SCALING EFFECTS OF INKJET MICROFABRICATED 3D GOLD ELECTROCHEMICAL SENSORS FOR AQUEOUS LEAD DETECTION

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ABSTRACT

This paper presents the scaling effects of the microfabricated inkjet printed (IP) gold microelectrochemical sensor (μECS) for aqueous lead detection. The microfabrication of the reported μECS utilizing IP additive manufacturing technology on shape memory polymer (SMP) is introduced for the first time in case of electrochemical sensing applications. The reported microsensor is simple, cost-effective, sensitive, and disposable. The dimension and area of the fabricated μECS is 4.23×4.23×1.52 mm^3 and 2.25 mm^2 respectively. The combination of IP and SMP for microfabrication offers quick maskless fabrication (10 minutes), simple and easy miniaturization (simultaneous curing and shrinking), cost-effectiveness (low sample volume), and high sensitivity (increased effective electrode surface area despite miniaturizing the device).

KEYWORDS

Additive Manufacturing; Inkjet Printing; Micro-electrochemical Sensor; Microfabrication;

INTRODUCTION

Lead (II) contamination causes severe damage to human and children (learning, behavioral, and developmental delay) [1]. Recently, the most adapted and widely used technologies for lead (II) detection are screen printed electrodes (SPE) [2] and lithography [4]. SPE is chosen due to its cost-effectiveness, favorable quality (bulk fabrication), and flexibility in the design [2]. However, this technology fails to provide consistency for batch to batch fabrication/materials and limits materials waste [3]. On the other hand, lithography (etching and lift-off) is extremely time consuming, expensive, and requires cleanroom facility and hazardous materials [4]. Hence, researchers have started focusing on inkjet-printing (IP) additive manufacturing technology for sensor fabrication [5]. This technology ensures high resolution, consistent fabrication quality, and cost-effectiveness. Our group has reported IP macro electrochemical sensor on shape memory polymer (SMP) for the first time for lead (II) detection at Sensors 2021 [6]. The dimension of our previously reported sensor was 13×10×1.52 mm^3 (after curing and shrinking). Currently, we are focusing on microsensor fabrication as it provides simplicity, cost-effectiveness, low fabrication time (macro sensor - 180 minutes and microsensor - 10 minutes), high reproducibility, and fast response time (120 seconds). We are considering IP and SMP for microfabrication as this combination offers quick maskless fabrication (simultaneous curing and shrinking), simple miniaturization (heating the printed sensor/substrate above glass transition temperature and below melting temperature), and high sensitivity (increased effective electrode surface area - miniaturization does not have any impact on effective electrode surface area). The fabrication, characterization, and evaluation of the reported microelectrochemical sensor (μECS) is illustrated in the following sections. Figure 1 represents IP gold (Au) μECS for aqueous lead (II) detection.

FABRICATION

The reported microsensor cell consists of an Au working electrode (WE), Au counter electrode (CE), and silver chloride (AgCl) reference electrode (RE). The pattern for the reported μECS is designed using CAD software (GIMP 2.10.30). We have changed the design compared to our previous sensor [6] because after downscaling (less than 500 μm spacing between electrodes), the electrodes were shorted after shrinking and curing. The pattern is then loaded onto the inkjet printer (DMP-2850). 50 nanometer diameter silver (Ag) nanoparticle conductive ink (ANP-DGP-40-LT-15-C) is used to print the pattern with 10 pL drop-on-demand piezoelectric nozzle. The drop spacing, cartridge temperature, platen temperature, and number of printed layers were investigated for microfabricating the μECSs. After critical investigation, the reported microsensor is fabricated with 20 μm drop spacing, 30°C cartridge temperature, 50°C platen temperature, and single layer of Ag ink. Each Ag IP pattern with dimension of 10.20×10.20×0.52 mm^3 (macro sensor) were placed in a preheated laboratory oven at 180°C for 2 minutes. Patterned Ag μECS is cured and shrunk simultaneously with approximately 58.5% reduction factor [6]. The sintered RE of the μECS cell is chlorinated using 3% sodium hypochlorite solution for 60 seconds. Au WE and CE are obtained with 24K brush gold plating technology. Figure 2 illustrates fabrication processes of the reported microsensor. Finally, scanning electron micrograph (SEM) images were analyzed to characterize the 3D topology of the nanomaterials used for microfabrication.

