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Transdermal microneedle sensor arrays based on palladium: Polymer composites

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ABSTRACT

The solvent based casting of metal particle-polymer mixtures has been investigated as a rapid means through which to produce a 10 × 10 array of pyramidal (200 × 200 × 350 μm) microneedles for electroanalytical sensing applications. The incorporation of nanoparticulate palladium powder within either a polycarbonate or polystyrene binder is shown to result in mechanically robust microneedles. The electrochemical properties of the resulting structures have been investigated and their application for transdermal sensing applications has been demonstrated through the use of epidermal/skin mimic.

1. Introduction

The application of microneedles for drug delivery applications is well established [1–4] but there has been an increasing interest in the transfer of the technology for sensing purposes [5–10]. The near painless transdermal insertion of the microneedle array offers considerable advantages over conventional sampling routes [4] but, in most cases, the devices are produced using relatively sophisticated microfabrication and micromachining processes that can severely compromise the accessibility of the technology [5–10]. The availability of silicone moulds for the production of polymer composite microneedles however, has revolutionised research into transdermal drug delivery [3,11–12] and, it could be envisaged that such systems would be an invaluable tool through which to develop electrochemical sensors. It can be postulated that the incorporation of metallic micro and nanoparticles within the composite formulation could speed the production of conductive microneedle arrays suitable for a range of biomedical applications. In this communication, the production of palladium microneedles has been investigated and their potential applicability for transdermal electroanalysis is demonstrated.

Palladium modified electrodes have been extensively exploited in a wide variety of electrochemical sensing applications in environmental [13,14], industrial [15,16] and biomedical contexts [17,18] and are typically employed in the form of micro-nanoparticulate catalytic clusters within composite constructions [13–16]. The latter typically involves carbon [13], carbon nanotubes [14] or graphene/graphene oxide [15–17] but, as yet, there are few reports of the use of Pd in microneedle architectures. Chandrasekaren et al. produced intricate Pd and Pd-Co alloy microneedles through electrodeposition onto micromachined substrates but their electroanalytical performance was not investigated [19]. It was therefore of interest to determine the viability of constructing microneedle structures based on a more accessible microparticulate Pd composite. The proposed strategy centred on the encapsulation of Pd powder (<1 μm diameter) within either polycarbonate or polystyrene binders. While the exploitation of these polymeric systems in microneedle fabrication is well established [3,20,21], the challenge here was to determine whether or not the inclusion of the metallic particles, at the ratio necessary to ensure adequate conductivity for electroanalytical purposes, would compromise the mechanical integrity and cohesiveness of the needle structure. The proposed approach is based on solvent casting mixtures of powder and polymeric binder into a silicone mould which, upon release, should produce a 10 by 10 array of needles with the dimensions indicated in Fig. 1A. Ideally, the needles should be of sufficient length and mechanical rigidity to penetrate the epidermis of the skin (typically 100 μm) without triggering the sensory cells [22]. In this communication, the formulation of a skin mimic (Fig. 1B) based on a calcium alginate hydrogel loaded with ferrocyanide as a redox probe was used to determine the electroanalytical properties of the composite Pd microarray. A parafilm™ barrier (~130 μm thick) was employed to act as the epidermal layer such that the ferrocyanide probe would only be accessible upon the needles successfully puncturing the top film.

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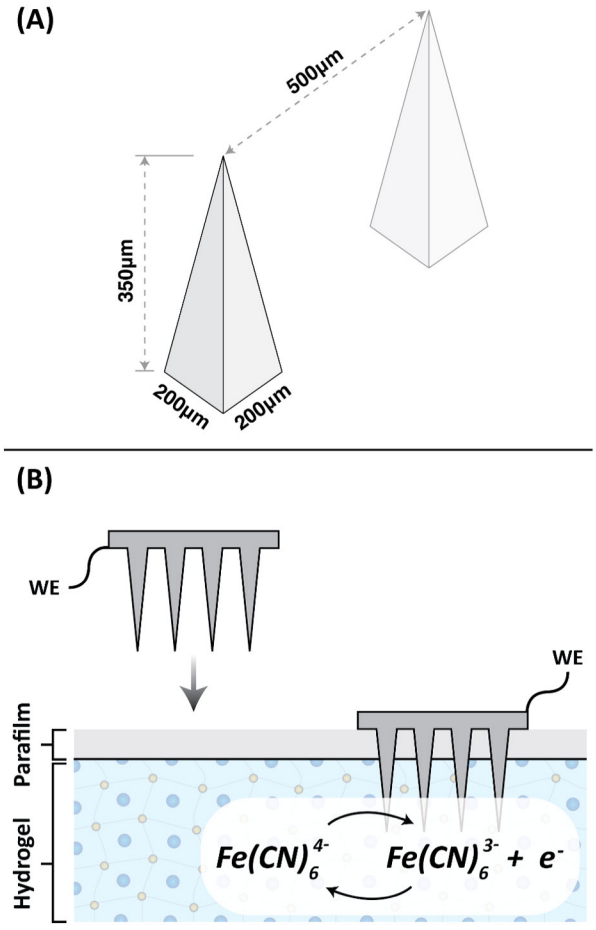

Fig. 1. A) Microneedle dimensions and B) Skin mimic employing a nonporous parafilm™ barrier and alginate hydrogel loaded with a ferrocyanide redox probe.

