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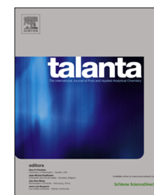

Disposable microfluidic sensor arrays for discrimination of antioxidants

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A microfluidic colorimetric sensor array was developed for detection and identification of various antioxidants. The sensor was fabricated by a photolithographic method, and consists of an array of printed cross-responsive indicators. The microfluidic design also incorporates pre-activation spots to allow printing of chemically incompatible components separately. Separately printed oxidizer allowed an oxidation of adjacent redox indicators only when aqueous sample was added to the sensor cartridge. Antioxidants were primarily detected by measuring the extent of inhibition of this oxidation reaction. Using this flow-based technique, a clear differentiation of 8 different antioxidants and 4 different teas has been demonstrated with 98.5% sensitivity.

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1. Introduction

Oxidative stress is a biochemical imbalance in which production of reactive oxygen species (ROS) or reactive nitrogen species (RNS) exceeds the cellular antioxidant capacity. While ROS are produced during normal cellular metabolism, excess ROS can cause oxidative stress, resulting in tissue damage and dysfunction through the chemical modification of structural or functional molecules (e.g., lipids, proteins, and nucleic acids) and alteration of redox-sensitive signaling pathways [1]. Consumption of antioxidants from fruits and vegetables has been suggested as a method to mitigate such oxidative damage, leading to increased popularity of antioxidant-rich foods, beverages, and supplements and a clear demand for identification and quantification of the antioxidant capacity in food and beverages.

Several direct and indirect methods have been developed to evaluate antioxidant activity of foods and beverages [2]. While there is no standardized method for measuring antioxidant capacity, common *in vitro* methods, such as ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) [3–5], DPPH (2,2-diphenyl-1-picrylhydrazyl) [3–5], and ORAC (oxygen radical absorbance capacity) [6–9] assays are often used. Other approaches include CUPRAC (cupric ion reducing antioxidant capacity) [10,11], FRAP (ferric reducing-antioxidant power) [9,12], electrochemical [13], and ESR (electron spin resonance) assays [6], along with Folin–Ciocalteu method [8,14]. All of these methods, however, are solution-based tests, requiring cumbersome sample preparation and handling.

Colorimetric sensor arrays (CSAs) present a new opportunity to measure antioxidant capacity, requiring little to no sample preparation while also allowing for discrimination of chemical components. Our CSA has been shown to discriminate a wide variety of chemical species based on their interaction with cross-responsive chromogenic dyes [15,16]. These CSAs have successfully differentiated various volatile analytes, including volatile organic compounds [17], toxic industrial chemicals [18–20], and microbial VOCs [21–23]. Zhang et al. first investigated liquid sensing capabilities of the CSA, and were able to discriminate 18 different aqueous solutions of organic compounds [24] and complex mixtures (represented by 14 commercial soft drinks and 18 commercial beers) [25,26]. Key to their success was employing a hydrophobic membrane and water-insoluble dyes, which minimized cross-reactivity to water and indicator leaching. By default, this approach is limited to the use of hydrophobic dyes and is not compatible with non-aqueous carrier solvents. A later generation array converted soluble dyes into insoluble nanoporous pigments by immobilizing the dyes in sol-gel matrices [27,28]. This improved sensor durability and performance for detection and identification of sugars. However, this method required pretreating sugars in the solution with boronic acid prior to any sensing experiments.

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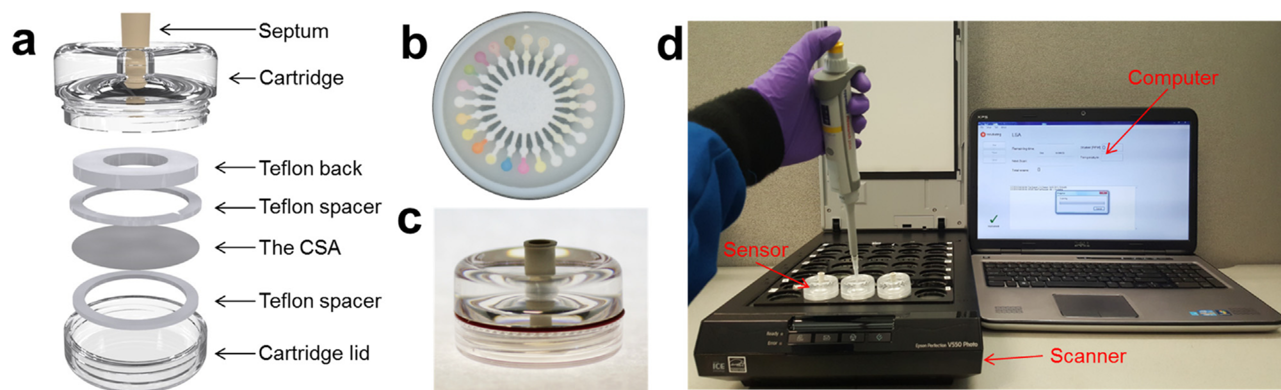

Fig. 1. Images of the disposable microfluidic sensor array used in study. (a) Exploded view of the sensor cartridge. (b) The CSA with 24 chromogenic indicators and 10 activators. (c) Fully assembled cartridge. (d) The CSA sensors on a flatbed scanner and a computer.

