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DIRECTING FUNCTIONAL CHEMISTRIES ON MICROPATTERNED CONDUCTING POLYMERS FOR All-POLYMER CELL ANALYSIS MICROSYSTEMS

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ABSTRACT

Micrometer scale electrical circuits of PEDOT (poly(3,4-dioxythiophene)) were created by locally oxidizing PEDOT thin films with an agarose stamp containing the oxidizing agent NaOCl. The oxidized PEDOT was removed completely by applying detergents. The process was sufficiently mild that chemical groups on the underlying substrate, such as azides or alkynes, were preserved for subsequent specific functionalization. Moreover entire PMOXA (poly(2-methyl-2-oxazoline)) films preventing cell binding could be hidden below the PEDOT and be re-exposed upon stamping, allowing for cell capturing microelectrodes on a cell non-adhesive background. Chemically functionalized PEDOT types permitted the introduction of multiple additional types of micropatterned chemistry.

KEYWORDS: PEDOT, Conducting polymers, click chemistry, micropatterning, surface modification

INTRODUCTION

Microfluidic systems are becoming an important part of the chemical and bio-medical industries and research. However, conventional micro systems are currently not useful in many potential applications due to high fabrication costs. This limitation can be overcome by basing the systems exclusively on polymeric materials that allow large scale production at low cost. New functional materials and processing methods must be developed to produce versatile all-polymer devices. Relevant properties of microfluidic systems, such as electrical contact to specific surface areas and locally defined surface (bio)chemistry, should be supported by these novel materials and methods. Also, both materials and processing methods should be inexpensive.

Conducting polymers are highly useful materials for incorporating electrical functionalities into microfluidic systems, without the use of metals or silicon. PEDOT (poly(3,4-dioxythiophene)) is of particular interest due to its high conductance, chemical stability, cellular compatibility, and low cost. In this report we demonstrate a fast and chemically mild route for making conductive polymer PEDOT microelectrodes. The method avoids cleanroom processing and additionally allows presentation of multiple functional surface chemistries.

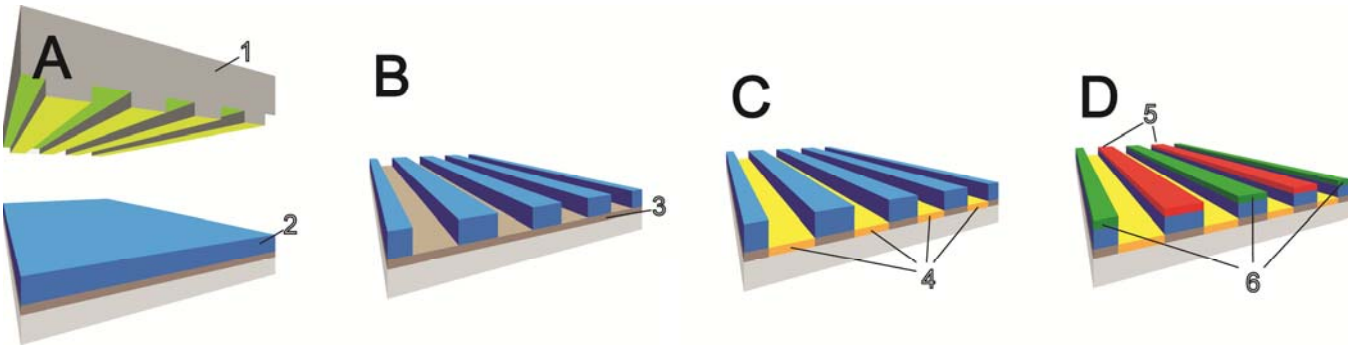

Figure 1: Scheme indicating the principle of the stamping procedure. A PEDOT, PEDOT-azide or PEDOT-hydroxide layer (2, blue) may be coated onto a click-reactive thin film (3). (A) Stamping with a micropatterned stamp (1) incubated with an oxidant (light green) will locally oxidize the PEDOT that (B) may be removed by washing, without affecting the underlying click-reactive groups. (C) These click-reactive groups can then be functionalized (4, yellow), or alternatively, a pre-functionalized surface can be used as substrate for the PEDOT thin film. (D) PEDOT-azide electrodes may subsequently be modified by separate types of chemistry (here illustrated by red (5) and green (6) coatings on alternating electrodes).

