3D printable conductive materials for the fabrication of electrochemical sensors: A mini review

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Abstract

The review presents recent developments in the use of conductive materials that can be printed using additive manufacturing (3D printing), enabling the development of mass-produced electrochemical sensors of varying geometries. This review will highlight some key electroanalytical applications of 3D-printed electrochemical sensors and discuss their potential future capabilities.

Keywords: 3D printing; additive manufacturing; electrochemistry; conductive electrode; 3D printed electrode; electrochemical sensor

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Contents

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1. Introduction

Three-dimensional (3D) printing technology, also known as additive manufacturing, has been widely used to make complex devices and microfluidic channels which can be used as platforms to house sensors made by conventional methods [1–6]. However, exploiting the capabilities of 3D printing technology to fabricate materials that can function as electroanalytical sensors has been a recent development, due to the availability of conductive materials that can be used in printing [7–10].

The process of printing 3D objects usually starts by creating a model using computer-aided design (CAD) software. This model must then be converted into the Standard Triangle Language (STL) file format which stores information on the 3D object surfaces as a list of coordinates of triangulated sections. This process is then followed by a slicing procedure, where the 3D model is divided into several layers with 2D cross-sections, which are then sent to a 3D printer to process. Finally, the 3D printer starts to deposit a filament onto the print bed until the entire 3D object has been created. There are a number of processes that can be used for 3D printing, which are detailed in a review by Ambrosi and Pumera [7]. The most commonly used technique is a process of extrusion using fused deposition modelling (FDM). This technique uses an additive approach, in which a continuous thermoplastic filament is heated to a semi-molten state before extrusion for layer-by-layer deposition [11,12]. This approach is simple and can be utilised to print multi-material structures at low cost, which in turn provides high versatility. However, the accuracy and surface quality can be relatively poor when compared to those of powder-based plastic additive manufacturing processes [12].

3D printing of electrochemical sensors offers several interesting advantages over conventional manufacturing methods as it can lower the production cost, provide rapid prototyping, increase the manufacturing speed, and allow for the development of sensors with complex geometries. Herein, we highlight the conductive materials that have been used for the development of electrochemical sensors through 3D printing and their applications.

2. Conductive materials developed for 3D printing of electrodes

Various materials have been employed for 3D printing in different sectors, in particular for the development of electronic components [9,13,14] However very few studies have transformed these materials into electrodes for sensing.

The majority of studies that have developed electrodes using 3D printing methods have involved the printing of metals. In these studies, 3D stainless-steel electrodes were printed and then electroplated with gold (Au) [15–20], bismuth (Bi) [20], nickel (Ni) [21], platinum (Pt) [21] and iridium oxide (IrO_2) [21,22] to make electrodes suitable for a host of analytical applications. However, printing of metal materials requires expensive equipment and, in most cases, an additional fabrication step is required, where the stainless-steel electrodes are electroplated with another metal to make the electrodes suitable for sensing. Certain electrodeposited metals may also not be biocompatible or suitable for environmental monitoring. Metal electrodes also offer a limited electrochemical potential window, reducing their scope for use as sensors.

For these reasons, carbon-based materials are more attractive for the development of 3D printed electrodes. To produce conductive carbon filaments, composite materials are produced from conductive materials such as carbon nanotubes, graphene and carbon black mixed with thermoplastic materials such as polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS). Printing of carbon composite filaments could offer significant advantages in the development of conductive electrodes [23] when compared to carbon paste and carbon nanotube-epoxy composite electrodes [24–26] as dispersion is better regulated, providing enhanced batch-to-batch precision. However, the development of a printable conductive filament is not a simple task, as an appropriate balance needs to be struck between the fraction of conductive material that allows for a semi-molten state to be achieved during printing, and appropriate conductivity of the printed electrode. At present there are reports on conductive 3D printable polymer materials based on PLA/graphene filaments [27–29], ABS/carbon black filaments [30,31], polypropylene/carbon black filaments [9], polybutylene terephthalate/carbon nanotube/graphene filaments [32] and carbon nanofiber/graphite/polystyrene composite filaments [33,34].

Studies to date have shown that printing with carbon composite materials must be carried out with care, as anisotropy and orientation of printing [30,31] can result in significant variations in the electrochemical performance of the printed sensors, as shown in Figure 1 [31]. These studies highlight the importance of understanding the key parameters in printing and their influence on the conductivity of composite electrodes, as these variables can influence conductive pathways in composite materials.