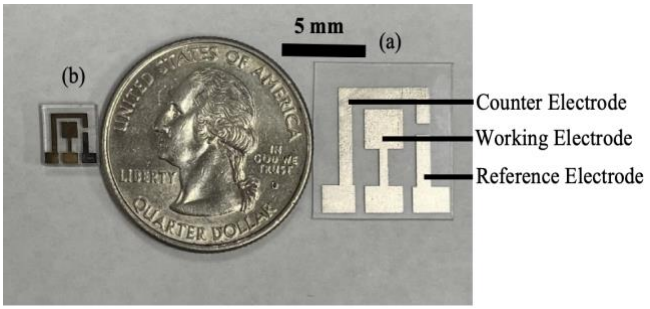

Figure 1: (a) Inkjet printed (IP) silver (Ag) working electrode (WE), counter electrode (CE), reference electrode (RE) (before shrinking and curing) with dimension 10.20×10.20×0.52 mm^3, (b) IP gold (Au) WE, Au CE, and silver chloride (AgCl) RE (after shrinking and curing) with dimension 4.23×4.23×1.52 mm^3.

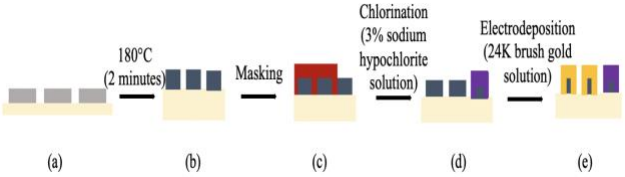

Figure 2: Step by step microfabrication of the gold (Au) inkjet printed (IP) microelectrochemical sensor (μECS) (cross-sectional view): (a) IP silver (Ag) electrodes on shape memory polymer (SMP) - before shrinking and curing (dimension:10.20×10.20×0.52 mm^3 and working electrode area: 19.36 mm^2), (b) IP Ag conductive electrodes on SMP - after curing and shrinking (dimension: 4.23×4.23×1.52 mm^3 and working electrode area: 2.25 mm^2), (c) counter electrode (CE) and working electrode (WE) are covered with masking tape and reference electrode (RE) is exposed for chlorination, (d) silver chloride (AgCl) RE and Ag CE and WE, (e) AgCl RE and Au CE and WE (Au plating immersion technology).

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RESULTS

The reported µECS is characterized with 3mM lead (II) contaminated aqueous solution (optimized with 0.1 M HCl). Cyclic voltammogram (CV) analysis of the microsensor is performed for optimized aqueous solution with (sample 2) and without (sample 1)

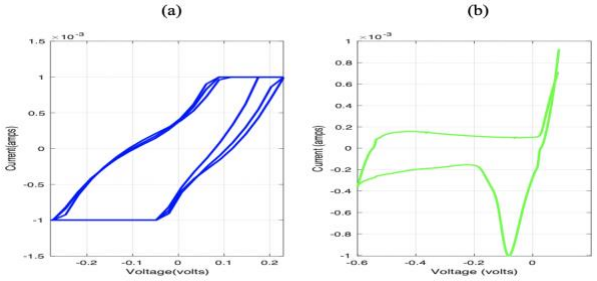

Figure 3: Cyclic Voltammogram (CV) for the microfabricated inkjet printed (IP) gold (a) microsensor and (b) previously reported macro sensor for optimized drinking water without lead (II) ions (0.1 M HCl).

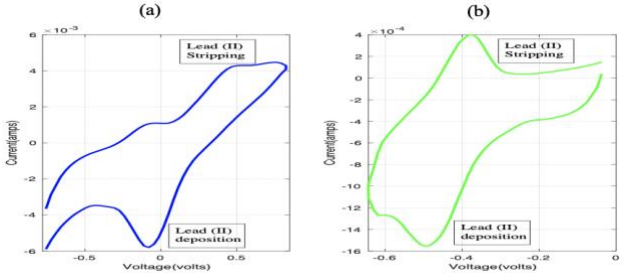

Figure 4: Cyclic Voltammogram (CV) for the microfabricated gold inkjet printed (IP) (a) microsensor and (b) previously reported macro sensor for optimized (0.1 M HCl) drinking water with 3 mM lead (II) ions.

