

High-Resolution Inkjet Printing of a Functional Polymer for On-Chip Biosensing

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Summary

We present a surface functionalisation method based on high-resolution electrohydrodynamic inkjet printing of an azide-functional polymer bearing a reversible protein reporter layer for small-molecule detection. As proof of principle, we demonstrate a fluorescence assay of biotin on a silicon chip and localised functionalisation of a packaged photonic crystal, opening a route towards highly multiplexed label-free biosensing.

Keywords: Functional polymers, localised surface functionalisation, electrohydrodynamic inkjet printing, photonic integrated circuit, photonic crystals.

1. Introduction

In conventional on-chip assays, bioreceptors are delivered via microfluidics, which limits the minimum footprint available for multiplexing. Inkjet printing enables local functionalisation to reduce this footprint [1], and printing a target-specific functional polymer adds a further level of control [2]. However, conventional inkjet printing is limited to feature sizes larger than 20 μm and thus far these polymers have not yet been applied to photonic sensors. In contrast, electrohydrodynamic inkjet (EHD) printing can reach sub-micrometre resolution [3] but has mostly served flexible electronics and light-emitting diodes (LEDs) [4]. Here we demonstrate, for the first time, detection of a small molecule (biotin) by EHD printing of a commercially available functional polymer, and its local application on a packaged photonic crystal (PhC), expanding our previous work on printed polymer [5].

2. Materials and Methods

The reporter layer is a double-stranded alkyne-DNA (ds-alk-DNA) covalently grafted to EHD printed azide-polystyrene via copper-catalysed azide-alkyne cycloaddition (CuAAC). The DNA carries desthiobiotin, enabling reversible, competitive displacement of the protein streptavidin by biotin [6]. Az-PS at 2 mg/ml in dichlorobenzene was EHD-printed on untreated silicon with a sub-2 μm nozzle (SIJ-S050, SIJ Technology Inc.), then reacted by CuAAC with desthiobiotinylated ds-alk-DNA and incubated with Alexa Fluor 647–streptavidin for fluorescence readout

(FV1200 confocal microscope). Printing was also performed on a fibre-packaged SOI photonic integrated circuit containing PhCs, characterised by transmission around telecom wavelengths ($\sim 1.55 \mu\text{m}$).

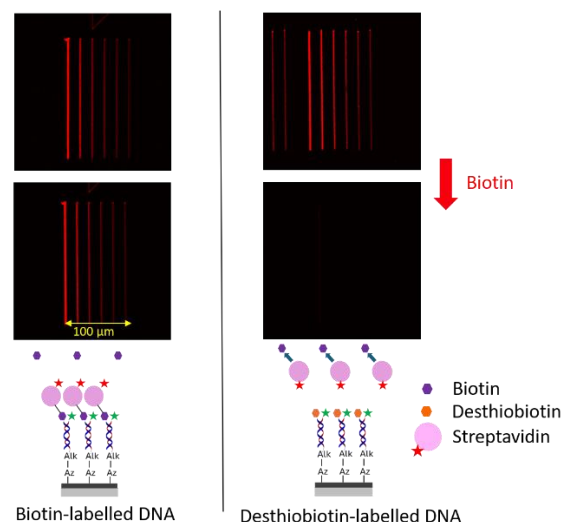


Fig. 1. Biotin sensing with streptavidin-bound to EHD-printed az-PS strips of variable thicknesses ($\sim 100 \text{ nm}$ to $\sim 10 \text{ nm}$ left to right). The fluorescence microscopy images were obtained from the fluorophore on the streptavidin (5% laser power)

3. Discussion

Az-PS strips $\sim 3 \mu\text{m}$ wide and 10–100 nm thick (AFM) were printed on untreated silicon. Following click chemistry with ds-alk-DNA and

incubation with streptavidin the fluorescence signal was localised to printed strips, scaling with strip height, with $S/N > 40$, confirming specific binding to the DNA-bound polymer (Fig. 1). Incubation in 1 mM biotin for 30 min returned the signal to near noise level for the desthiobiotinylated DNA while a biotin-modified DNA control showed no significant change, as expected. The result was reproduced on a nanostructured PhC surface and the surface regenerated by re-injecting streptavidin, demonstrating reversible biotin sensing (not shown here). On a slotted PhC packaged with optical fibres, post-printing transmission showed a photonic stop-gap with a sharp resonance, consistent with cavity creation at the printed centre (Fig. 2). This constitutes a clear demonstration of post-fabrication enhancement of a photonic stopgap by high-resolution inkjet printing while simultaneously establishing a route to local biofunctionalisation using the same clickable polymer platform. The polymer can subsequently be removed in an appropriate solvent to recover the initial PhC state.

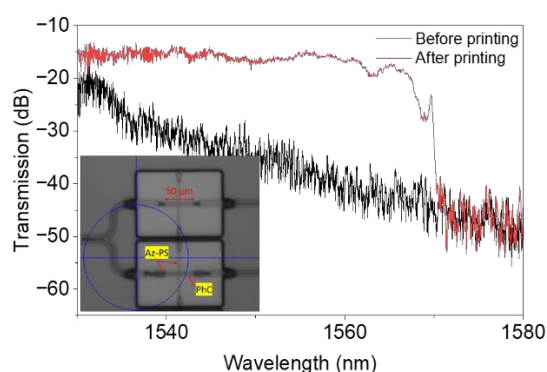


Fig. 2. Transmission spectra in water of a slotted PhC before and after EHD-printed az-PS. Inset: optical micrograph of the packaged PhC sensor with printed az-PS across and along the PhC waveguide.

References

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