Figure 1

3. Electroanalytical applications of 3D printed electrodes

There have been a host of electroanalytical applications using 3D printed electrodes, among which we will highlight some key developments. Most of these applications have employed metal printed devices developed by Pumera and colleagues [7,8], utilising a 3D printed helical stainless-steel electrode, which was then electroplated with various metals for sensing applications [15,17–20].

Using the stainless-steel helical template, gold films were electroplated to create a sensor for the detection of single-stranded DNA (ssDNA). Using a self-assembled monolayer DNA sensor, complementary ssDNA concentrations in the range 1 nM–1000 nM were detected [15]. In a similar approach, 3D printed gold-plated electrodes were utilised for the detection of phenol and *p*-aminophenol, where lower anodic potentials were observed when compared to glassy carbon (GC) electrodes. However, the 3D printed electrodes only showed higher sensitivity towards the detection of *p*-aminophenol, not phenol [17]. Gold electroplated 3D metal electrodes were also shown to have enhanced sensitivity for the determination of acetaminophen and dopamine when compared to GC and gold (Au) disk electrodes [19]. To study heavy metal detection, thin films of Au and Bi were separately electrodeposited on stainless-steel 3D printed electrodes. Figure 2 shows that both 3D printed electrodes (3D-Au and 3D-Bi) showed higher sensitivities than a GC electrode for the detection of lead (Pb) and cadmium (Cd). However, the limit of detection (LOD) values for Pb and Cd obtained were higher than for the GC electrode [20]. Most recently, these 3D printed stainless-steel gold electroplated electrodes have been shown to be more sensitive for the detection of 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and fenitrothion (FT) than GC electrodes [18]. These studies all highlight the potential of 3D printing of metal to make electrodes, but their electrochemical behavior was only achieved through electroplating.

Figure 2

Carbon composites offer a more promising approach for the direct use of printed conductive material. There are very few applications of carbon-based 3D printed electrodes for sensing applications. An all polystyrene 3D printed electrochemical device with an embedded carbon nanofiber/graphite/polystyrene composite electrode was shown to provide excellent responses for the detection of Pb^{2+} via anodic stripping [33]. Using the same electrode material, differential pulse anodic stripping voltammetry was used to analyse Zn^{2+} in a sample of tap water [34]. An alternative approach for the detection of Cu^{2+} cations was achieved using gold-coated 3D printed PLA/graphene electrodes with immobilised cadmium sulfide nanoparticles present at the electrode surface as an active semiconductor, where the LOD was lower than that obtained using indium tin oxide/fluorine-doped tin oxide glass electrodes [29]. Most recently, a study used a PLA/graphene filament to make 3D printed ring and disc electrodes for the detection of picric and ascorbic acid. The electrodes, shown in Figure 3, demonstrated exceptional linearity for measurement of picric acid (5 and 360 ppm) and ascorbic acid (10 and 500 ppm) [28]. These initial studies have shown that 3D printed conductive materials can function as sensors and offer enhanced performance compared with commonly utilised electrodes such as GC electrodes.

Figure 3

4. Conclusion and Future work

The availability of conductive materials suitable for 3D printing is likely to shape a new wave of sensor development for electroanalytical applications. Carbon composite sensors fabricated by 3D printing show enhanced precision when compared to carbon composite electrodes produced by conventional approaches. To date, 3D printed metal or carbon materials have been shown to have exceptional performance for the detection of metals and organic compounds when compared to GC electrodes. The ability to make robust, high-throughput, precisely fabricated electrodes using 3D printing technology provides a new and attractive proposition for sensor development. However, there has still not been enough comparison of 3D printed conductive materials with screen-printed electrodes or other commonly used sensing materials. This is critical to understand the niche of these sensing materials and future studies need to provide appropriate analytical comparison.

However, the use of 3D printing in the development of sensors is still in its infancy and there is tremendous potential in the strategies that can be utilised for printing sensors and in the exploration of geometries. As 3D printing occurs through the layer-by-layer deposition of conductive materials, there is still plenty to explore in the most appropriate printing parameters to ensure enhanced conductivity of the electrode material. Within FDM, the print layer thickness, pattern of infill and printing orientation can all be altered and therefore researchers have the opportunity to explore whether these parameters can alter the electrochemical performance of carbon composite sensors. A study has already shown that anisotropy and printing orientation can have a dramatic influence on the current density and anodic peak potential of redox species [31].