Recently, microfluidic paper-based analytical devices (μPADs) have attracted a lot of interest due to their simplicity, low cost and rapid analysis [29]. A variety of fabrication techniques, including photolithography [30–33], wax printing [34–37], inkjet printing [38–42], flexographic printing [43,44], and paper cutting-shaping [45–47], have been applied for the colorimetric determination of various analytes, such as metal ions [36,41,48], biomarkers [49], DNA [50], and foodborne pathogens [51]. Colorimetric μPADs are well suited to the consumer market, because they can be manufactured cheaply and only require a simple imaging device (e.g., a scanner or a digital camera) for sensor response measurement. Sharpe et al. have reported a colorimetric metal oxide paper-based sensing array for the analysis of antioxidant-containing samples [52]. Several classes of antioxidants, including flavonoids, phenolic acids and amides, and polyphenols, were used to generate a colorimetric database for antioxidant identification and quantification in the mM range. Their sensor has recently been used to study the effect of brewing conditions on the antioxidant capacity of commercial green teas [53]. However, this sensor has been developed for spot test analysis and not a multichannel microfluidic device.

Integrating paper-based microfluidics and colorimetric array technology will expand liquid sensing applications to the identification of a variety of chemical compounds and complex mixtures in solution. Herein, we report the development of such a device for the detection and quantification of antioxidants in solution. We enhanced the discriminatory power of the CSA for antioxidants by colorimetrically characterizing redox response. The sensor array primarily relies on the ability of antioxidants to prevent an activator-mediated oxidation of chromogenic redox indicators, which is reflected by a reduction in the intensity of color change. By printing an oxidizer adjacent to the redox indicators, we obviate the need to pre-treat the liquid analyte and analysis is accomplished in a single step in under 10 min. This sensor device can provide rapid, facile detection and discrimination of liquid solutions based on their antioxidant capacity. It also introduces the possibility of adding other types of solid state pre-activation agents to future generations of the CSA.

2. Experimental

2.1. Photolithographic patterning

All reagents were used as received without further purification. Photocurable monomers EBECRYL-8602 (aliphatic urethane acrylate) and EBECRYL-130 (cyclic aliphatic diacrylate) were acquired from Allnex. Photoinitiator Darocure 1173 (2-hydroxy-2-methylpropiophenone) was purchased from BASF. The two monomers were mixed in a 1:1 ratio, along with 1.0 wt% of photoinitiator. Cellulose paper (Whatman filter paper, Grade 4) was soaked in the resulting solution until air pockets were completely removed from the paper membrane. Photoresist soaked paper was then sandwiched between a photomask and a black plastic board. The photomask was prepared using an inkjet printer and a transparency film. Excess monomers were removed by flattening the photomask against the black board. The monomers were selectively polymerized with 70 mW/cm^2 of UV light (IntelliRay 600, UVitron) for 2 s. Patterned substrate was washed with acetone several times to remove any unreacted monomer. The patterned cellulose paper was re-exposed to the UV light for 1 min for complete curing before washing again in acetone and drying in air on a 50 °C hot plate.

2.2. The colorimetric sensor array printing

The pattern designed for the colorimetric liquid sensor array is shown in Fig. 1. The CSAs manufacturing procedures have been described previously, and the list of indicators used in this study is shown in Table 1 [33]. Each microfluidic channel has a unique indicator immobilized in plasticized polystyrene formulation (MW=35,000 g/mole, Sigma-Aldrich, ratio of polystyrene, Triton X-100, 1,2-dichlorobenzene and 2-methoxyethanol was 1:1:9:9 by weight; for redox indicators (indicators 1–10) 2-methoxyethanol was replaced with 1,2-dichlorobenzene to improve the dye solubility). Aqueous $Fe(NO_3)_3$ solutions (25 mM or 100 mM) were used to print activation spots for channels 1–10. Each indicator and activation solution was sonicated for 5 min before printing on the patterned cellulose paper with 50 nL slotted pins (V&P scientific). Printed arrays were dried under dry nitrogen at room temperature for at least 3 days prior to any sensing experiment.

The printed sensor was mounted inside a small plastic screw-top cartridge. Teflon spacer rings were placed on each side of the sensor to prevent the microfluidic channels from directly contacting the cartridge lid (Fig. 1). An additional Teflon ring was placed behind the sensor spots for uniform light reflection. A hole drilled in the cartridge lid allowed liquid sample to be injected through the septum in the center, so that the liquid sample traveled uniformly through 24 fluidic channels. To limit evaporation of the liquid analyte and ensure uniform analyte response, the lid hole was plugged with a rubber septum and the cartridge joint was wrapped with parafilm.

2.3. Sensing experiments

Ascorbic acid, caffeic acid, chlorogenic acid, citric acid, *p*-coumaric acid, gallic acid, glutathione, and salicylic acid were

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