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3D-printed electrodes for the detection of mycotoxins in food

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ABSTRACT

Additive manufacturing, also termed 3D printing, enables economical, dynamic and rapid fabrication of customisable three-dimensional (3D) devices catering for specialised functions. Herein, we report the fabrication of 3D-printed graphene electrodes by fused deposition modelling (FDM), which were then used for the electrochemical detection of the mycotoxin zearalenone (ZEA). Chemical and electrochemical pre-treatment procedures were applied to remove the inert polylactic acid external layer from the graphene electrodes, exposing and activating the inner graphene surface. These procedures enhanced the sensitivity of the electrodes towards electrochemical detection of ZEA. The activated 3D-printed graphene electrodes displayed a good linear response ($r = 0.995$) over a wide concentration range (10 to 300 μM). This proof-of-concept application opens up a wide range of possibilities for the fabrication of 3D-printed electrochemical devices for use in food analysis and food safety.

1. Introduction

Food security and safety have become increasingly important topics for discussion among international and regional agencies, particularly in view of the potential threats from terrorism as well as new strains of resistant pathogens. Additionally, with the spread of fungi, bacteria and other microorganisms, food inspectors and regulatory bodies are placing increasing emphasis on the shelf life of food products. One class of compounds which is of high interest is that of mycotoxins. Mycotoxins are poisonous secondary metabolites of low molecular weight produced by naturally occurring fungi which cause food products to turn mouldy under certain conditions [1]. Consumption of such compounds is known to adversely affect human health, possibly leading to cancer and even death. As such, stringent regulations have been put in place to mitigate the spread of mycotoxins in foodstuffs. Zearalenone (ZEA) is a mycotoxin produced by the *Fusarium* species of fungi and is found mainly in maize products and cereals such as wheat [2]. It is crucial to have reliable and rapid methods for detecting ZEA in food samples to enable the relevant authorities and food inspectors to take prompt action to mitigate the spread of ZEA, especially in food storage facilities.

The increasing emphasis on accurate and sensitive detection of mycotoxins has spurred researchers to develop a variety of methodologies with the aim of lowering detection limits and improving analytical detection. One such approach involves the use of electrochemical techniques. Research into improving electrochemical detection of mycotoxins has primarily focused on improving the limits of detection and sensitivity through the development of electrochemical methodologies [3] such as the optimisation of immunoassay systems [3–6] as well as the incorporation of novel transducer platforms [7–9] The detection of food contaminants is of the utmost importance and the evolution of techniques has to keep pace with advances in technology. In this respect, additive manufacturing, also known as three-dimensional (3D) printing, can be seen as a useful tool for printing customisable electrodes for the selective detection of mycotoxins. Additive manufacturing allows for the rapid printing of 3D objects designed using 3D modelling software. The 3D object is fabricated by digitally controlled deposition of successive layers of materials until the final structure is created. The use of 3D printing in electrochemistry has been widely reported for applications in energy devices [10,11] and biomedical applications [12–15]. However, to the best of our knowledge, there have not been any reported applications of 3D printing in electrochemical food analysis, or more specifically for the detection of mycotoxins.

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A 3D-printed detector would be a useful alternative to current detection methodologies, with the possibility of fabricating customisable on-site point-of-care diagnostic devices at lower cost while incorporating complex designs [16]. 3D-printed metal electrodes have been shown to perform reliably for the electrochemical detection of multiple pollutants and contaminants [17–19]. Herein, the detection of ZEA using a 3D-printed graphene electrode is studied as a proof-of-concept of a customisable electrode for rapid point-of-care detection of mycotoxins in food samples. The graphene electrodes were fabricated by fused deposition modelling (FDM) and then subjected to chemical and electrochemical pre-treatments before being tested for the electrochemical detection of ZEA.

2. Experimental

2.1. Materials and apparatus

Zearalenone (ZEA) and phosphate buffer saline (PBS) in tablet form were purchased from Sigma-Aldrich (Singapore). *N*,*N*-dimethylformamide (DMF) and acetonitrile (ACN) were obtained from Merck (Singapore). Graphene/polylactic acid (PLA) filaments were obtained from Black Magic 3D, New York. Deionised water (DI) purified using the Milli-Q system (Millipore, MA, USA) with resistivity of 18.2 MΩ cm was used. A stock solution of ZEA was prepared in ACN and stored in the dark at 4 °C. Working solutions were prepared daily by diluting suitable amounts of stock solution with PBS, which serves as the supporting electrolyte.

The Ag/AgCl reference electrode, platinum counter electrode and glassy carbon (GC) working electrode (diameter 3 mm) were obtained from CH Instruments (Texas, USA). Edge-plane pyrolytic graphite (EPPG) (diameter 3 mm) was obtained from Autolab (The Netherlands). The surfaces of the EPPG and GC electrodes were renewed by polishing with alumina particles using a polishing pad.

