PFS PHOTONIC CRYSTALS FOR OPTICAL AND ELECTROCHEMICAL GLUCOSE SENSING

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ABSTRACT

We propose the construction of a biosensor based on photonic crystals of polyferrocenylsilane (PFS). The redox-activity of PFS, combined with the color of the photonic crystal, will allow for both optical and electrochemical readout. The photonic crystal will be directly written into a layer of polymer using two-photon lithography. We show that we are able to build structures of PFS using two-photon lithography and can perform electrochemical sensing using PFS. These are two important steps towards PFS photonic crystals for optical and electrochemical glucose sensing.

KEYWORDS: Electrochemical Glucose Sensing, Polyferrocenylsilane, Photonic Crystal, Impedance

INTRODUCTION

Polyferrocenylsilane (PFS) is a redox active polymer, with two functionalizable side groups per monomer (see figure 1). Multiple applications of this polymer have been suggested, from sensors [1] to displays made of photonic PFS crystals [2]. We aim at constructing a biosensor composed of PFS photonic crystals, which will allow for both optical and electrochemical readout. Fabrication of a PFS inverse opal photonic crystal with a colloidal opal as template was previously demonstrated [2]. Alternatively, we are directly writing the photonic crystal into a layer of polymer using two-photon lithography. This allows us to tailor the geometry of the crystal to the desired application, thus setting the wavelength at which the crystal is reflective. The swelling ratio of the polymer can be controlled by the amount of crosslinkable groups in the polymer and can therefore be optimized to give a desired color or impedance change of the crystal.

EXPERIMENTAL

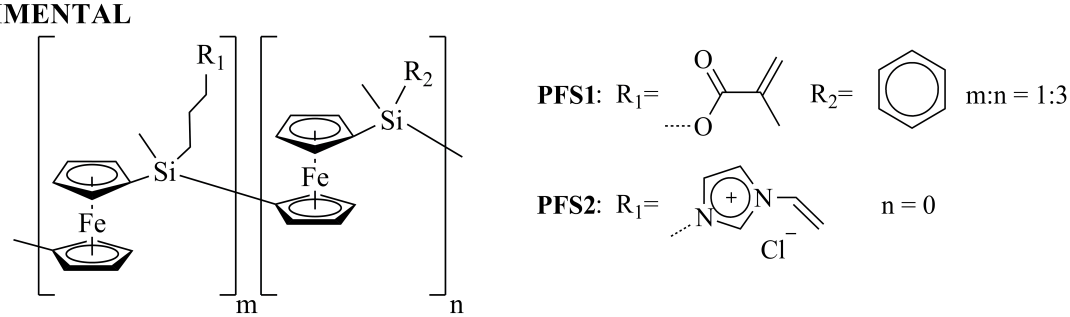

Figure 1: Polyferrocenylsilane (PFS) structures as used in this research.

Photonic crystals: For the two-photon polymerization we use **PFS1** (see figure 1). **PFS1** is a copolymer containing 75% phenyl-PFS-groups to increase the glass transition temperature and stiffness of the polymer and 25% methacrylate-PFS-groups to enable photocrosslinking of the polymer. Structures of **PFS1** were fabricated by crosslinking the polymer chains using two-photon lithography. A 1.5 wt.% concentration of Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one) was used to initiate the crosslinking.

Enzymatic sensing: Preliminary electrochemical glucose sensing measurements were performed with an aqueous solution (0.2 mg/mL) of **PFS2** (see Fig.1). Besides PFS, the measurement solution contained 0.2 mg/mL glucose oxidase (GOx), 0.1 M potassium chloride, and 50 mM acetic acid-sodium acetate buffer (pH 5.1). To this solution aliquots of a 0.1 M D-glucose solution were added. After every addition a cyclic voltammogram (CV) was measured between 0 and 0.8 V vs. Ag/AgCl (3M NaCl) with a scan rate of 50 mV/s. The working electrode was a screen-printed carbon electrode; a platinum spiral was used as counter electrode.

Electrochemistry of a PFS membrane: A porous PFS membrane was fabricated on top of a platinum electrode by mixing a layer of **PFS2** with poly(acrylic acid) (PAA) and weak base treatment. Electrochemical measurements on this layer were performed in a 0.1 M $NaClO_4$-solution containing 50 mM acetic acid-sodium acetate buffer (pH 5.1). A Ag/AgCl (3M NaCl) reference electrode and a platinum spiral counter electrode were used. CVs were measured between 0 and 0.8 V vs. Ag/AgCl, with a scan rate of 10 mV/s.

