Selective Deposition of Conductive Polymer Films Using Agarose Stamps

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Statement of Purpose: Conductive polymers are attractive materials for biomedical applications due to their unique and tunable properties. Through adjusting the synthesis parameters, different properties of these polymers including volume, color, wettability, conductivity, and biocompatibility can be precisely tailored. These polymers have, therefore, attracted an increasing interest for a variety of applications ranging from flexible electronics and sensing to drug delivery and cell engineering. In particular, The biocompatible nature of polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) has enabled the application of these two conductive polymers for cell and tissue engineering, and biosensing. Surfaces with micro-patterned conductive polymers offer ideal platforms for high-throughput studies of cell differentiation, growth, and attachment. Here, we present an innovative and simple approach based on agarose hydrogel stamping (Majd S. Angew. Chem. Int. Ed. 2005; 44:6697-6700) to positively pattern conductive polymers on conductive substrates. This method allows for controlled and selective deposition of conductive polymers in a single-step process. The hydrated environment of hydrogel stamp is also ideal for inclusion of biomolecules, drugs, and growth factors in the deposited polymer network. In addition, this technique affords simultaneous deposition of different types of conductive polymers or different polymer/dopant compositions on a substrate in a one-step process.

Methods: In this study, we use PPy due to its biocompatible nature. Figure 1 displays the patterning process of PPy. First, agarose gel is cast in a negatively patterned PDMS mold with desired features. Upon gelation, the hydrogel is removed from the mold and its positive features are immersed in a solution of pyrrole and poly(styrenesulfonate) (PSS). After this absorption period, the "inked" stamp is placed on a conductive gold-coated or indium-tin oxide (ITO) substrate. A working electrode is attached to the conductive substrate, while reference and counter electrodes are placed in contact with the hydrogel stamp. Upon application of a voltage, polymerization and selective deposition of conductive polymer films occur on the substrate in areas of contact between the gel and the substrate.

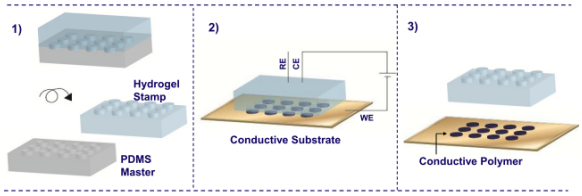

Figure 1. Direct printing of PPy on conductive substrates using hydrogel stamps.

Results: Using this technique, we patterned PPy films with circular features of 40 µm-1 mm diameter in ~1 cm^2 areas. We optimized the hydrogel stamping and film synthesis process by varying electrodeposition time (2-30 minutes), current density (0.2-0.8 mA/cm^2), hydrogel agarose content (1-4% *w/v*), and substrate material. Resultant patterned films (Figure 2) were characterized using optical microscopy, scanning electron microscopy, and impedance spectroscopy.

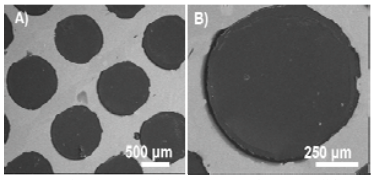

Figure 2. SEM image of patterned PPy films on gold..

We examined the changes in polymer film thickness with variation of electrodeposition time and found that average film thickness increased linearly from 550 ± 84 nm after 3 min deposition to 2200 ± 145 nm after 15 min deposition, as shown in Figure 3.

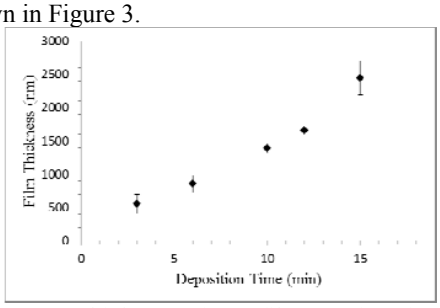

Figure 3. Thickness of PPy film as a function of deposition time at a constant current density.

Impedance spectroscopy measurements revealed a reduction in substrate impedance upon polymer film growth by approximately 16 %. This reduction is due to partial coverage of substrate with films of conductive polymer.

Conclusions: Here, we introduce a novel and simple approach to selectively deposit conductive polymers using agarose stamps. In this approach, topographically-patterned agarose hydrogels act as stamps that absorb monomer and dopant solutions and deliver these materials to conductive substrates where a polymer film is synthesized in areas of contact between the stamp and substrate upon voltage application. We examined the effect of different parameters on thickness, impedance, size, and topography of the resulting PPy films. The hydrogel stamp may be tailored to transfer different concentrations or types of monomers/dopants to the substrate by inking of individual posts of a stamp with different solutions. Future studies aim to incorporate drugs and biomolecules in patterned conductive polymer films for selective manipulation of cell adhesion, growth, or differentiation through local release of different drugs/proteins and selective electrical stimulation.