Spiropyran Modified Microfluidic Chip Channels for Photonically Controlled Sensor Array Detection of Metal Ions

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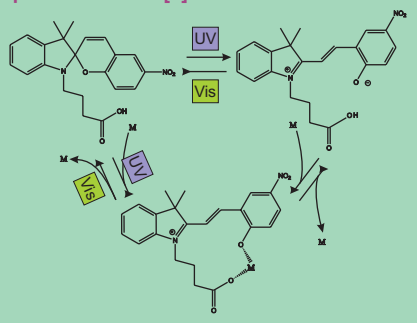
Introduction

Microfluidic chips are particularly attractive for analytical purposes because they provide a convenient small platform for rapid analysis and detection. Small sample volumes are required and the movement of the analyte through the channels enables real-time measurements with very rapid sample turn-around.[1]



Scheme 1: Reversible photochromic reactions of spiropyran

Furthermore, spiropyrans dyes in solution or following surface immobilization can be used as photonically controlled, self-indicating molecular recognition agents for the fabrication of sensors.[2]

When the colourless spiropyran (SPCOOH) absorbs UV light it switches to the highly coloured merocyanine form (MC), and this structure has an active binding site for certain metal ions. By shining white light on the colored complex, the closed spiropyran form is regenerated, and the metal ion is released (Scheme 1).

Array Fabrication

The microfluidic chip (3.5 x 1.5 cm) was fabricated using soft lithography techniques and it consists of five independent 94 μm depth by 160-210 μm width rectangular channels fabricated in polydimethylsiloxane (PDMS)/glass, Fig.1.

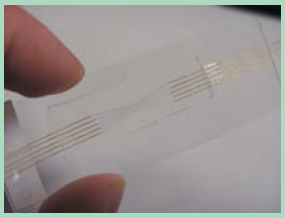


Figure 1: chip picture

SPCOOH is covalently bond and/or physisorbed in the PDMS microchannel surfaces after UV/ozone plasma (UV/O_3) activation.

Figure 2 shows the microscope images of the channels after each functionalization step and their contact angles. The UV/O_3 activated surface is more hydrophilic which increases SPCOOH adsorption into PDMS.

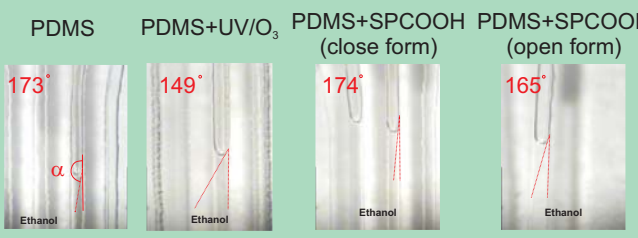


Figure 2: Optical microscopy images of the ethanol meniscus inside the channel after each functionalization step of the chip

1- L. Basabe-Desmonts *et al. Anal. Bioanal. Chem.* (2008) *390*: 307-315.
2- R.J. Byrne *et al. J. Mat. Chem.* (2006) *16*: 1332-1337.

Results

Switching properties of the immobilized SPCOOH on PDMS chip walls

Channel walls containing SPCOOH were first irradiated with UV light for 1 min. to obtain the MC form and followed by green light to regenerate the SPCOOH form. Fluorescence was measured every 3 s. untill the fluorescence completely vanished, Fig.3a. Switching cycles SPCOOH↔MC were performed 5 times, and repeatable photo switching behaviour was evident , Fig.3b.

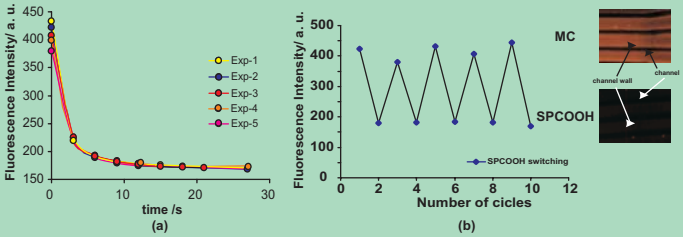


Figure 3: a) Channel wall fluorescence decreases while green light irradiation is applied. b) Fluorescence plotted from the channel walls during switching cycles

Metal ion interactions with SPCOOH immobilized on the PDMS chip walls

Stock solutions of several ion metals (Ca^{2+}, Zn^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}) were pumped independently through the four channels; different optical responses were observed for each metal. Fluorescence intensity increases or reduces differently for each metal, Fig.4.

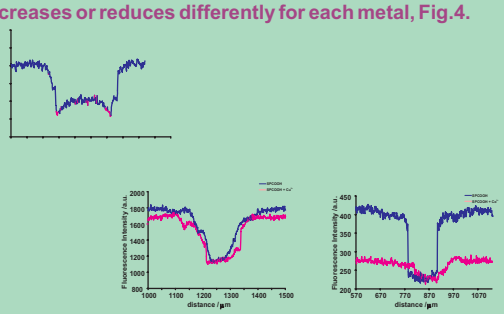


Figure 4: Fluorescence intensity of the MC form adsorbed in the PDMS channel walls in the presence of different metal ion solutions

Conclusions

The results presented here show that an array of microchannels in a PDMS chip which are functionalized with photochromic spiropyran can be fabricated as a non-specific fluorescent probe for online monitoring of metal cations.

The sensing effect can be activated/desactivated using light and metal ions can be easily captured and released.

This method combines the advantages of microfluidic arrays and the cost-effectiveness of microanalytical devices to develop microfluidics systems for chemical sensing. The combination of easily accessible microfabrication techniques and the straightforward channel functionalization enhance the toolbox for the fabrication of microfluidic systems for sensing application.

Acknowledgments

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