THEORY

Micropatterning of conducting polymers normally requires expensive photolithography. We have earlier reported an alternative patterning method, based on the observation that PEDOT loses its conductivity upon over-oxidation due to degradation of polymer conjugation [1]. The patterning method is based on physically contacting the film with a hydrogel stamp containing oxidizing agents (Fig. 1A). We have recently found that oxidization makes the PEDOT soluble, using proper

detergents (Fig. 1B). In this process, PEDOT is oxidized and removed, while alkyne or azide chemical groups hidden below the PEDOT film are spared. Thus fabrication of microelectrodes with a well-defined (bio)chemistry of not only the electrodes, but also of the areas between the electrodes, can be obtained over large surface areas in few steps and without photolithographic processing.

EXPERIMENTAL

PEDOT, hydroxyl-modified PEDOT, and azide-modified PEDOT films were deposited on various substrates as described in [1-4]. Substrates tested included polystyrene-alkyne and polystyrene-azide thin films, azide functionalized glass, and PMOXA functionalized glass. Agarose stamps were fabricated as described in [1]. The agarose stamp was soaked in a 1-2.5wt% NaOCl aqueous solution, and blown dry prior to stamping. The surfaces were stamped for 2-5mins. After stamping the surfaces were rinsed in deionized water, washed for 10 mins in 0.1% Triton X-100 / 2% sodium ascorbate at 60°C, 20 mins in deionized water, and 10 mins in 80%/20% DMSO/H_2O, before finally re-oxidizing the samples in 10% Baytron C in water, and rinsing in deionized water. Alternatively 1% Triton X-100 was included in the NaOCl solution in which case the Triton X-100 washing step was left out. Following the stamping and washing procedure, the samples were functionalized using standard wet chemical reactions or by electroclick reactions as described in [2-4]. Cellular adhesion tests were conducted as in [3].

RESULTS AND DISCUSSION

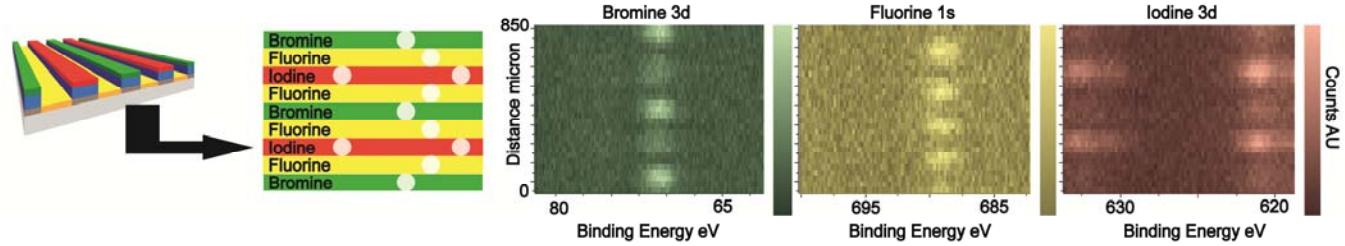

Figure 2: Demonstration of spatially defined triple chemistries on 100 µm wide PEDOT-N3 electrodes produced by stamping. The sketch (far left) shows the targeted chemical line patterns with alternating electrodes presenting bromine- or iodine-containing compounds with a fluorine-containing compound between electrodes. An XPS line scan perpendicular to the long axis of the electrodes reveals the presence of peaks from bromine (left line scan), fluorine (center line scan), and iodine (right line scan) at the intended surface locations. The electrodes were selectively functionalized with 1-bromo-4-ethynylbenzene and 5-iodo-pentyne marker molecules by applying electro-click reactions as described in [2-3]. Additionally the underlying PS-alkyne film was functionalized specifically with 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl azide, using a click reaction similar to in [4].

The use of a click-chemistry reactive azide-functionalized PEDOT film in combination with electro-click chemistry [2-3] permits individual functionalization of the conducting polymer electrodes (Fig 1D and Fig. 2). In combination with an underlying chemically orthogonal alkyne-functional polystyrene film, three types of localized chemistry can be introduced. This is illustrated in Fig. 2, where a local reaction of three types of click reactive molecules positioned at three different locations was conducted. Each of the reactants contained a specific halogen marker for individual identification by X-ray Photoelectron Spectroscopy (XPS).

In addition to demonstrating re-exposure of reactive functional groups as in Fig. 2, we have also found that an entire film of PMOXA (poly(2-methyl-2-oxazoline) can be hidden below the conducting polymer films and be re-exposed upon stamping. PMOXA films have antifouling properties similar to those of PEG, and are well suited for our process due to a higher hydrophilicity and higher oxidative stability than PEG. A PEDOT-azide film was patterned on top of a PMOXA substrate, and the PEDOT-azide electrodes were subsequently functionalized with a mixture of PEG-alkynes (cell non-adhesive) and RGD-tripeptide containing alkynes (cell adhesive). The samples were tested for cellular adhesion of 3T3 fibroblasts as shown in Fig. 3. Here we found that the PMOXA coating was intact and served as an low-binding background, whereas the cells attached to the functionalized electrodes.