One of the major advantages of 3D printing is the ability to create electrodes of different geometries. At present all studies using 3D metal electrodes have been carried out using helical [22] and gauze [21] shaped 3D printed devices, while carbon printed sensors have mainly been rectangular [33] or disc electrodes [27–29,31]. With the ability to develop complex geometries, the consequences of varying the shapes and sizes of electrodes have yet to be explored. Due to limitations in fabricating different shapes, little is known about how differently shaped electrodes behave in electrochemical sensing and we have

yet to explore more appropriate shapes to enhance electrode and mass transfer activity for sensing. In this light, not only will 3D printing sensors be able to explore new analytes for measurement but there may also be new applications where sensors can be shaped to suit specific applications where conventional geometries do not perform well.

Finally, there is plenty of potential for the development of conductive materials for 3D printing. At present the range of 3D printed conductive materials is limited and, particularly in the case of composite conductive filaments, there is scope for the development of more interesting conductive materials that can increase the array of analytes that can be monitored. In the future, conductive carbon filaments may also have additional chemical modifiers or mediators that allow for specific tailoring of the printed conductive material for electocatalytic reactions or to serve as base electrodes for biosensors. More complex filaments consisting of a mixture of conductive materials and polymers for specialized sensing applications are also likely to be developed.

In summary, conductive materials that can be used to fabricate electrodes using 3D printing have been developed and show significant promise. This is only the tip of the iceberg, however, as there is tremendous potential in the conductive materials that can be printed and the geometries that can be produced, opening up new avenues for electroanalytical sensing.

Total words (Abstract to Section 4 = 1925 words)

Conflict of interest statement

The authors declare no conflict of interest.

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Figures

Figure 1. 3D printed electrodes. (A) shows the approach in which the horizontal and vertical print of the ABS/carbon black material was used to generate vertical printed (VP), horizontal printed smooth surface (HPSS) and horizontal printed rough surface (HPRS) electrodes. The cross-section of the electrode is shown on the right. (B) Photographs of 3D printed carbon black/ABS electrodes showing electrodes printed vertically and horizontally. Cyclic voltammetric responses on the printed electrodes. (C) Voltammograms of glassy carbon (GC), VP, HPRS and HPSS for 1 mM ferrocene carboxylic acid in 0.1 M NaOH measured at a scan rate of 100 mV/s. Responses of (D) anodic peak current normalised to electrode surface area (i_{pa}) and (E) anodic peak potential (E_{pa}) for 1 mM ferrocene carboxylic acid. Statistical analyses were performed using one-way ANOVA followed by a post hoc Tukey test. Data are shown as mean ± S.D., $n = 4$, $^{*}P < 0.05$,$^{**}P < 0.01$ and $^{***}P < 0.001$. Adapted and reprinted with permission from ref 23. Copyright (2018) Nature Publishing Group

Figure 2. (A) Schematic of the electrode design as obtained by CAD software. Photographs of 3D-printed electrodes (B) as printed (3D-steel), (C) after electroplating with Au (3D−Au) and (D) after electroplating with Bi (3D−Bi). Scale bar corresponds to 1 cm. Square-wave stripping voltammograms for increasing concentrations of Pb in 50 ppb steps for (E) GC, (F) 3D-steel, (G) 3D−Au and (H) 3D−Bi electrodes, with a concentration range of 50–300 ppb. Also shown are the corresponding blank voltammograms (black lines). Experimental conditions: deposition potential of −1.3 V for 120 s, scans with frequency of 25 Hz, potential step of 4 mV and amplitude of 25 mV. 0.1 M acetate buffer (pH 4.5) was used as supporting electrolyte. Adapted and reprinted with permission from ref 13. Copyright (2018) Wiley-VCH

Figure 3. (A) 3D-printed electrode dimensions and shapes. Cyclic voltammograms of 3D-printed graphene electrodes recorded for different concentration levels of (B) picric acid in acetate buffer 0.1 M pH 4.6 (inset: calibration plot using anodic peak intensity) and (C) ascorbic acid in KCl 0.1 M (inset: calibration plot). Dashed line: nonactivated electrodes in the presence of the highest concentration of analyte. Discontinuous line: blank current in the supporting electrolyte. Full lines from light gray to black: activated electrodes in the presence of increasing analyte level (5 to 360 ppm for picric acid and 10 to 500 μM for ascorbic acid). Adapted and reprinted with permission from ref 21. Copyright (2018) American Chemical Society.

