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Doped pencil leads for drawing modified electrodes on paper-based electrochemical devices

Nicolò Dossi *, Rosanna Toniolo, Flavia Impellizzieri, Gino Bontempelli

Department of Food Science, University of Udine, via Cotonificio 108, I-33100 Udine, Italy

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ABSTRACT

A simple strategy is here described for assembling graphite-based pencil leads doped with electrode modifiers suitable for drawing electrochemical devices on porous materials such as paper in a very reproducible and easy way. They were prepared by mixing controlled amounts of the chosen modifier with different quantities of carbon powder (conductive material), sodium bentonite (binding agent) and sodium silicate (hardening agent). After pressurisation, these mixtures were extruded at room temperature from a suitable die in thin rods which were then inserted in commercial lead holders to facilitate their use for drawing electrodes on paper. Lead composition (80% graphite powder; 8% sodium bentonite; 12% potassium silicate) and their fabrication procedure were optimised by drawing working electrodes for paper-based electrochemical cells with leads prepared with different contents of their components and evaluating their performance by voltammetric measurements conducted on hexacyanoferrate(II). Two prototype species (decamethylferrocene and cobalt(II) phtalocyanine, chosen as model compounds displaying a reversible redox process and versatile electrocatalytic properties, respectively) were assayed for doping leads. A quite satisfactorily reversible electrochemical behaviour was observed for decamethylferrocene incorporated into graphite-based working electrodes drawn on paper-based cells (RSD% for peak height and peak potential of 4.1 and 2.4, respectively) and a good electrocatalytical activity towards cysteine and hydrogen peroxide was displayed by graphite-based working electrodes modified by cobalt(II) phtalocyanine.

1. Introduction

Nowadays there is an exponential increase of interest in the development of affordable, robust and user-friendly analytical apparatus. Microfluidic devices, with their reduced dimensions, low reagent consumption, poor waste production and easy portability, offer an excellent synthesis of these peculiarities and their suitability has been successfully proved by several applications to food, environmental and clinical analysis [1–8].

Recently, the use of both economic and sustainable substrates such as paper and emerging fabrication techniques exploiting commercial printers, have opened up new horizons for easily assembling simple and disposable devices representing valuable alternatives to sophisticated instrumentations which frequently require well-trained operators [9–15].

Electrochemical detectors (ECDs) appear to be particularly advantageous for paper-based devices, thanks to their small size, portability, low cost and high sensitivity [16–27]. Moreover, ECDs are usually driven by simple instrumentation requiring low electrical power sources which can be conveniently miniaturised and integrated in analytical systems suitable for in-field controls. Several paper-based electrochemical sensing platforms, characterised by high sensitivity and short analysis time, have recently been proposed for conducting analysis in either liquid or gas phase [28–31]. In these devices, electrodes are frequently assembled by screen printing technologies, using inks or pastes prepared by mixing suitably conducting materials such as carbon or metals powders with polymeric binders [32,33]. This procedure is rather time consuming because it involves three operative steps (printing, curing and final thermal treatment of the obtained pattern) and almost expensive in view of the large amount of ink required with respect to the yield achieved [34,35].

Only more recently, the use of commercial lead pencils, consisting of graphite particles mixed with clay, which are well suited to mark lines on paper, has been proposed for drawing on paper electrodes with the desired geometry [36,37]. This approach proved to be profitable for rapidly assembling paper-based amperometric detectors with hand-drawn graphite-based electrodes. The use of portable writing tools such as lead pencils

* Corresponding author. Tel.: +39 0432 558835; fax: +39 0432 558803.
E-mail address: nicolo.dossi@uniud.it (N. Dossi).

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for electrode fabrication, already recently applied to the development of chemoresistive gas sensors and microfluidic devices [38–41], appears to be particularly attractive for assembling inexpensive devices in developing countries and resource-limited remote regions where advanced technologies and infrastructures are not available. This notwithstanding, electrodes drawn by commercial pencil leads make only possible the detection of analytes which are electroactive at bare carbon surfaces, because immobilisation onto pencil lines of suitably tailored modifiers to improve sensitivity and/or selectivity appears to be quite difficult. Hence, to achieve a significant extension of the use of pencil drawn electrochemical sensors assembled on paper or other porous supports, the development of pencils leads doped with modifiers displaying mediator, enzymatic or electrocatalytical properties appears to be particularly desirable.

In this article we describe for the first time a simple procedure for assembling homogeneously doped pencil leads. They are prepared by a procedure different enough from that usually employed for commercially available pencils, to avoid undesired heating steps able to cause modifier decomposition. It involves mixing of controlled amounts of the desired mediator with carbon powder (conductive material), sodium bentonite (binding agent) and sodium silicate (hardening agent). The resulting mixture is then forced within a thin metal tube to build up rods which can be mounted on lead holders. The performance of these pencil leads was evaluated by voltammetric measurements conducted in miniaturised paper-based cells, each defined by a circular hydrophobic wax barrier, where three electrodes with the desired design and size were hand-drawn carefully. We report here the good results found by assaying pencil leads both undoped (in the presence of hexacyanoferrate(II) as the prototype redox species) and doped with either decamethylferrocene or cobalt(II) phtalocyanine. The first modifier was chosen as model compound displaying an excellent reversible behaviour, while the latter was used as a prototype species displaying electrocatalytical properties towards thiols [42] and hydrogen peroxide [43].