RESULTS AND DISCUSSION

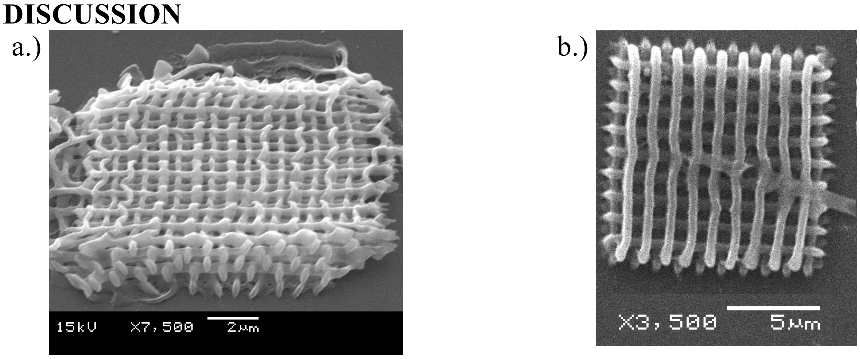

*Figure 2: Scanning electron microscope (SEM) images of woodpiles made of **PFS1**, fabricated using two-photon lithography. a.) The horizontal spacing between the rods is 1 μm; the vertical spacing between layers is 0.4 μm. b.) Horizontal spacing: 1.2 μm; vertical spacing: 0.4 μm.*

Photonic crystals: PFS1 woodpiles—composed of alternating layers of rods, with the rods in each layer perpendicular to the neighboring layers—were constructed by two-photon lithography. SEM-pictures of two of these woodpiles are shown in figure 2. Optimizing the process and designing the correct structure should in the future lead to PFS photonic crystals that swell upon oxidation and hence change color in response to the presence of an analyte such as glucose. Furthermore, the swelling of these structures will be measurable by impedance spectroscopy, allowing for exact quantification of the amount of analyte present.

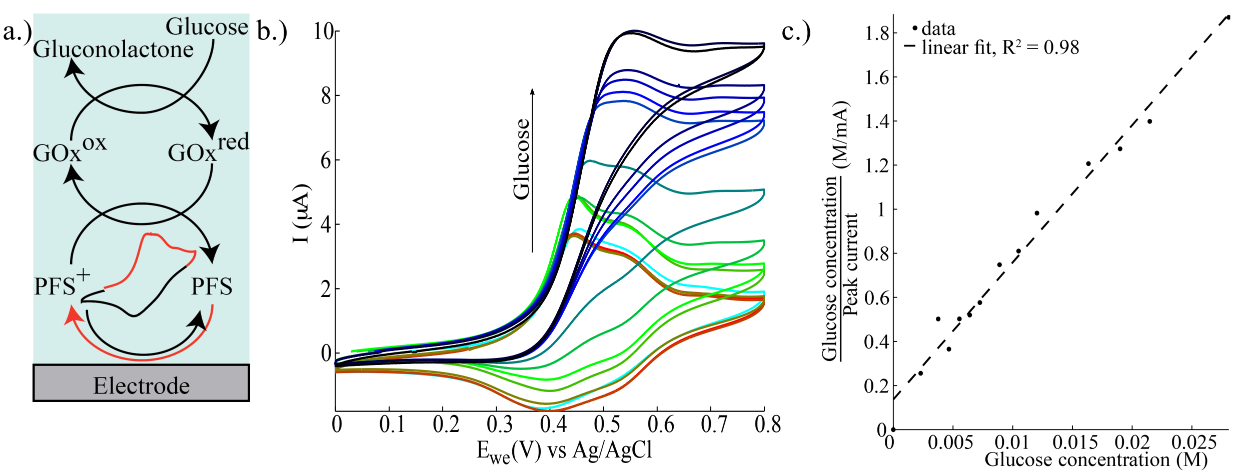

*Figure 3: Glucose sensing with **PFS2** in solution. a.) The (electro)chemical reactions that occur in the solution and at the electrode. b.) CVs showing increased oxidation peak current of PFS at the electrode with increasing glucose concentration. c.) Glucose concentrations and respective peak currents from the CVs plotted in a Hanes-Woolf plot. The linear relationship in this plot follows from Michaelis-Menten kinetics of the glucose oxidase enzyme.*

Enzymatic sensing: Preliminary electrochemical glucose sensing measurements were performed with an aqueous solution of **PFS2** (see Fig.1), the result of which is shown in figure 3. The response of this measurement follows the typical Michaelis-Menten kinetics in the range of 2.3 to 28.1 mM glucose, with a current increase of approximately 0.8 mAM^{-1} at the lowest glucose concentrations.

