3-D printed adjustable microelectrode arrays for electrochemical sensing and biosensing

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ABSTRACT

Printed electronics has emerged as an important fabrication technique that overcomes several shortcomings of conventional lithography and provides custom rapid prototyping for various sensor applications. In this work, silver microelectrode arrays (MEA) with three different electrode spacing were fabricated using 3-D printing by the aerosol jet technology. The microelectrodes were printed at a length scale of about 15 μm, with the space between the electrodes accurately controlled to about 2 times (30 μm, MEA30), 6.6 times (100 μm, MEA100) and 12 times (180 μm, MEA180) the trace width, respectively. Hydrogen peroxide and glucose were chosen as model analytes to demonstrate the performance of the MEA for sensor applications. The electrodes are shown to reduce hydrogen peroxide with a reduction current proportional to the concentration of hydrogen peroxide for certain concentration ranges. Further, the sensitivity of the current for the three electrode configurations was shown to decrease with an increase in the microelectrode spacing (sensitivity of MEA30:MEA100:MEA180 was in the ratio of 3.7:2.8:1), demonstrating optimal MEA geometry for such applications. The noise of the different electrode configurations is also characterized and shows a dramatic reduction from MEA30 to MEA100 and MEA180 electrodes. Further, it is shown that the response current is proportional to MEA100 and MEA180 electrode areas, but not for the area of MEA30 electrode (the current density of MEA30:MEA100:MEA180 is 0.25:1:1), indicating that the MEA30 electrodes suffer from diffusion overlap from neighboring electrodes. The work thus establishes the lower limit of microelectrode spacing for our geometry. The lowest detection limit of the MEAs was calculated (with $S/N = 3$) to be 0.45 μM. Glucose oxidase was immobilized on MEA100 microelectrodes to demonstrate a glucose biosensor application. The sensitivity of glucose biosensor was 1.73 μA mM^{-1} and the calculated value of detection limit ($S/N = 3$) was 1.7 μM. The electrochemical response characteristics of the MEAs were in agreement with the predictions of existing models. The current work opens up the possibility of additive manufacturing as a fabrication technique for low cost custom-shaped MEA structures that can be used as electrochemical platforms for a wide range of sensor applications.

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1. Introduction

An array of microelectrodes (MEA) shows many advantages over a conventional (individual) microelectrode such as increased mass transport, fast response times, decreased influence of the solution resistance, enhanced sensitivities, and the lower limit of detection (LOD) [1–3]. Further, studies have shown that individual microelectrodes show high mass-transfer flux and a low value of the potential drop, but have a very low current carrying capability due to the low cross section area. The MEAs are shown to increase the current carrying capability while maintaining the advantages of a single microelectrode with respect to mass diffusion and ohmic drop [4]. Each microelectrode of an MEA, however, has a diffusion layer associated with it. In order to make each electrode work as an individual microelectrode, the spacing between electrodes (for a given electrode width) in an MEA needs to be sufficiently large to avoid the diffusion layer overlap with the adjacent electrodes [5,6]. Since the noise level depends on the dimension of the individual electrodes whereas the signal strength depends on the total surface area of the electrodes, the size reduction of each

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individual electrode and the increase of the total number of electrodes, as in an MEA, is shown to improve the signal-to-noise (S/N) ratio and achieve lower LOD [5,7]. An excellent sensor action can be obtained by controlling the space between each microelectrode of MEAs to achieve maximum number of electrodes and avoid the overlap of the diffusion layer, while using the individual microelectrode for the sensing action.

Previously, lithography, template methods, or chemical self-assembly were explored to fabricate micro/nanoelectrode arrays [8–12]. Such methods typically involve the use of harmful chemicals, multiple fabrication steps and create material waste [13,14]. In addition, the material choices for sensor platforms are rather restricted due to the substrate compatibility with the chemical processes used. Lastly, a need for customized biosensors to each individual is emerging in specific applications which requires rapid changes in sensor circuitry to change the detection range and/or limit. The above fabrication techniques are not suitable for such rapid and customized changes to circuitry without resulting in a significant cost increase. Recently, direct write 3-D printing has become a valuable technique in a wide variety of applications, such as chemistry reaction container [15,16], microfluidics [17], sensors [18], photodetectors [19], graphene interconnects [20], and biomimetic structures [21]. However, few works have been achieved on the fabrication of microelectrode arrays with 3D printing technique [22]. The direct write printing method can 'write' microelectronic circuit on any surface without requiring the use of harmful chemicals and without creating material waste [23,24]. In addition to being scalable, this technique can allow rapid and customized changes to sensor design. Lastly, direct-write techniques can create sensors on any substrate as long as the substrate is hydrophilic and it allows highly complex/dense metal-polymer circuitry required for the electrochemical detection.