2. Experimental section

2.1. Chemicals and instrumentation

Potassium chloride, potassium hexacyanoferrate(II), cobalt(II) phtalocyanine, decamethylferrocene, sodium acetate, acetic acid, sodium bentonite, cysteine, hydrogen peroxide and potassium sylicate were purchased from Sigma-Aldrich (St. Louis, MO, USA). Conductive carbon powder (325 mesh) was obtained from Alfa Aesar (Ward Hill, MA, USA).

0.5 M potassium chloride, 0.1 M sodium perchlorate or 0.1 M sodium phosphate (whose pH was adjusted to either 3.5 or 7.5 with phosphoric acid) solutions were prepared in pure deionised water and used as supporting electrolytes for voltammetric measurements. In all instances, high purity deionised water, purified by an Elgastat UHQ-P (Elga, High Wycombe, UK) system, was used.

Standard solutions (0.1 M) of potassium hexacyanoferrate(II) and cysteine were prepared by adding weighed amounts to known volumes of pure deionised water. Stock hydrogen peroxide solutions (0.1 M) were prepared by suitable dilution of the 30% w/w commercial product. Controlled amounts of these stock solutions were then added to the adopted electrolyte prior to each experiment, to achieve the desired concentrations.

All voltammetric and amperometric measurements were performed using a model 430 potentiostat (CH Instruments, Austin, TX, USA) driven by a CHI software 2.07 installed on a Pentium IV computer.

2.2. Pencil lead fabrication

Pencil leads were fabricated by using a stainless steel extruder, resembling a syringe, assembled on purpose. It consisted of a plunger moving inside a cylindrical tube, whose outlet was a circular orifice of 3 mm in diameter, which allowed cylindrical pencil leads to be extruded at room temperature. 0.4 g (80% w/w) of graphite were carefully mixed with 0.04 g (8% w/w) of sodium bentonite and 0.06 g (12% w/w) of potassium silicate (as a 26% w/w solution) and the resulting mixture was loaded inside the barrel and pressed with the plunger, by keeping the extruder gripped by a pipe vice, with the outlet opening plugged up. After removal of the plug, the plunger was pushed in order to extrude thin rods which were cut into pieces of about 30 mm. After drying for about 24 h at room temperature, they were inserted in lead holders.

Doped leads were prepared following the same procedure, but adding to the graphite mixture above 1% decamethylferrocene or 8% cobalt(II) phtalocyanine, respectively, both dissolved previously in dichloromethane. Such a procedure for pencil lead fabrication is schematically illustrated in Fig. 1A.

2.3. Preparation of paper-based electrochemical devices (PEDs) with pencil-drawn electrodes

Paper-based electrochemical cells were prepared by wax printing to pattern filter paper, according to a previously reported method [44]. Briefly, PEDs were prepared by printing with a Xerox Phaser 8570 DN printer a series of rings with black wax-based ink onto chromatography paper foils type 1 from Whatman (Maidstone, UK), to define the area of a set of cells. Heating at 120 °C for 10 min allowed the wax into the printed paper to be melted. Then, paper foils were cut into pieces, each consisting of a circular pad (12 mm in diameter) displaying a hydrophilic area of 50.24 mm^2, defined by a hydrophobic barrier. The back face of patterned paper was insulated by thermally laminating a polyethylene (PET) layer (0.1 mm) to prevent any electrolyte leakage during analysis. Subsequently, reference, counter and working electrodes with the desired design and size were drawn on the

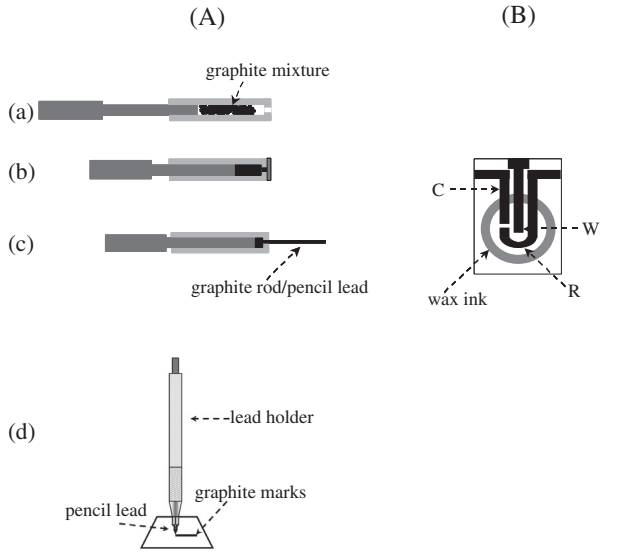

Fig. 1. (A) Schematic illustration of the fabrication process of pencil leads. (a) Graphite-based mixture is loaded inside the extruder; (b) pressure is applied by keeping the extruder outlet opening plugged up; (c) the plug is removed and the plunger is pressed to extrude graphite rods which are then cut into pieces; (d) pencil leads are inserted in commercial holders. (B) Layout of the pencil-drawn paper-based electrochemical cell (PED). W, R and C are working, pseudo-reference and counter electrodes, respectively.