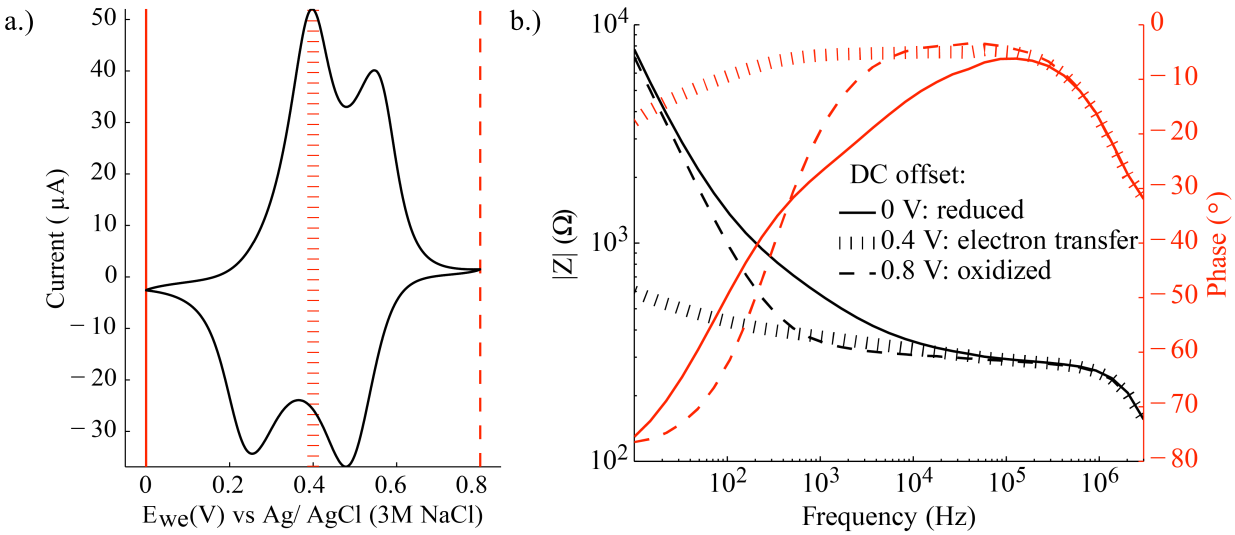

Figure 4: Electrochemistry of a porous PFS-membrane. a.) Cyclic voltammogram of a porous PFS membrane on a gold electrode. Red vertical lines correspond to the DC offsets used for impedance spectroscopy. b.) Impedance spectra of a porous PFS/PAA membrane, measured at DC offsets of 0 V (reduced; solid curves), 0.4 V (striped curves) and 0.8 V (oxidized; dashed curves).

Electrochemistry of a PFS membrane: A porous PFS membrane was fabricated by mixing a layer of **PFS2** with poly(acrylic acid) (PAA). Figure 4a shows a cyclic voltammogram of this membrane; figure 4b shows the impedance spectra of this membrane, measured at three DC offsets, showing clearly identifiable redox states. Combining the enzymatic sensing with a PFS-functionalized electrode will be our next step towards an enzymatic sensor with photonic crystals of PFS.

CONCLUSION

We are able to build structures of PFS using two-photon lithography. The next step is to build photonic crystals of PFS with a color that changes upon oxidation/reduction. Secondly, we show that we can perform electrochemical sensing using PFS. This makes us confident that we can eventually construct a PFS-based photonic crystal for enzymatic sensing which can be used for colorimetric, as well as electrochemical readout.

ACKNOWLEDGEMENTS

This work is part of the research program ChemThem Out-of-equilibrium Self assembly, which is financed by the Netherlands Organisation for Scientific Research (NWO).

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