In this paper, we report design and direct-write fabrication of MEAs with adjustable array spacing as a platform for electrochemical sensing. The space between microelectrodes of the three fabricated MEAs is controlled to be 30, 100, and 180 μm, respectively. By using direct write 3D printing technique, it is easy to find the minimum spacing between electrodes on MEAs to get the maximum signal-to-noise (S/N) ratio. Sensor performance is demonstrated through the detection of hydrogen peroxide and glucose, chosen as model analytes. The sensitivity and accuracy of detection was determined as a function of the printed MEA structure geometry. The potential applications of this method for other types of electrochemical sensors are also discussed.

2. Experimental

2.1. Micro-electrode array fabrication

The MEAs were fabricated using aerosol jet (AJ) based direct-write technology that allows deposition of solvent based nanoparticles with solution viscosity ranging from 1 to 1000 cP. A schematic of the AJ system (AJ 300, Optomec Inc., Albuquerque, NM, USA) is shown in Fig. 1 and includes two atomizers (ultrasonic and pneumatic), a programmable XY motion stage, and a deposition head. Solvent based nanoparticle ink is placed in the atomizer which creates a continuous and dense mist of nanoparticles with a droplet size of 1–5 μm which is then transferred to the deposition head with the help of a carrier gas N_2. The mist or dense vapor is then focused and driven towards the nozzle with the help of a secondary gas (also N_2) to form a micro-jet. A UV apparatus (UJ35 UV cure subsystem, Panasonic Corporation, Osaka, Japan) connected to the machine can instantaneously cure the (UV curable) polymer. Primary materials used to fabricate the biosensor were silver nanoparticle ink (Perfect-TPS 40 G2, Clariant Group, Frank-
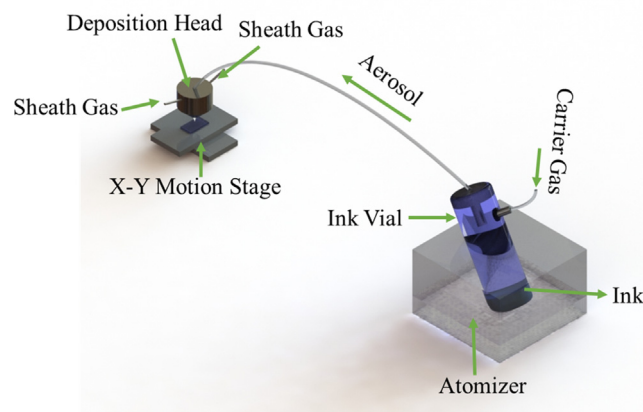

Fig. 1. Schematic of an aerosol jet micro-additive printer.

furt, Germany) and a UV curable polymer (Loctite 3105, Henkel Corporation, Düsseldorf, Germany). The silver nanoparticles had a size of about 30–50 nm with about 40 ± 2 wt% particle loading in the ink and a viscosity of about 1.5 cP according to the manufacturer data sheet. The viscosity of Loctite 3105 was 300 cP and was printed using pneumatic atomizer of the AJ system. Before printing the structures, ink material was placed in a tube which was rotated continuously around its axis for 12 h using a tube roller (Scilogex MX-T6-S, Rocky Hill, CT, USA) to prevent nanoparticle agglomeration within the ink. UV curable Loctite 3105 was stored without exposure to ambient light prior to printing. A transparent glass slide (Thermo Fisher Scientific, Waltham, MA, USA) was used as the substrate. Prior to printing, the substrates were cleaned in DI water followed by isopropyl alcohol. In order to make the substrate surface hydrophilic and to promote better adhesion of the printed material, the substrate was treated with an atmospheric plasma (Atomflo^{TM} 400, Surfx® Technologies LLC, Redondo Beach, CA, USA) at 100 W for 5 min.

In the current study, we used both, the ultrasonic and the pneumatic atomizer. The nozzle exit diameter to print the Ag electrode lines was 150 μm (the minimum line width is about 10 times smaller than the nozzle diameter based upon the sheath gas pressure). Three types of nozzle exit diameters, 150 μm, 250 μm, and 300 μm was used to print Loctite 3105 in order to achieve different trace width 30 μm, 100 μm, and 180 μm. While printing, the tip-to-substrate distance was always kept at 3 mm. All other parameters mentioned in Table 1 were optimized for the current work. The details for Ag and polymer printing is presented in following subsections.

a) Additive fabrication of micro electrode: a nanoparticle Ag ink is dispensed on the glass substrate using ultrasonic atomizer in order to fabricate conductive Ag traces at a length scale down to tens of micrometre. Before printing geometry of the conductive part was drawn in AutoCad (Autodesk, 2015) and converted to prg file compatible to the AJ software. The nozzle exit diameter used to print Ag traces was 150 μm. An atomizing flow rate of 25 sccm and a sheath gas flow rate of 50 sccm was used for printing. Width of the printed traces measured by a compound microscope was 15 ± 1.04 μm. The fingers of the sensors including interconnect and probing pad was printed using a single layer of printed material. During printing platen temperature was set to 80 °C.

b) Additive fabrication of micro-scale polymer trace: after printing the conductive silver traces, polymer traces were printed perpendicular to the silver traces in order to create micro electrodes.