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Surface Sunctionalization Strategies for the Design of Thermoplastic Microfluidic Devices for New Analytical Diagnostics

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Abstract : The development of micro total analysis systems is of major interest for contaminant and biomarker analysis. As a lab-on-chip integrates all steps of an analysis procedure in a single device, analysis can be performed in an automated format with reduced time and cost, while maintaining performances comparable to those of conventional chromatographic systems. Moreover, these miniaturized systems are either compatible with field work or glovebox manipulations. This work is aimed at developing an analytical microsystem for trace and ultra trace quantitation in complex matrices. The strategy consists in the integration of a sample pretreatment step within the lab-on-chip by a confinement zone where selective ligands are immobilized for target extraction and preconcentration. Aptamers were chosen as selective ligands, because of their high affinity for all types of targets (from small ions to viruses and cells) and their ease of synthesis and functionalization. This integrated target extraction and concentration step will be followed in the microdevice by an electrokinetic separation step and an on-line detection. Polymers consisting of cyclic olefin copolymer (COC) or fluoropolymer (Dyneon THV) were selected as they are easy to mold, transparent in UV-visible and have high resistance towards solvents and extreme pH conditions. However, because of their low chemical reactivity, surface treatments are necessary. For the design of this miniaturized diagnostics, we aimed at modifying the microfluidic system at two scales : (1) on the entire surface of the microsystem to control the surface hydrophobicity (so as to avoid any sample wall adsorption) and the fluid flows during electrokinetic separation, or (2) locally so as to immobilize selective ligands (aptamers) on restricted areas for target extraction and preconcentration. We developed different novel strategies for the surface functionalization of COC and Dyneon, based on plasma, chemical and /or electrochemical approaches. In a first approach, a plasma-induced immobilization of brominated derivatives was performed on the entire surface. Further substitution of the bromine by an azide functional group led to covalent immobilization of ligands through “click” chemistry reaction between azides and terminal alkynes. COC and Dyneon materials were characterized at each step of the surface functionalization procedure by various complementary techniques to evaluate the quality and homogeneity of the functionalization (contact angle, XPS, ATR). With the objective of local (micrometric scale) aptamer immobilization, we developed an original electrochemical strategy on engraved Dyneon THV microchannel. Through local electrochemical carbonization followed by adsorption of azide-bearing diazonium moieties and covalent linkage of alkyne-bearing aptamers through click chemistry reaction, typical dimensions of immobilization zones reached the 50 µm range. Other functionalization strategies, such as sol-gel encapsulation of aptamers, are currently investigated and may also be suitable for the development of the analytical microdevice. The development of these functionalization strategies is the first crucial step in the design of the entire microdevice. These strategies allow the grafting of a large number of molecules for the development of new analytical tools in various domains like environment or healthcare.

Keywords : alkyne-azide click chemistry (CuAAC), electrochemical modification, microsystem, plasma bromination, surface functionalization, thermoplastic polymers
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