRAY FOR LOCALIZED SYNTHESIS OF FUNCTIONAL MATERIALS IN PICOLITER VOLUMES

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ABSTRACT

Microreactors enclosing volumes of a few hundred picoliters have been designed to facilitate localized synthesis of micro- and nanostructured metal-organic materials formed from fast reacting precursors. We demonstrate in three applications the potential of the device, including a two-step reaction process and the integration of in situ formed conductive systems with electrode arrays for direct characterization and application.

KEYWORDS: Micro-chamber, Functional materials, Charge-transfer complexes, Crystals

INTRODUCTION

The synthesis of chemical compounds with a high throughput and in large amounts is most conveniently done in bulk synthetic approaches. However, for assembling of nano- or microsized materials in tiny amounts, it is of high importance to precisely meter the reagents and to control the reaction conditions including diffusion times of the reagents [1,2]. Here, we present a microreactor array designed to create micro-sized functional assemblies and to characterize their electrical properties directly on chip. Metering of reagents and initiation of the reaction is controlled by pneumatically actuated valves. We demonstrate the parallel production of fluorescent metal-organic complexes and crystalline charge-transfer materials in these picoliter volume microchambers. The device bridges the gap between in situ formation of organic-based functional materials and micro scale read out components.

EXPERIMENTAL

The microfluidic device is made of poly(dimethylsiloxane) (PDMS, Dow Corning) by soft lithography as described elsewhere [1]. It consists of two layers, one bottom layer for fluid supply and another top layer for pneumatic actuation of integrated valves. Ten parallel reaction chambers are implemented on this platform which are operated by three parallel control lines (Figure 1). The bottom layer is covered by a thin glass slide that is patterned with a platinum electrode array by means of a lift-off process. The glass slide is positioned below the microchambers so that either one or two electrode pairs are reaching the microchambers (Figure 1B).

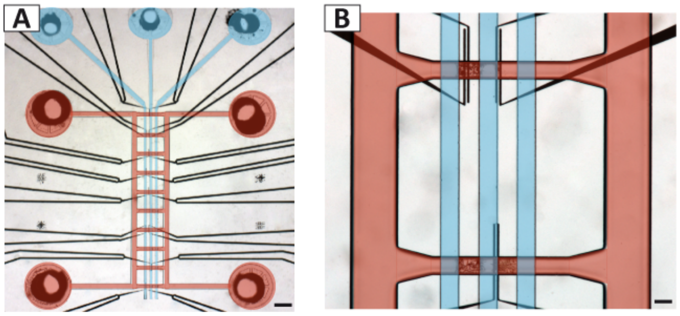

*Figure 1. (**A**) Micrograph of the multilayer poly(dimethylsiloxane) (PDMS) chip with an array of 10 reaction chambers, each is controlled by 3 pneumatic valves. The central valve is closed during the filling procedure, the outer valves are closed during reaction. (**B**) Magnification of two reaction chambers. Either two pairs of electrodes, or one central electrode pair patterned on a glass slide are aligned below the microchambers. (blue: control layer, height: 100 µm; red: fluidic layer, height: 10 µm; black: platinum electrodes, height: 100 nm; Scale bars: A: 500 µm; B: 100 µm)*

Two reactants are supplied from either side of the microchip into the microchambers, which are initially separated by the central valve (Figure 2). Afterwards, the two outer valves are actuated to enclose a volume of about 100 pL of each reagent solution. Opening the middle valve allows diffusion of the reagents towards the centre of the reaction chamber and hence, the reaction is initiated. Diffusion of the reagents across the entire chamber occurs within seconds up to a few minutes, and complete formation of the functional assemblies is demonstrated to happen only in a few minutes. In this configuration, the volumes of reactants are precisely predefined, as well as the interface of the two reagent solutions resulting in a convection-free process. Furthermore, all valves can be opened to flush residual solution out of the channels, or to allow fresh reagents to enter the chamber. Since the reaction chamber is larger (300 pL) than the initially supplied volumes (2 x 100 pL), the microchamber is slightly under low pressure, which is partly balanced by the flexibility of the chamber walls, and partly equalized by air diffusing through the PDMS into the chamber.

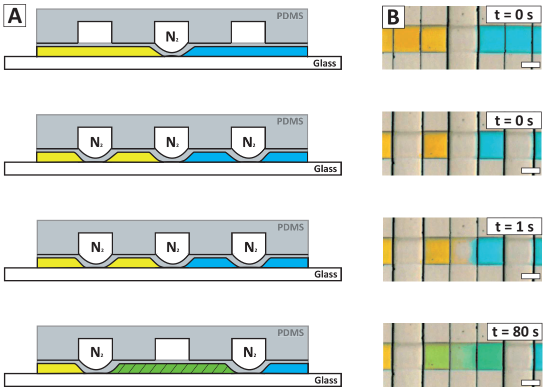

*Figure 2: Schematic illustration (**A**) and optical images (**B**) of the device and operation procedure showing the mixing of two food dyes. Scale bar: 100 µm*

RESULTS AND DISCUSSION

We first proved the functionality of the device by inducing the reaction of an aqueous solution of $Zn(NO_3)_2$ (20 mM) with a solution of 1,4-bis(imidazol-1-ylmethyl)benzene in ethanol (bix, 20 mM) yielding the blue fluorescent metal-organic complex (Zn(bix)) [3]. Figure 3 shows a sequence of micrographs monitoring the reaction inside the micro-chamber at different times.