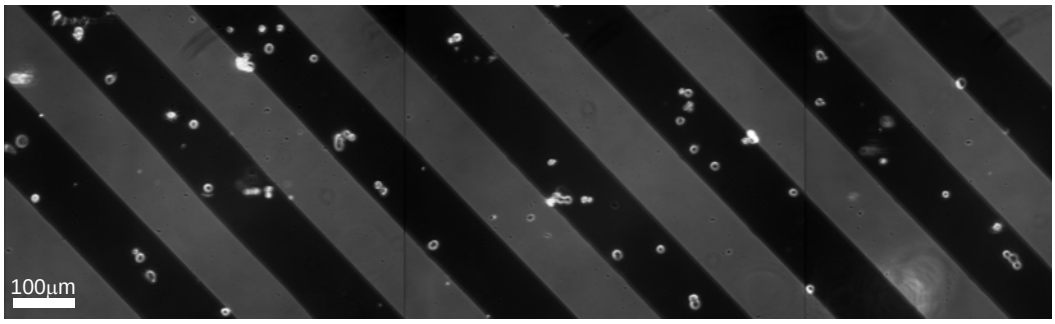

Figure 3: Phase contrast image of cells (bright spots) bound to 100 µm wide PEDOT-azide electrodes (darker areas) produced by the stamping procedure described and subsequently reacted with a mixture of RGD-alkynes (cell binding ligands) and PEG-alkynes (cell non-adhesive) to achieve specific cell attachment. The PEDOT-azide layer is deposited on a thin film of PMOXA that retains its cell non-adhesive properties upon re-exposure after the stamping procedure (brighter areas).

CONCLUSION

We have demonstrated a simple route for micro-patterning electrically conducting circuits by complete removal of conducting polymer thin films of the PEDOT type. The method is fast and inexpensive and avoids clean-room processing. The major advantage of the method presented, is that it is sufficiently chemically mild to preserve the underlying chemistries. This makes it possible to introduce multiple types of surface chemistries across all surface areas of the system by a simple process. The method allows micropatterning of (bio)molecules or cells, along with introducing localized conductivity. These features makes it is well suited for fabrication of advanced all-polymeric micro devices to be used in micro total analysis systems

ACKNOWLEDGEMENTS

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REFERENCES

[1] T.S. Hansen, K. West, O. Hassager, N.B. Larsen, “Direct Fast Patterning of Conductive Polymers using Agarose Stamping“ *Adv. Mater.*, vol. 19, pp. 3261-3265 (2007)

[2] T.S. Hansen, A.E. Daugaard, S. Hvilsted, N.B. Larsen, “Spatially Selective Functionalization of Conducting Polymers by "Electroclick" Chemistry” *Adv. Mater.*, 44, pp. 4483-4486. (2009)

[3] T.S. Hansen, J.U. Lind, A.E. Daugaard, S. Hvilsted, T.L. Andresen, N.B. Larsen, ”Complex surface concentration gradients by stencilled ”Electro Click chemistry“ *Langmuir*, 26, pp. 16171-16177 (2010)

[4] J.U. Lind, T.S. Hansen, A.E. Daugaard, S. Hvilsted, T.L. Andresen, N.B. Larsen, “Solvent Composition Directing Click-Functionalization at the Surface or in the Bulk of Azide-Modified PEDOT Macromolecules“ *Macromolecules*, 44, pp. 495–501 495 (2011)

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J.U. Lind[1], A.E. Daugaard[1], T.L. Andresen[1], C. Acikgöz[2], M. Textor[2], and N.B. Larsen[1]
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T. Scharnweber[1], R.K. Truckenmüller[2], A. Welle[1], and S. Giselbrecht[1]
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[2]*University of Twente, THE NETHERLANDS*

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[1]*McGill University, USA,* [2]*Northeastern University, USA, and*
[3]*University of Toronto, CANADA*

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[1]*University of Colorado, USA and*
[2]*National Institute of Standards and Technology (NIST), USA*

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[1]*Boston University, USA,* [2]*Boston Medical Center, USA, and*
[3]*Beth Israel Deaconess Medical Center, USA*

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[1]*Columbia University, USA and* [2]*University of South Carolina, USA*

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[1]*RIKEN Advanced Science Institute, JAPAN and* [2]*University of Tokyo, JAPAN*

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