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Paper electrodes for bioelectrochemistry: Biosensors and biofuel cells

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ABSTRACT

Paper-based analytical devices (PAD) emerge in the scientific community since 2007 as low-cost, wearable and disposable devices for point-of-care diagnostic due to the widespread availability, long-time knowledge and easy manufacturing of cellulose. Rapidly, electrodes were introduced in PAD for electrochemical measurements. Together with biological components, a new generation of electrochemical biosensors was born. This review aims to take an inventory of existing electrochemical paper-based biosensors and biofuel cells and to identify, at the light of newly acquired data, suitable methodologies and crucial parameters in this field. Paper selection, electrode material, hydrophobization of cellulose, dedicated electrochemical devices and electrode configuration in biosensors and biofuel cells will be discussed.

1. Introduction

Paper (and paper-related) is probably one of the oldest manufactured material. From the early China and Egypt to the first book impression, paper is a support for transmission of knowledge. During the industrial revolution, paper together with the advances in printing has allowed the access to information to nearly everyone (as long as they were able to read). This has even been more popular with the access to personal printer and personal computers. In the scientific world, paper publications is the basis of scientific spreading and, despite most of the resources are nowadays electronically available, articles are still often printed by scientists. Paper itself has also lead to high achievement in science as depicted by the famous Whatman paper #1 found in every lab in the world.

The second part of the 20th century was the reign of silicon, when computers and the World Wide Web (internet) replaced progressively newspapers. Even in the lab, paper filters are replaced by polymeric beads, silica membranes for chromatography or by organic filters. One could expect that the age of paper should end soon but it is without considering the exhaustion of non-renewable resources and of the availability of silicon of high purity. Therefore paper will probably remain an important material for data storage and dissemination in the next years.

Paper could offer some new alternatives and opportunities as material because it benefits for centuries of accumulated knowledge. It is obtained from renewable (inextinguishable) resources and could be manufactured in different form (filter paper, glossy paper, kraft paper …) to achieve the desired properties. It could be as strong as cardboard or as light as rice paper. One of its main interests is its low price and high availability worldwide.

Interestingly, the most important application of paper in the scientific community during the last five years was the development of single-use and wearable point-of-care diagnostic devices (POCD).

The key publication in this field is the assembly in 2007 of a microfluidic paper-based analytical device (PAD) by members of the Whitesides' group (Martinez et al., 2007). In this work, microfluidic channels and individual test zones were designed in a chromatography paper using a photoresist to allow the simultaneous colorimetric detection of glucose (using glucose oxidase and horseradish peroxidase) and protein (using a tetrabromophenol blue as protein specific dye) in the same sample. This work has yet unveiled the main interests of what is now called microfluidic paper-based analytical devices (μPAD): sample volume is as low as 5 μL, multiplex analysis of single sample is possible in a short time range (about 11 min for all analytes), solid contaminants do not migrate on the test zones and the overall device cost is low. Moreover, it could be used by non-trained person, it does not require any pumping system or specific reader and it is easily wearable. Therefore, these simple assays are suitable for emerging

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Table 1
Analytical characteristics of ePAD used as biosensors.

