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A novel microelectrode array combining screen-printing and femtosecond laser ablation technologies: Development, characterization and application to cadmium detection

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ABSTRACT

The elaboration of a new kind of microelectrode array based on femtosecond laser ablation and screen-printing process was reported. The electrochemical behavior of this sensor, constituted by a square array of 8×8 screen-printed carbon-based microelectrodes, was characterized by cyclic voltammetry (CV) and compared with macroelectrodes. With an interelectrode distance-to-electrode diameter ratio of 21, this screen-printed microelectrode array (SPμEA) has shown a superior diffusion behavior and a greater mass-transport. The analytical performances of this mercury modified SPμEA were evaluated for cadmium detection. Promising results were obtained with synthetic cadmium solutions in acetate buffer by square-wave anodic stripping voltammetry (SWASV) technique with a detection limit of 1.3 $\mu g\,L^{-1}$ and were confirmed with application to a river sample.

1. Introduction

Microelectrodes are regarded as powerful tools in many fields of electrochemistry. Indeed, due to their small dimensions, they offer many advantageous features such as low interfacial capacitance, low ohmic drop and faster mass-transport rate than conventional electrodes [1,2]. Their properties permit to exhibit steady-state currents without forced convection such as rotating disk electrodes. As a consequence these micro-sized electrodes open up a lot of interesting opportunities for clinical analysis [3] or environmental analysis [4].

If the use of microelectrodes shows a lot of advantageous properties, the very low currents recorded can be problematic and emphasize the need of a very sensitive equipment and a correct electrical isolation of the experimental device [5–7]. In the last decade, microelectrode arrays have been consequently developed in order to obtain higher current output compared to a single microelectrode [8–10].

Several microelectrode arrays arrangements have been published, but the most adopted layout is the array of microdisks electrodes. The number of disks in these arrays varied from a few disk electrodes [11] up to tens of thousands [12], with dimensions ranged from a few micrometers [11] to tens of micrometers [13]. The most adopted spatial disks distributions are square and hexagonal arrays. In all cases, the distance between microelectrodes must be sufficient to avoid shielding effects due to the overlapping of diffusion layers of adjacent electrodes. An interelectrode distance of at least 10 times the diameter of electrode was reported with the aim of circumventing this phenomenon [4,11].

These microelectrode arrays can be fabricated using different methodologies such as photolithography [10], sonochemical ablation of thin polymer films [14], or the randomly dispersion of conducting carbon microdisks in epoxy resin [7].

Only a few works have related to the use of screen-printing technology for microelectrode arrays development [15–17], although this technology represents a very attractive approach for the mass production of inexpensive and highly reproducible sensors [18,19].

In this paper, a new kind of sensor, micromachined by femtosecond (fs) laser ablation of a thin polymer membrane prior to screen-printing step was presented. Laser ablation was performed with a fs laser what permits to obtain a higher precision ablation with minimal damage due to a much smaller thermal diffusion depth than the most of conventional laser device. Another advantage of this technique is the reproducibility of micromachining [20]. Moreover, the screen-printing of an ablated membrane provides microarrays without modification of the characteristics of the conductive ink, due to the warm-up [21]. Furthermore, only recessed microelectrodes [22] or nanovials [23] can be obtained if the laser ablation occurs on a screen-printed membrane, which limits the

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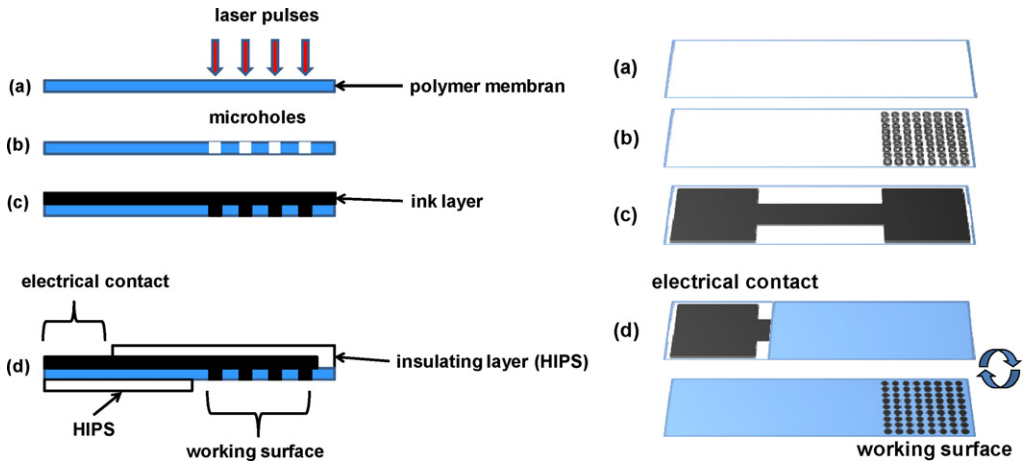

Scheme 1. Side and top views of different steps for microelectrode array fabrication (a) membrane of mylar (b) membrane after laser ablation, (c) ablated membrane after screen-printing, (d) side of screen-printed membrane after insulation showing the electrical contact and the other side of screen-printed membrane after insulation, showing the working surface.

mass-transport. With the process proposed in this article, the holes can be filled by the ink.

