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Lind, Johan Ulrik; Daugaard, Anders Egede; Andresen, Thomas Lars; Acikgöz, Canet; Textor, Marcus; Larsen, Niels Bent

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

J.U. Lind¹*, A.E. Daugaard¹, T.L. Andresen¹, C. Acikgöz², M. Textor² and N. B. Larsen¹

¹Technical University of Denmark, DENMARK and ²Eidgenössische Technische Hochschule Zürich, SWITZERLAND

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 micro-electrodes 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/H2O, 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.

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CONTACT
*J.U. Lind, tel: +45-22902060 Joli@nanotech.dtu.dk
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M. Ebara, K. Uto, N. Idota, J.M. Hoffman, and T. Aoyagi
National Institute for Materials Science, JAPAN

M10F HYDROGEL REACTIVE MICROBONDING (HRMB) METHOD FOR THE USE OF TETRA-PEG GEL AS A STRUCTURAL MATERIAL FOR MICROFLUIDIC DEVICES
University of Tokyo, JAPAN

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C.I. Rogers, J.V. Pagaduan, G.P. Nordin, and A.T. Woolley
Brigham Young University, USA

M12F CHEMICAL-LESS CELL PATTERNING VIA ELECTRICALLY ALTERED ITO SURFACE
J. Chang and L. Lin
University of California, Berkeley, USA

M13F DIRECTING FUNCTIONAL CHEMISTRIES ON MICROPATTERNED CONDUCTING POLYMERS FOR ALL-POLYMERIC CELL ANALYSIS MICROSYSTEMS
J.U. Lind1, A.E. Daugaard1, T.L. Andresen1, C. Acikgöz2, M. Textor2, and N.B. Larsen1
1Technical University of Denmark (DTU), DENMARK and 2ETH Zürich, SWITZERLAND

M14F GETTING THE GROOVE INTO SILICONE – LET LIGHT DO THE JOB
T. Scharnweber1, R.K. Truckenmüller1, A. Welle1, and S. Giselbrecht1
1Karlsruhe Institute of Technology (KIT), GERMANY and 2University of Twente, THE NETHERLANDS

M15F SUPERHYDROPHOBIC PERFLUOROPOLYMER MICRO- AND NANOSTRUCTURES BY EMBOSING
P. Suvanto, V. Jokinen, and S. Franssila
Aalto University, FINLAND

M16F CHARACTERIZING ELASTIC AND VISCOELASTIC PROPERTIES OF YOUNG AND AGED MOUSE OOCYTES USING A PDMS MICRODEVICE
X. Liu1, J. Shi1, Z. Zong1, R. Fernandes2, R.F. Casper3, A. Jurisicova3, K.-T. Wan2, and Y. Sun3
1McGill University, USA; 2Northeastern University, USA, and 3University of Toronto, CANADA

M17F MICROFLUIDIC TRANSPORT AND SENSING OF FUNCTIONALIZED SUPERPARAMAGNETIC BEADS WITH INTEGRATED SPIN-VALVES
W.R. Altman1, J. Moreland2, S.E. Russek2, B.W. Han3, and V.M. Bright1
1University of Colorado, USA and 2National Institute of Standards and Technology (NIST), USA

M18F A DISPOSABLE MICROFLUIDIC CHIP FOR DETECTION OF INFLUENZA TYPE A IN CLINICAL SPECIMENS INTEGRATING RNA ISOLATION, REVERSE TRANSCRIPTION, AND CONTINUOUS FLU PCR
M. Mahalanabis1, Q. Cao1, J. Chang1, C.A. Odell2, N. Pollock3, P. Mitchell2, J. Feldman2, and C.M. Klapperich1
1Boston University, USA, 2Boston Medical Center, USA, and 3Beth Israel Deaconess Medical Center, USA

M19F A MICROFABRICATED DIELECTRIC AFFINITY SENSOR FOR CONTINUOUS GLUCOSE MONITORING
X. Huang1, S. Li2, E.N. Davis2, R. Peltzman2, Q. Wang2, and Q. Lin1
1Columbia University, USA and 2University of South Carolina, USA

M20F A SELF-REFERENCING PAPER T-SENSOR FOR ANALYTE DETECTION
J.L. Osborn, L. Marshall, C. Holstein, C. Ball, B. Lutz, E. Fu, and P. Yager
University of Washington, USA

M21F BIOCHEMICAL SENSOR TUBING FOR POINT-OF-CARE MONITORING OF INTRAVENOUS DRUG INFUSION AND URINARY METABOLITES
C.J. Choi, H.Y. Wu, S. George, J. Weyhenmeyer, and B.T. Cunningham
University of Illinois, Urbana-Champaign, USA

M22F FIELD-PORTABLE REFLECTION AND TRANSMISSION MICROSCOPE FOR TELEMEDICINE APPLICATIONS
G. Biener, A. Greenbaum, S.O. Isikman, K. Lee, D. Tseng, and A. Ozcan
University of California, Los Angeles, USA

M23F FLOW-VALVE DIAGNOSTICS FOR SIMPLE, POINT-OF-CARE ANALYTE QUANTITATION
D. Chatterjee, S. Subedi, D.S. Mansfield, and A.T. Woolley
Brigham Young University, USA

M24F HIGHLY SENSITIVE MICRORNA DETECTION USING GOLD-NANO-PARTICLES ON POWER-FREE MICROFLUIDIC CHIP: TOWARDS POINT-OF-CARE EARLY-STAGE CANCER DIAGNOSIS
K. Arata1, H. Komatsu1, B. Han1, K. Hosokawa1, and M. Maeda1,2
1RIKEN Advanced Science Institute, JAPAN and 2University of Tokyo, JAPAN

M25F INVESTIGATION OF MOLECULAR TRANSPORT ACROSS SMALL BLOOD VESSELS IN A MICROFLUIDIC FORMAT
S. Pinto, Z. Abd Dezfouli, S. Vasothyran, S.-S. Bolz and A. Günther
University of Toronto, CANADA

M26F MICROFILTRATION DEVICE FOR CONTINUOUS, LABEL-FREE BACTERIA SEPARATION FROM WHOLE BLOOD FOR SEPSIS TREATMENT
K. Aran1, M. Morales1, L.A. Sasso2, J. Lo3, J. Zheng4, I. Johnson1, N. Kamdar1, A. Undar5, and J.D. Zahn1
1Rutgers University, USA and 2Penn State College of Medicine, USA