Analyte	Electrode	Detection	Paper	LOD	Dynamic range	Sensitivity	Stability	Reference
Amperometry								
Ascorbic acid, uric acid, paracetamol	Pencil drawn electrode	$[Fe(CN)_6]^{3-}$	Whatman #1					Dossi et al., 2013a, 2013b
Uric acid, ascorbic acid	Gold	Direct oxidation	Whatman #1	0.2 mM		64–152 nA mM^{-1}		Carvalhal et al., 2010
H_2O_2	SPE	Prussian Blue	Whatman #1	3.6 μM	3.6–100 μM	1.3 μA mM^{-1}		Dungchai et al., 2009
Glucose				210 μM	2–100 mM	64 μA mM^{-1}		
Uric acid				360 μM	5–35 mM	6 μA mM^{-1}		
Lactic acid				1380 μM	2–50 mM	40 μA mM^{-1}		
Glucose	SPE	Prussian Blue			0.5–5 mM	1 μA mM^{-1}		Dungchai et al., 2011
Iron	None (colorimetric)	Phenanthrolin						
Glucose	Carbon ink	$[Fe(CN)_6]^{3-}$	Whatman #1	0.35 mM	0–20 mM	0.041 μA mM^{-1}		Zhao et al., 2013
Lactic acid				1.76 mM	0–25 mM	0.0076 μA mM^{-1}		
Uric acid				0.52 mM	0–10 mM	0.048 μA mM^{-1}		
Single-strand DNA	Golds NPs on SPE	HRP (direct oxidation)	Whatman #1	6.3 fM	10.0 fM to 100 nM			Wang et al., 2014a
Glucose	Graphite pencil	Glucose oxidase/4-aminophenol	Whatman #1	0.38 μM	0.01–1.5 mM		5 days at 2–8 °C	Santhiago and Kubota, 2013
Carcinoembryonic antigen	Golds NPs on SPE	NADH oxidation	Whatman #1	0.85 pg mL^{-1}	0.001–1000 ng mL^{-1}			Wang et al., 2014b
Lactate	Prussian Blue SPE	Lactate oxidase/H_2O_2	Cotton	0.3 mM	0.1–5 mM	0.3169 mA mM^{-1}		Malon et al., 2014
Glucose	SPE	$[Fe(CN)_6]^{3-}$ dried on paper with Glucose oxidase	Whatman #1	0.22 mM	0.43 mA mM^{-1}			Nie et al., 2010b
Cancer cells (SK BR-3)	Platinum NPs on SPE	H_2O_2	Whatman #1		0.10 nM–1.0 mM			Liu et al., 2014b
Adenosine	SPE	Glucose oxidase $[Fe(CN)_6]^{3-/4-}$ concentration difference	Whatman #1	11.8 μM	0–250 μM	0.48 mA mM^{-1}		Liu et al., 2012b
Lactate	Graphene	H_2O_2		0.3 μM	0.1–15 μM	13.1 nA μM^{-1}		Labroo and Cui, 2014
Glucose				0.3 μM	0.1–15 μM	13.3 nA μM^{-1}		
Cholesterol				0.3 μM	0.1–15 μM	29.3 nA μM^{-1}		
Xanthine				0.3 μM	0.1–15 μM	14.6 nA μM^{-1}		
Cholesterol	Polyaniline/poly (vinylpyrrolidone)/Graphene on SPE	Cholesterol oxidase/H_2O_2	Whatman #1	1 μM	0.05–10 mM	35 μA mM^{-1} cm^{-2}		Ruecha et al., 2014
Photo-induced amperometry								
Carcinoembryonic antigen	CdS/ZnO CNTs on SPE	Ascorbic acid	Whatman #1	4 pg mL^{-1}	0.01–50 ng mL^{-1}			Wang et al., 2013a
ATP	CdS quantum dot and CNTs on SPE	H_2O_2/Gold	Whatman #1	0.2 pM	1–1000 pM	27 nA pM^{-1}	4 weeks at 4 °C	Ge et al., 2013a
Single wave voltammetry or cyclic voltammetry								
ssDNA	Gold nanoparticles on carbon	Methylene Blue		30 nM			Four weeks under nitrogen	Cunningham et al., 2014
Thrombin				16 nM				
Carcinoembryonic antigenalpha-fetoprotein Cancer antigen 125Carbohydrate antigen 153	Graphene oxide/chitosan on SPE	HRP/tetramethylbenzidineHRP/phenylene diamine	Whatman #1	0.01 ng mL^{-1}	001–100 ng mL^{-1}(CEA)		3 weeks at 4 °C	Wu et al., 2014b, 2013b
Glucose	SPE	Glucose oxidase /tetrathiafulvalene	Japanese paper		1–100 mM	0.055 μA mM^{-1}		Shitanda et al., 2013b
Carcinoembryonic antigen	CNTs/Chitosan on screen-printed electrodes	HRP/phenylene diamine	Whatman #1	0.01 ng mL^{-1}	0.05–50.0 ng mL^{-1}			Wang et al., 2012a
Cysteine	Doped pencil	Co(II) phtalocyanin	Whatman		0.5–10 mM	0.92 μA mM^{-1}		Dossi et al., 2014