2.2. Electrochemical procedures

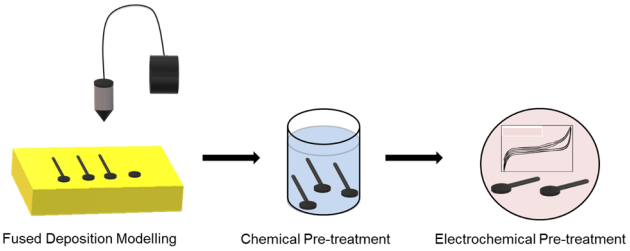
Voltammetric measurements were performed at room temperature (25 °C) using a three-electrode configuration and an Autolab Type III electrochemical analyser (Eco Chemie, The Netherlands) controlled by NOVA 1.10 software (Eco Chemie). Cyclic voltammetry (CV) experiments were performed at a scan rate of 100 mV s^{-1} unless otherwise stated.

2.3. Fabrication of 3D-printed graphene electrodes

Graphene/polylactic acid filaments were used to print the electrodes, which were designed using Fusion 360 CAD software (Autodesk). The design of the electrodes was inspired by our previous works and consists of a 1.6 mm thick disc (diameter 8 mm) attached to a rectangular stem. The design was exported to a .stl file, sliced and converted to a .gcode file using Slic3r software. 3D printing was performed using a Prusa i3 MK3 printer (Prusa Research) with a Olsson Ruby ruby-tipped 0.4 mm nozzle (3DVerkstan, Sweden). The nozzle and bed temperatures were set to 220 °C and 60 °C, respectively. The rest of the printing parameters were adopted from the Prusa Slic3r configuration known as PLA.

2.4. Pre-treatment of 3D-printed electrodes

A chemical pre-treatment was performed by soaking the 3D-printed graphene electrodes in DMF for 10 min [20]. Subsequently, the treated electrodes were washed with ethanol and deionised water before drying overnight under ambient conditions. Electrochemical activation was then performed in 0.01 M PBS (pH 7.2) by applying a constant potential of 2.5 V (vs. Ag/AgCl) for 250 s [21].



Scheme 1. Schematic representation of the fabrication from graphene/polylactic acid filaments of 3D-printed graphene electrodes and their pre-treatment for the detection of ZEA.

3. Results and discussion

Pre-treatment activation is crucial to enhancing the sensitivity and detection capabilities of the fabricated electrodes [22–24]. For graphene electrodes printed from commercially available graphene/polylactic acid filaments, pre-treatment to activate the underlying graphene layers for electrochemical applications by removing the polylactic acid layer on the surface greatly enhances the performance of the 3D-printed graphene electrodes [20]. The electrochemical response has been reported to be further enhanced by a combination of chemical and electrochemical pre-treatments [21]. The use of specific enzymes has also been reported to expose the underlying graphene layer for potential biosensing applications [24]. In this study, a previously reported chemical and electrochemical pre-treatment procedure [20] was adopted as it produces significantly improved output signals which would potentially maximise voltammetric measurements for the detection of ZEA (Scheme 1). In summary, the electrodes were first designed using the 3D sketch-up modelling software before being printed via fused deposition modelling (FDM). The printed graphene electrodes were then soaked in *N*,*N*-dimethylformamide (DMF). Chemical pre-treatment resulted in the corrosion of the outer polylactic layer, as is evident from the black particulate matter that appeared in the DMF solution (**Fig. S1**). After washing and drying, electrochemical activation was performed at a constant potential of 2.5 V (vs. Ag/AgCl) in phosphate buffer solution. Further details of the pre-treatment procedures are outlined in the Section 2. The 3D-printed graphene electrodes were of uniform dimensions with a length of ~4.5 cm and with a circular closed disc at one end (**Fig. S2**). The end with the circular closed disk was immersed in the sample solution during all electrochemical studies reported in this paper.

The electrochemical sensing performance of the activated 3D-printed electrodes was compared with those of bare glassy carbon (GC) and edge-plane pyrolytic graphite (EPPG) electrodes, to analyse any apparent differences in current signals obtained towards the detection of ZEA. Additionally, the voltammetric signals obtained from the GC and EPPG electrodes provide a baseline comparison with an inert electrode and a sensitive electrode surface with reactive edge plane sites, respectively. It can be seen from Fig. 1 that broad anodic peaks centred at ~0.7 V (vs. Ag/AgCl) and 0.75 V (vs. Ag/AgCl) were observed for the GC and EPPG electrodes, respectively. A defined anodic peak was observed when experiments were performed with the activated 3D-printed graphene electrode. However, the voltammetric signal shifted to a higher potential of ~0.9 V (vs. Ag/AgCl). The 3D-printed graphene electrode appears to be less electroactive than the GC and EPPG electrodes. Despite that, the presence of an anodic peak demonstrates its ability to electrochemically detect ZEA. Potassium hydroxide was considered as an alkaline alternative to DMF in the chemical pre-treatment process in an attempt to improve the voltammetric signals. However, no anodic peaks corresponding to ZEA were observed, with a strong background signal produced (**Fig. S3**). Further modifications might have to be made to improve and optimise the performance of the 3D-printed electrode.