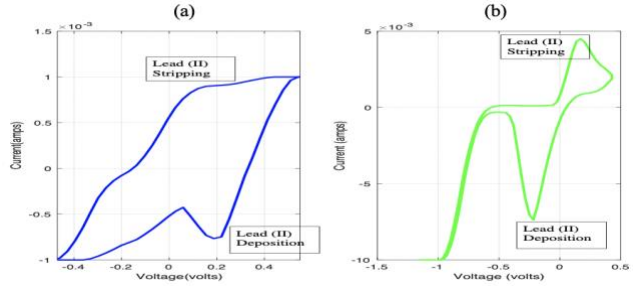

Figure 5: Cyclic Voltammogram (CV) for the fabricated gold inkjet printed (IP) (a) microsensor and (b) previously reported macro sensor for optimized (0.1 M HCl) drinking water with 14.4 µg/L lead (II) ions.

lead (II) ions. Figure 3 and 4 represent the CV graphs for both sample 1 and 2 respectively. It is observed from Figure 3 that there is no indication of lead (II) deposition and stripping in case of lead (II) free aqueous solution. However, a significant pair of peaks i.e. cathodic @ ~ -78.6 mV and anodic @ ~ 470.3 mV are representing lead (II) deposition and stripping respectively in case of 3 mM lead (II) contaminated optimized aqueous solution in Figure 4 (µECS). Figure 5 represents CV analysis of µECS (a) and macro sensor (b) for 14.4 µg/L lead (II) contaminated optimized aqueous solution (according to US Environmental Protection Agency (EPA) the approved lead (II) level in drinking water is 15 µg/L). It is observed that the reported µECS has enough potential to detect lower lead (II) level in the optimized aqueous solution. We have included the CV analysis of our previously reported macro sensor (13×10×1.52 mm^3) alongside the performances of our newly fabricated µECS (4.23×

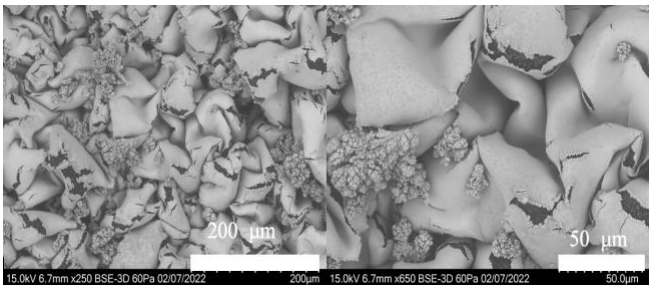

Figure 6: Scanning electron micrograph (SEM) images of the gold inkjet printed microelectrochemical sensor (µECS).

4.23×1.52 mm^3) for each case to understand and analyze the scaling effects in case of microfabrication of the reported microsensor. It is known that electrode surface area is proportional to stripping peak currents for CV analysis. But it is observed that the down scaling of the lateral dimension has bare minimum influence in case of the novel microfabricated µECS as miniaturizing the device using SMP provides increased effective electrode surface area despite reducing the lateral dimension of the electrodes. The twisted, tangled, and squeezed 3D topology shown in the SEM images in Figure 6 supports the claim of increased effective electrode surface area while miniaturization using SMP.

CONCLUSION

The reported IP Au µECS is an effective and efficient microsensor for lead (II) detection in the optimized aqueous solution. The µECS showed consistency and reproducibility in case of 14.4 µg/L lead (II) detection. In comparison to macro sensor, this 3D microsensor has performed potentially promising enough to be considered for further developments and different electrochemical sensing applications. However, the reported analytical results/data exhibits that the proposed additive technology (inkjet printing on SMP) and specific reported parameters for microfabrication has ensured green, direct, and maskless microfabrication of a simple, cost-effective, sensitive, and disposable µECS for lead (II) detection in the optimized aqueous solution.

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