2. Experimental details

2.1. Materials

Palladium powder (<1 μm), polystyrene (avg. MW 192,000), L-cysteine (97%), potassium ferrocyanide (≥99%), acetone (≥99.8%), dichloromethane (DCM, ≥99.8%), and Parafilm M® were obtained from Sigma-Aldrich Company Ltd. (Dorset, England). Potassium chloride (99%) was obtained from Alfa Aesar (Lancashire, England) and silicone MPatch™ microneedle templates were purchased from Micropoint Technologies Pte Ltd. (CleanTech Loop, Singapore). All chemicals purchased were of analytical grade and used without any further purification.

2.2. Microneedle fabrication

Microneedle templates were cleaned prior to each use by way of sonication in acetone for 600 s and allowed to dry at room temperature. Needle casting involved a three stage process in which an initial 50 μL aliquot of DCM was introduced into a separate beaker, along with 50 mg of Pd powder. The Pd suspension was pipetted into the template and allowed to dry at room temperature - the intention being to precoat the needle surface with a greater quantity of interfacial Pd and enhance the electroanalytical performance. The second stage casting solution was prepared by dispersing 50 mg of Pd within 50 μL of a 50% w/v solution of polystyrene in DCM to form the bulk of the needles and initial baseplate. The final stage involved the introduction of a further 50 μL of 50% PS/DCM containing 50 mg Pd to form the top of the baseplate backing. The templates were subjected to centrifugal force at 3000 rpm for 300 s to facilitate the removal of air bubbles and enable efficient packing of the polymer/particle mixture within the needle structure. Following this, the remaining DCM was allowed to evaporate at room temperature and pressure for 4 h prior to demoulding of the microneedle array using adhesive tape. Electrical connection to the MN array was achieved through using silver conductive paint (RS Components Ltd., Northants England) to bond a length of silver wire (0.5 mm diameter, Goodfellow UK) to the front surface of one corner of the microneedle array to maximise the usable electrochemical surface area.

In order to improve the electron transfer kinetics of the microneedle array, surface modification by way of a self-assembling monolayer was employed. Due to the presence of thiol functional groups which can be readily adsorbed onto metallic surfaces, the array was submerged in a solution of 10 mM L-cysteine for 60 min. The array was then rinsed with distilled water prior to any electrochemical analysis.

2.3. Alginate preparation

Alginic acid sodium salt slowly was added to 0.1 M potassium chloride to produce a 1.5% w/v viscous solution. The mixture (typically 10 mL) was stirred for 4 h at 45 °C after which a 5 mL solution of 0.2 M calcium chloride in deionised water was added drop-wise against the edge of the beaker until the alginate solution was completely covered. The solutions were covered with parafilm and left overnight to induce complete cross-linking. In the case of gels containing the redox probe, solid potassium ferrocyanide was added to prior to adding the calcium cross linker to provide the required concentration (0.5 mM, 1 mM or 2 mM) based on a 15 mL total volume and stirred until dissolution was complete.

2.4. Characterisation

The fabricated microneedle arrays were characterised by way of digital optical microscopy (Nexus Aigo GE-5, Brunel Microscopes Ltd., England), focused ion beam scanning electron microscopy (Quanta 200 3D FIB/SEM, FEI Company, USA), and electrochemically (PG581 Portable Potentiostat, Bio-Logic SAS, France). Electrochemical measurements were carried out at room temperature 20 °C (±2 °C). Microneedles were sputtered under vacuum prior to scanning electronic microscopy using a 80:20 Pd/Au target at 30 mA for 3 min (Emitech K500X Sputter Coater, Quorum Technologies Ltd., England). An accelerating voltage of 5 kV was used to obtain the micrographs.

3. Results and discussion

Scanning electron micrographs of the resulting palladium-polymer microneedles are shown in Fig. 2A–C. The needle array is lifted directly from the mould and, as such, mechanical flexing of the latter is minimised and, it can be seen, the integrity of the needle structure is preserved upon removal. While the needles exhibit well defined geometry, there is, however, a degree of distortion where the sides of the pyramid can be seen to curve inwards. It is likely that this artefact is caused by shrinkage of the polymer resulting from the gradual removal of the solvent. No difference in morphology was observed when comparing Pd:polycarbonate or Pd:polystyrene structures with both displaying a granular surface highlighted in Fig. 2A–C and is attributed, primarily, to the particulate nature of the Pd component. The effect of the latter is emphasized when compared with the relatively smooth morphology of MNs composed solely of polymer. One such example is highlighted in Fig. 2D where the homogeneity of a polystyrene casting solution ensures more efficient filling of the needle void and results in greater definition.

It could be anticipated that the surface roughness observed in Fig. 2A–C could be addressed through increasing the proportion of polymer