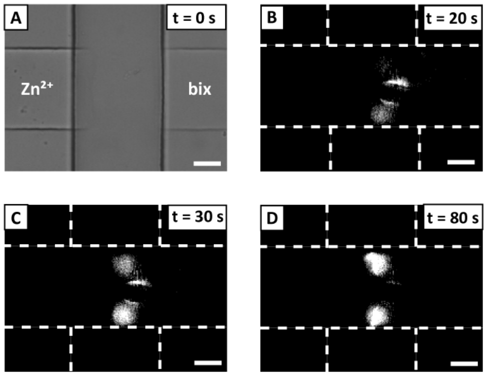

*Figure 3: Sequence of optical microscope images showing the formation of fluorescent Zn(bix) complexes in our device. (**A**) brightfield image taken before the synthesis, (**B**), (**C**) and (**D**) fluorescence images captured at different times. Note: The reaction starts at the sides of the channel due to the slightly slower opening of the valve in the middle. Scale bars: 50 µm*

We found reproducible diffusive mixing and reaction times, as well as reproducible location of the resulting coordination polymer demonstrating the convection-free condition of the device. Note that the preferred reaction at the sides was due to the delayed opening of the valve in the centre of the chamber.

In a modified microchip, electrode pairs, patterned on the bottom channel (glass slide), were aligned underneath the microreactor allowing the electrical characterization of assembled material. This microchip was employed for the reaction between tetrathiafulvalene (TTF, 24 mM) and hydrogen tetrachloroaurate (6 mM), both in acetonitrile (Figure 4) [4].

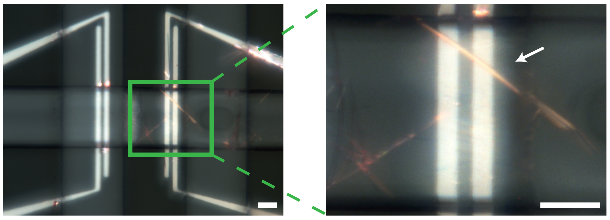

Figure 4: Micrographs of the Au-TTF hybrid wires (polarized light is used) formed above the electrode pairs. Scale bars: 50 µm

Upon opening the central valve to allow diffusion, the assembly of isolated crystalline Au-TTF wires with diameters ranging from 1 µm to 5 µm and lengths up to 200 µm could be observed. Due to the slower diffusion of TTF molecules compared to the gold ions, formation was preferentially induced at the TTF solution chamber. The wires settled down on the electrode pairs and the electrical properties could be straightforward characterized. Figure 5 shows the I/V curves for wires formed in 8 chambers in parallel, which have the same characteristic than Au-TTF wires produced with other methods [4].

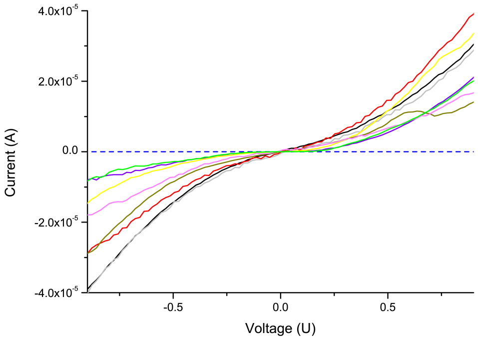

Figure 5: I/V curves of the conductive Au-TTF hybrid wires formed in parallel inside the micro-chambers (solid lines). Dashed line: Non-bridged electrode pair in an empty microchamber.

Finally, we performed a localized two-step reaction creating silver-tetracyanoquinodimethane (Ag-TCNQ) wires. In this case, first silver was deposited inside the chamber by the reaction of a silver salt with reducing agent (both HE-300 solutions, Peacock-Laboratories) (Figure 6A). After rinsing the surplus solution the chip was dried and a saturated TCNQ solution in acetonitrile was added, keeping one of the outer valves closed to allow only diffusion of TCNQ into the reaction chamber and hence, the formation of Ag-TCNQ wires (Figure 6B).

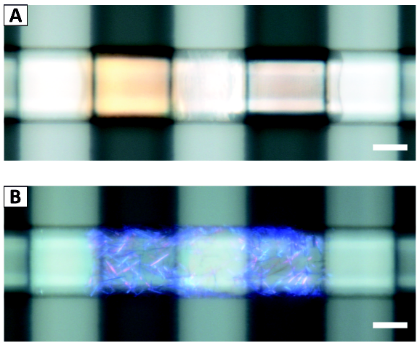

*Figure 5: Two-step reaction to form Ag-TCNQ wires. (**A**) Micrograph of the silver layer formed in the first step. The film covers the microchamber walls and the glass surface over the entire length of 300 µm. (**B**) Wires formed after addition of TCNQ solution. Scale bars: 50 µm*

CONCLUSION

In conclusion, we developed a microfluidic device, where (i) the reactions takes place in a very small confined region of the microchip, (ii) reproducible reaction conditions are provided, and (iii) further interfaces such as electrode arrays can be integrated. We focus in future on the assembly of nanosized materials, which have potential use for sensing or electronic applications.

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