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Disposable electrochemical paper-based devices fully fabricated by screen-printing technique

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ABSTRACT

This work presents a novel method for the full fabrication of electrochemical paper-based cells by screen-printing technology. Firstly, a mixture of ultraviolet curable inks was used for patterning hydrophobic barriers into chromatography paper. Afterwards three-electrode systems were coupled for electrochemical detection by printing successively carbon and silver/silver chloride inks over the hydrophilic areas. The resulting electrochemical cells were characterized by cyclic voltammetry in different redox systems and used for amperometric detection of ferricyanide.

1. Introduction

Paper has been used as substrate in analytical testing for a long time. However, there is a renewed interest around paper applications since the Martinez et al. report in 2007 [1]. In this work, the authors created well-defined, millimetre-sized channels, patterning photoresist onto chromatography paper to form defined areas of hydrophilic paper separated by hydrophobic walls. This simple device could be considered the origin of what are now called paper-based analytical devices (PADs). Two years later, Dungchai et al. introduced the electrochemical detection in PADs for the first time [2]. It was a very promising way to get analytical quantification for PADs and, since then, the research in this field has been intensive. The interest in electrochemical PADs (ePADs) relies on the own characteristics of the electrochemical detection, such as the availability of low cost readers, the selectivity by modifying the electrode surface and/or the adequate working potential, the feasibility of low detection limits and high sensitivities, but also relies on the inherent advantages of the paper such as self-power fluid transport by capillarity, high surface area/volume ratio, high capacity for reagent storage, biodegradable, easy hazardous waste disposal by incineration, etc. [3–6].

There are several patterning methods for the effective, simple and low cost fabrication of PADs, i.e. photolithography, analogue plotting, plasma treatment, inkjet printing, inkjet etching, paper cutting, wax printing, flexography printing, laser treatment or screen printing [7]. Surprisingly, even though screen-printing has been successfully used for massive production of disposable low-cost (bio)sensors [8], there are few reports about the full fabrication of PADs and ePADs by this technique. W. Dungchai et al. used a screen-printing machine for rubbing solid wax through a patterned screen onto filter paper. The patterned papers were heated so that the wax melted into the substrate to form hydrophobic barriers [9]. Another approach deals with polymer solutions. These mixtures can be used as conventional screen-printing inks. In this case, the solvent provides the penetration of the polymer chains to the bottom of the paper, creating 3D patterned hydrophobic barriers [10,11]. Banks et al. evaluated different kinds of paper for fully fabricated ePADs by serigraphy [12]. In this work, the authors demonstrated that functional ePADs can be printed on conventional papers, preferably universal office paper 80 $g \cdot m^2$. However, they also advised some problems with thick and high porous papers, such as filter papers, because the dielectric paste used for patterning the hydrophobic walls was ineffective to prevent the capillary wicking of the solution from the hydrophilic areas.

In this work we presented ePADs fully fabricated by screen-printing. Firstly, a mixture of commercial ultraviolet curable screen-printing and ink-jet inks was used to pattern hydrophobic walls across chromatography paper. Carbon and silver/silver chloride electrodes were subsequently printed. The resulting ePADs were characterized for several redox systems by cyclic voltammetry. Finally, the feasibility of these

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devices for electroanalytical applications was also demonstrated by amperometric detection of ferricyanide.

2. Experimental

2.1. Reagents and materials

Ortho-phosphoric acid 85% (w/w) and sulphuric acid 98% (w/w) were purchased from Scharlab (Sentmenat, Spain). Other chemicals were obtained from Sigma-Aldrich (Spain). They were analytical grade and were used without any further purification. Electrochemical measurements were carried out with a PGSTAT 128N potentiostat-galvanostat from Autolab (KM Utrecht, The Netherlands), using the software package NOVA 1.9. Screen stencils on aluminium frames with L-140.30 polyester meshes (mesh opening 39 μm) from NBC Meshtec Inc. (Kagoshima, Japan), Whatman chromatography paper 1# from GE Healthcare Life Sciences (Barcelona, Spain), two conductive inks (BQ 242 carbon and 5874 silver/silver chloride, from Dupont (Bristol, UK)), three UV curable inks (white Ultraswitch UVSW from Maribu (Barcelona, Spain), white IJR-400 from Taiyo Ink MFG. Co. (Saitama, Japan) and blue Jet UV curable CMYK from Collins Inkjet (Ohio, USA)), Thieme 110E screen-printing machine from Thieme GmbH & Co (Teningen, Germany), UV tabletop dryer Aktiprint T/A 40-2 from Technigraf (Hessen, Germany) and a natural convection oven PN 200 from Carbolite (Hope Valley, UK) were used for the ePADs fabrication. Rheological measurements were carried out on a Rheometer AR2000EX from TA Instruments (New Castle, USA).