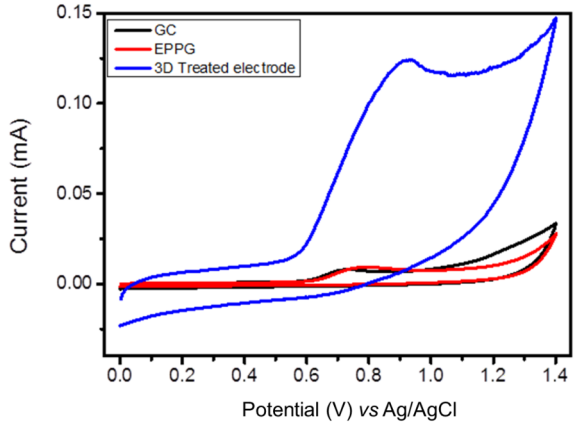


Fig. 1. Cyclic voltammograms of glassy carbon (GC), edge-plane pyrolytic graphite (EPPG) and 3D-printed electrodes (the latter fabricated from graphene/polylactic acid filaments) in the detection of 100 μM ZEA (vs. Ag/AgCl). Conditions: 0.01 M phosphate buffer solution (pH 7.2) as electrolyte, scan rate 100 mV s^{-1}.

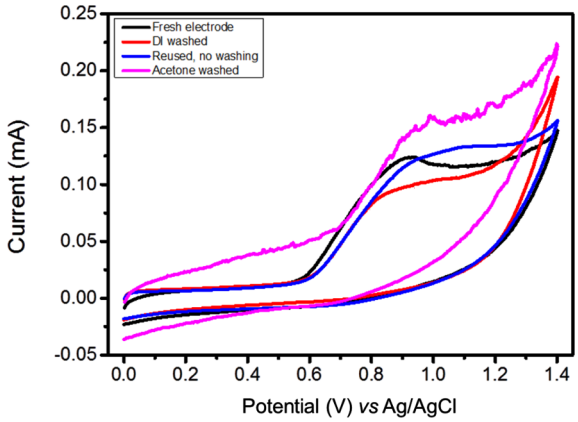


Fig. 2. Voltammograms of 3D-printed activated graphene electrodes washed with different solvents towards the detection of 100 μM ZEA (vs. Ag/AgCl). Conditions: 0.01 M phosphate buffer solution (pH 7.2) as electrolyte, scan rate 100 mV s^{-1}.

Having ascertained the ability of the 3D-printed graphene electrode to electrochemically detect ZEA, we next investigated the reusability of the 3D-printed electrodes by washing with different solvents (deionised water and acetone). 3D-printed electrodes which did not undergo this washing step were also re-used to investigate the significance of the washing step. From Fig. 2, it is noted that the absence of a washing step resulted in a broader anodic peak which had shifted to a higher voltammetric potential. This could be due to the detection of oxidised forms of ZEA which had previously adhered to the electrode surface. Thus, it is recommended to perform a washing step between measurements to mitigate the collection of unwanted side products. The voltammetric signals obtained from used 3D-printed electrodes washed with DI water did not display significant deviations. The oxidative peak obtained was similar to that of a newly activated 3D-printed electrode, although the observed peak height was lower. The number of active sites on the electrode surface could have been reduced prior to the second measurement, which could have produced the observed decrease in the current signal. Nonetheless, the voltammetric profiles were similar. However, the voltammetric signal obtained on washing with acetone resulted in a voltammogram with spikes attributed to the background noise. Furthermore, no apparent anodic peaks were observed. Upon closer analysis, the voltammetric profile obtained was similar to that of an unwashed reused 3D-printed electrode. The acetone used for washing might have partially corroded and reacted with the activated graphene layer, resulting in a 'noisy' voltammetric signal which hinders the application of the 3D-printed graphene electrode for detection purposes. Hence, it might not be appropriate to wash graphene-based electrodes with harsh chemicals in order to preserve the structural integrity of the surface layer. The results obtained show that a washing step between measurements is advantageous and crucial to obtaining reproducible results. Additionally, deionised water turns out to be an ideal solvent for washing used 3D-printed activated graphene electrodes.

