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Electroanalytical applications of screen printed microelectrode arrays

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ABSTRACT

We report the fabrication of screen printed microelectrode arrays which are comprised of six working electrodes (50 μm radii) which are separated from their nearest neighbour by an average distance of 2272 (±0.3) μm and arranged in a circular configuration around a common counter and reference electrode. Due to their facile fabrication, different inks can be used to give rise to both graphite- and gold-based screen printed microelectrode arrays. Additionally due to their fabrication design, the microelectrodes comprising the array are sufficiently separated to ensure no diffusional overlap which is commonly encountered by microelectrode arrays reported within the literature.

The electrochemical sensing characteristics of the graphite screen printed microelectrode arrays are evaluated using acetaminophen, dopamine and nitrite giving rise to limits of detection (3σ) of 4.29, 3.24 and 5.24 μM respectively. Further to this, the gold-based screen printed microelectrode arrays are explored towards the electroanalytical sensing of chromium (VI) yielding a limit of detection (3σ) of 8.28 μM. Proof-of-concept is further demonstrated through the determination of chromium (VI) within an environmental (canal water) sample.

Due to the analytically useful responses observed at the graphite and gold screen printed microelectrode arrays, these disposable and economical electrodes hold promise for in-the-field sensing applications. Additionally the working electrode composition can be readily changed through the use of the desired screen printing ink (i.e. Pd, Pt, Cu, etc.) allowing the tailoring of the electrode surface enabling electrocatalytic microelectrode arrays to be readily derived.

1. Introduction

Microelectrodes are utilised by electrochemists due to their reported benefits, which include; improved Faradaic-to-charging current ratios, steady-state (or quasi-steady state) responses for Faradaic processes, reduced ohmic (*IR*) drop, and most importantly when used in sensing, improved signal-to-noise ratios allowing low detection levels to be reached compared to macroelectrodes [1–5].

The caveat with microelectrodes is that a very small Faradaic current is produced which can be hard or impossible to measure, especially due to their susceptibility to mains interference such that the Faradaic signal is engulfed beneath capacitively coupled mains interference [6]. As pointed out by Fletcher and Horne [6], to overcome this – that is, to decrease the interference – one has to place all electrochemical apparatus inside earthed screens, and wire all circuits in a common ground plane, greatly complicating the experimental design and significantly limiting sensor implementation into the field.

The well-known solution to overcome these problems yet still use the benefits of microelectrodes is to assemble multiple microelectrodes wired in parallel, with ideally, each microelectrode independent of its neighbours; such an electrode will exhibit all the useful properties of a single microelectrode but generate a signal which is significantly greater [6–10].

Microelectrode arrays present an opportunity for the integration in 'lab-on-a-chip' devices which can be used in a plethora of applications, such as in vitro and in vivo biological biosensing [11–16]. Typically microelectrode arrays comprise noble metals and are constructed in a variety of approaches (see reference [17] for a thorough overview) which involve sealing the chosen noble metal microwire within an inert substance, for example glass, so as to allow for realisation of micron sized electrode diameters whilst providing sufficient spacing between the microelectrodes comprising the array [18].

Approaches such as photolithography are thus favoured for the design and production of microelectrode configurations since they offer the ability to fabricate microelectrode arrays with well-defined geometric and inter-electrode spacing [19] such that diffusional interaction from neighbouring microelectrode comprising the array is minimal. Other approaches for the fabrication of arrays have reported the use of screen printing technology [20–24].

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Such a method of fabrication is highly advantageous due to their single-shot use alleviating the requirement for preparatory steps such as electrode polishing and also their low-cost nature allowing for economical sensor production without comprising performance or reproducibility [17].

In this paper we report a screen printed microelectrode array which comprises six microelectrodes of 50 μm radii, arranged in a circular configuration around a common counter and reference electrode and are separated from their nearest neighbour by an average distance of 2272 (±0.3) μm. Due to their design, these screen printed microelectrode arrays are diffusionally independent such that no diffusional interaction occurs between the individual microelectrode comprising the array; such a configuration is seldom reported within the literature and additionally very few microelectrode arrays are produced via screen printing technology.

The microelectrodes comprising the screen printed microelectrode arrays are fabricated to have working electrodes comprised of either graphite or gold, though an array of any desired noble material could also be realised by using the desired corresponding metal ink (i.e. Pd, Pt, Cu, etc.). Clearly, screen printed electrodes have been fabricated previously utilising both carbon [25] and gold [26] inks however such sensors are macro in size in comparison with the screen printed microelectrode array discussed herein. The microelectrode arrays are first characterised utilising the common electrochemical probe hexaammine-ruthenium (III) chloride and explored, in the case of the graphite microelectrode array towards the electroanalytical sensing of acetaminophen, nitrite and dopamine in the case of the gold microelectrode array, chromium (VI) and in all cases are found to yield analytically useful results. In the latter case, the sensing of chromium (IV) in an environmental sample is shown to be feasible suggesting these sensors have potential merit in the possible screening of water samples.