2.2. Rheological characterization

The rheological tests were performed at 25 °C with parallel plate geometry (40 mm diameter stainless steel plane and 1 mm gap). A continuous ramp with an increasing shear rate from 1 to 1000 s^{-1} was applied during 5 min for each sample. The experimental data were fitted to the power law model ($\tau = K \cdot \gamma^n$), where τ is the shear stress, γ is the shear rate, n is the flow behaviour index (or a shear-thinning index when $n < 1$) and K is the power law coefficient or consistency.

2.3. Fabrication of the ePADs

100 ml Ultraswitch UVSW, 100 ml IJR-400 and 50 ml Jet UV curable CMYK were mixed and shaken manually. This mixture was rubbed onto the surface of the screen stencil with a squeegee, forcing the ink to pass through the mesh pores and penetrate into the chromatography paper. Then, the patterned papers were immediately introduced into the UV oven to cure the ink and define the hydrophobic walls of the ePADs. Afterwards, graphite and silver/silver chloride layers were successively printed and cured into the convection oven (120 °C, 5 min each). The paper area delimited by the hydrophobic walls was 65 mm^2 and the surface of the working electrode inside this area was 10 mm^2.

Table 1
Peak current and peak-to-peak potential values registered by cyclic voltammetry in different redox systems ($v = 100\ mV \cdot s^{-1}$).

Redox system	i_p (μA)	ΔE_p (mV)	n
Ferricyanide	−8.6 ± 0.6	56.4 ± 8.4	30
p-Aminophenol	14.4 ± 0.6	123 ± 10.4	15
Hydroquinone	10.4 ± 0.8	386.0 ± 15.6	15

2.4. Electrochemical measurements

The ePADs were connected to the potentiostat through a three pin connector (Fig. 1A). All electrochemical measurements were registered after dropping 5 μl inside the hydrophilic area and waiting 30 s for stabilization. The repeatability of the ePADs was tested for three redox systems [13–15], i.e. 1 mM ferricyanide in 0.1 M H_2SO_4, 1 mM p-aminophenol in 0.1 M phosphate buffer pH 7 and 1 mM hydroquinone in 0.1 M phosphate buffer pH 7. For this, cyclic voltammograms were registered at 100 $mV \cdot s^{-1}$ with ePADs of different printed sheets. In addition, kinetic studies for the ferricyanide system were also carried out by cyclic voltammetry. In this case, signals of 1 mM ferricyanide in 0.1 M H_2SO_4 were registered at scan rates between 100 and 1000 $mV \cdot s^{-1}$, and data were treated as described elsewhere [8]. Finally, amperometric measurements were also performed for ferricyanide in 0.1 M H_2SO_4. The currents registered after 5 s applying 0 V were considered for the calibration curve. The measurement of each point was repeated three times, using one ePAD for each repetition. The limit of detection was calculated as the concentration corresponding to three times the standard deviation of the estimate.

3. Results and discussion

Commercial screen-printing inks are not devised for patterning hydrophobic walls into hydrophilic cellulose fibre networks because they scarcely penetrate through the conventional paper substrates [12]. Conversely, the higher fluidities of ink-jet inks are more suitable for this goal although their rheological properties are inappropriate for conventional screen-printing technique. Taking into account these antagonistic properties, we considered that both kinds of inks could be mixed to get suitable UV screen-printing inks for patterning hydrophobic barriers in paper. Hence, different mixtures of one screen-printing ink (Ultraswitch UVSW) and two ink-jet inks (IJR-400 and Jet UV curable CMYK) were prepared and checked for screen-printing into

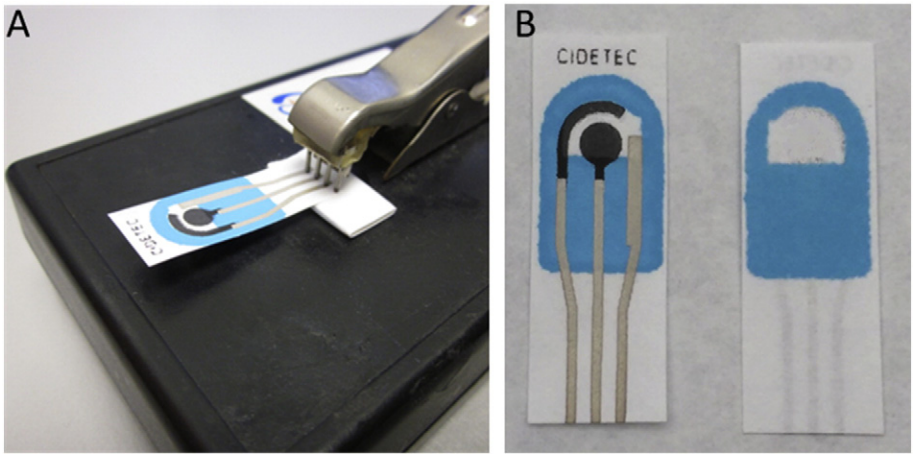

Fig. 1. (A) Three pin connector for the ePADs and (B) front and back side of the ePADs.