Having established the pre-treatment and washing procedure for the 3D-printed electrodes, the response of the 3D-printed electrode was analysed using voltammetry. ZEA has been reported to adsorb onto the surfaces of the electrodes before undergoing electrochemical oxidation [25–27]. The performance was compared to that of a conventional GC electrode. Linear plots for ZEA concentrations between 10 and 300 μM were obtained for both GC (Fig. 3A) and activated 3D-printed graphene electrodes (Fig. 3B). The activated 3D-printed graphene electrodes displayed good performance and linearity (r = 0.995) towards the detection of ZEA, comparable to that of the conventional GC electrode (r = 0.967). The limit of detection (LOD) was calculated by multiplying by 3 the quotient of the standard deviation of the peak height of the lowest concentration of ZEA and gradient of the calibration graph, while the limit of quantification (LOQ) was obtained by multiplying the same quotient above by 10 [28–32]. The LOD obtained for the GC electrode was 0.0683 μM with a LOQ of 0.228 μM. However, the activated 3D-printed graphene electrode had a higher LOD value of 0.340 μM with a LOQ of 1.13 μM. The LOD value achieved is greater than the detection limits reported previously (nanomolar concentration levels) [26,27,33] and the maximum detectable amount of ZEA permissible in food samples [34–36]. Despite this, the results provide a proof-of-concept insight into the potential incorporation of activated 3D-printed graphene electrodes [37] for the electrochemical detection of mycotoxins in food samples [39].

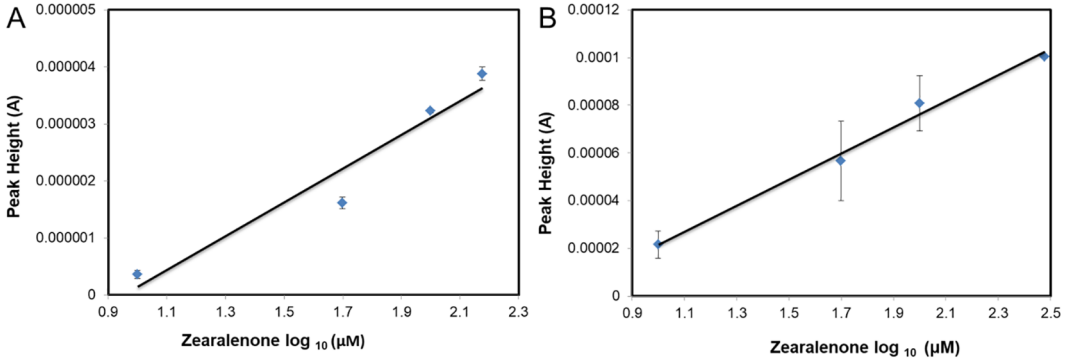


Fig. 3. Calibration plots of (A) glassy carbon (GC) and (B) activated 3D-printed graphene electrodes. Conditions: 0.01 M phosphate buffer solution (pH 7.2) as electrolyte, scan rate 100 mV s^{-1}.

This novel approach to electrochemical detection of mycotoxins opens up new avenues due to the incorporation of 3D-printing technology in electrochemical sensors. Further surface modifications of the 3D-printed electrodes can be explored, incorporating and printing biological elements [24,38] to improve their detection capabilities. Additionally, the electrode design could be optimised and improved by the use of alternative conductive materials to improve the sensitivity and electrochemical response of 3D-printed electrodes in future applications. One such possibility is the use of transition metal dichalcogenides (TMDs) [38], which have been reported to be good conductive materials with numerous applications in electrochemistry. These possibilities are also largely dependent on further developments in 3D printing technology and experimental optimisation [40–42]. Further work is also required to test the printed electrodes in real samples and study the possible effects of interferences on detection signals and sensitivities.

4. Conclusion

Additive manufacturing, better known as 3D printing, has been used to produce electrodes from graphene/polylactic acid filaments, which have been applied to detect the mycotoxin zearalenone (ZEA) by electrochemical means. A chemical pre-treatment complemented by electrochemical activation of the 3D-printed graphene electrodes has been shown to provide a cheap and effective method for the detection of ZEA within a wide range (10 to 300 μM) with good linearity ($r = 0.995$). The activated 3D-printed electrodes achieved a LOD of 0.340 μM with a LOQ of 1.13 μM. Despite these values being higher than the maximum approved levels, the results obtained provide a perspective regarding the applicability of 3D-printing technology in food regulation and inspection. This study opens the door for future improvements of 3D-printed electrodes to maximise their performance through better electrode design, better choice of materials and further functionalisation processes. Additionally, this proof-of-concept work opens the possibility of on-site customised fabrication of detection devices for food safety and inspection.

Author contributions

M.Z.N.M. performed electrochemical experiments and data analysis. F.N. fabricated and characterized the electrodes. M.P. conceived and supervised the research. All authors discussed the data and the implications of the data. All authors contributed to writing of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2020.106735.

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