2. Experimental

All chemicals used were of analytical grade and were used as received without any further purification and were obtained from Sigma–Aldrich. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm. Voltammetric measurements were carried out using a Palmsens (Palm Instruments BV, The Netherlands) potentiostat.

The screen printed microelectrode arrays electrodes were fabricated in-house with appropriate stencil designs using a microDEK 1760RS screen-printing machine (DEK, Weymouth, UK). A carbon–graphite ink formulation (Gwent Electronic Materials, UK) was first screen printed onto a polyester flexible film (Autostat, 250 μm thickness). This layer was cured in a fan oven at 60° for 30 min. Next a silver/silver chloride reference electrode was included by screen printing Ag/AgCl paste (Gwent Electronic Materials Ltd., UK) onto the plastic substrate. Last a dielectric paste ink (Gwent Electronic Materials Ltd., UK) was printed to cover the connection and define the carbon–graphite working electrode, and the resultant recessed surface. After curing at 60° for 30 min the screen printed microelectrode array is ready to use. The gold screen printed microelectrode array was made in the same fashion using a gold polymer paste comprising dendritic gold (83–87%) with particles sizes in the low micrometres range (Gwent Electronic Material Ltd., UK) which has previously been reported upon within the literature [27] in place of the previously utilised carbon–graphite ink formulation. Fig. 1 depicts a schematic representation of the fabricated screen printed microelectrode array. Also shown in Fig. 2 are optical and scanning electron microscope images showing the configuration of the screen printed microelectrode array. All measurements were conducted using the screen-printed microelectrode array configuration which comprises 6 carbon–graphite

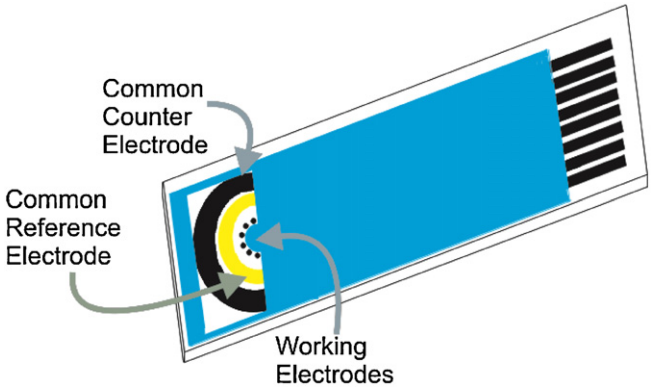

Fig. 1. A schematic representation of the SPMA fabricated entirely through screen printing technology.

geometric working electrodes with radii of 50 μm separated by an average of 2272 (±0.3) μm arranged in a circular configuration around a common carbon–graphite counter and a Ag/AgCl reference electrode.

Canal water was sampled at the edge of the canal bank (Rochdale Canal, Oxford Road, Manchester, UK) and collected in a polycarbonate bottle which was washed three times with canal water before being taken back to the laboratory. The sample was stored at room temperature and used within a day of sampling and was simply acidified with H_2SO_4 to a concentration of 0.05 M before electroanalytical measurements were commenced.

Scanning electron microscope (SEM) images and surface element analysis were obtained with a JEOL JSM-5600LV model having an energy-dispersive X-ray microanalysis package.

3. Results and discussion

3.1. Carbon screen printed microelectrode array (carbon SPMA)

The carbon screen printed microelectrode arrays (carbon SPMA) consist of six separate working electrodes (radii 50 μm) surrounding a common counter and reference electrode; images of the carbon SPMA are depicted in Fig. 2. Fig. 2A shows the entire screen printed disposable sensor, which upon closer inspection with an optical microscope (Fig. 2B) allows measurement of the centre-to-centre distance between the two closest microelectrodes. Since the electrodes are in a circular pattern, the top two microelectrodes are the closest electrodes together which have a separation corresponding to 2249.4 μm; this is relevant in discussions later in terms of the sensors electrochemical response. As shown in Fig. 2C, closer inspection with SEM reveals that the microelectrodes are not typically circular as is found in other microelectrode fabrication routes and is rather, akin to a matchstick head but should still approximate to that of a microelectrode. Note that the microelectrode size is controlled by the screen mesh size and this design is on the limit of fabrication; any smaller attempted electrodes sizes are not feasibly produced and is effectively limited by a combination of the screen mesh and graphite/carbon particle size (with agglomeration a significant factor) used within the commercially utilised screen printing inks. Last, further inspection of the microelectrode (Fig. 2D) reveals the surface to consist of conductive carbon particles and is consistent with previous reports of graphite screen printed electrodes [28,29].

The carbon SPMA were next electrochemically characterised using the redox probe hexaammine-ruthenium (III) chloride in 0.1 M KCl. Fig. 3 depicts the observed cyclic voltammetric signatures utilising the carbon SPMA using scan rates over the range 5–200 mV s^{-1}. It is evident through observation of Fig. 3 that at slow