These screen-printed microelectrode arrays (SPμEAs) have been characterized by microscopy and their electrochemical behavior studied by cyclic voltammetry (CV). Three different geometries of arrays, with different interelectrode spacing, have been tested and their electrochemical response compared.

The analytical performances of this sensor were evaluated for cadmium detection in aqueous solution with square-wave anodic stripping voltammetry (SWASV). This electrochemical technique, extremely sensitive for measurement of a large variety of trace elements, is particularly well adapted for the developed sensor [24]. Mercury, because of its large hydrogen overvoltage and fast electrode kinetics for many metals [25,26], was chosen for the modification of the carbon-based working electrode surface. Due to the small overall surface of the SPμEA, only a low quantity of mercury (less than 1 μg) was sufficient to perform trace analyses, what is more environmentally friendly than the most of macroelectrodes and would authorize field analyses [27].

Further to the analyses in a synthetic medium, the robustness of this sensor was tested with a real sample coming from a polluted river close to a mine area.

2. Experimental

2.1. Apparatus

Electrochemical experiments were performed with an Autolab PGSTAT 302 potentiostat (Eco Chemie BV, The Netherlands) in combination with the GPES version 4.9 software. All voltammetric experiments were carried out using a three electrode cell composed of an Ag(s)/AgCl(s)/KCl (3 mol L^{-1}) reference electrode, a platinum wire auxiliary electrode and screen-printed sensors as working electrodes: conventional-sized (disk of 3.3 mm diameter) carbon-based screen-printed electrodes (SPEs) and SPμEAs.

Laser ablation was performed with a femtosecond (fs) laser device (Alfamet, Novalase, France) fitted with a diode-pumped KGW-Yb laser, described in detail elsewhere [28]. This laser delivers 360-fs pulses at 1030 nm in the 0.1–100 μJ range (at the sample surface) with a repetition rate variable between 1 and 10–000 Hz.

Optical microscopic views were recorded with a microscope Olympus BX 60 equipped with a digital camera. Objectives UplanFL 10X/0.30, UplanFL 20X/0.50, UplanFL 40X/0.75, UplanFL 100X/1.3 oil are used.

The microelectrode arrays were examined by Atomic Force Microscopy (AFM). Measurements were performed to probe the surface of the films using an Innova AFM (Veeco Instrument, Inc.). The images were scanned in tapping mode under ambient condition. Rectangular silicon cantilevers from BudgetSensor (Multi75AI-G-5) with a resonance frequency of about 75 kHz were used.

2.2. Chemicals and reagents

All solutions were prepared with Milli-Q water. Standard solution of cadmium (1000 mg L^{-1} in 1 wt% nitric acid) was obtained from Alfa Aesar. Solution of Hg^{2+} was prepared from the corresponding acetate salt $Hg(CH_3CO_2)_2$ (Fluka) in acetate buffer (0.2 mol L^{-1}, pH 4.5). The hexafluorophosphate salt of (ferrocenylmethyl)trimethylammonium $[Fc(CH_2)NMe_3]^+$ (FcTMA) was obtained by metathesis of the corresponding iodide salt. An acetate buffer solution (0.2 mol L^{-1}, pH 4.5), prepared with acetic acid (Fluka) and suprapur sodium hydroxide (Merck), was used as supporting electrolyte. Commercial carbon ink Electrodag® PF-407A was purchased from Acheson Colloids and high-impact polystyrene (HIPS) from Sericol. Mesitylen used for dissolve HIPS was obtained from Fluka. Polyethylene terephthalate (polyester, PET, PETP) film, 13 μm thick, was obtained from Goodfellow Cambridge Limited.

2.3. SPμEA fabrication

The elaboration of sensors was broken down into several steps. At first, arrays of 64 microholes (8 × 8) were made in a polymer membrane of polyethylene terephthalate, 13 μm thick, with an IR femtosecond laser ablation device. The fs laser was fitted with a 25 mm focal length objective providing a nominal laser beam diameter of 9 μm. The laser source operated at 10 kHz in order to micromachine the sensor as fast as possible while keeping the optimal ablation quality.

In a first step, the polymer membrane was fixed on a high precision (<1 μm) motorized XY stage fitted on the laser device. An array of 8 × 8 holes (Scheme 1b) was then obtained by ablating the polymer according to a programmed array trajectory combining the XY stage movement with the laser shots sequence. Each hole was drilled using 1000 fs laser shots at very low fluence (4.3 J cm^{-2}). Spacing between holes was adjusted to the desired value directly on the software of the laser system. In these conditions the time required to micromachine one sensor is estimated to be in the range of 100 s. Membranes obtained were observed by optical microscopy