Figure 1

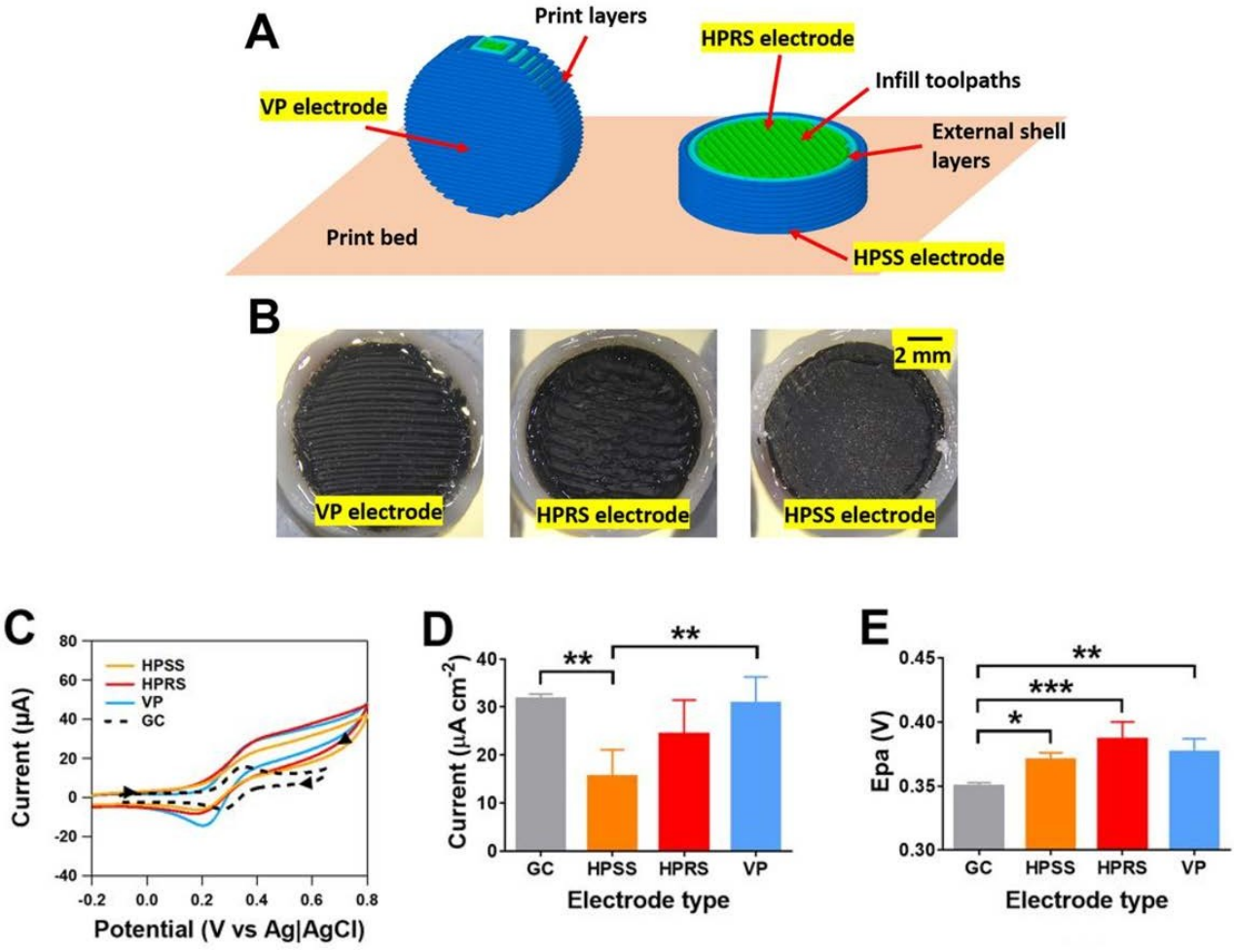
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Figure 2

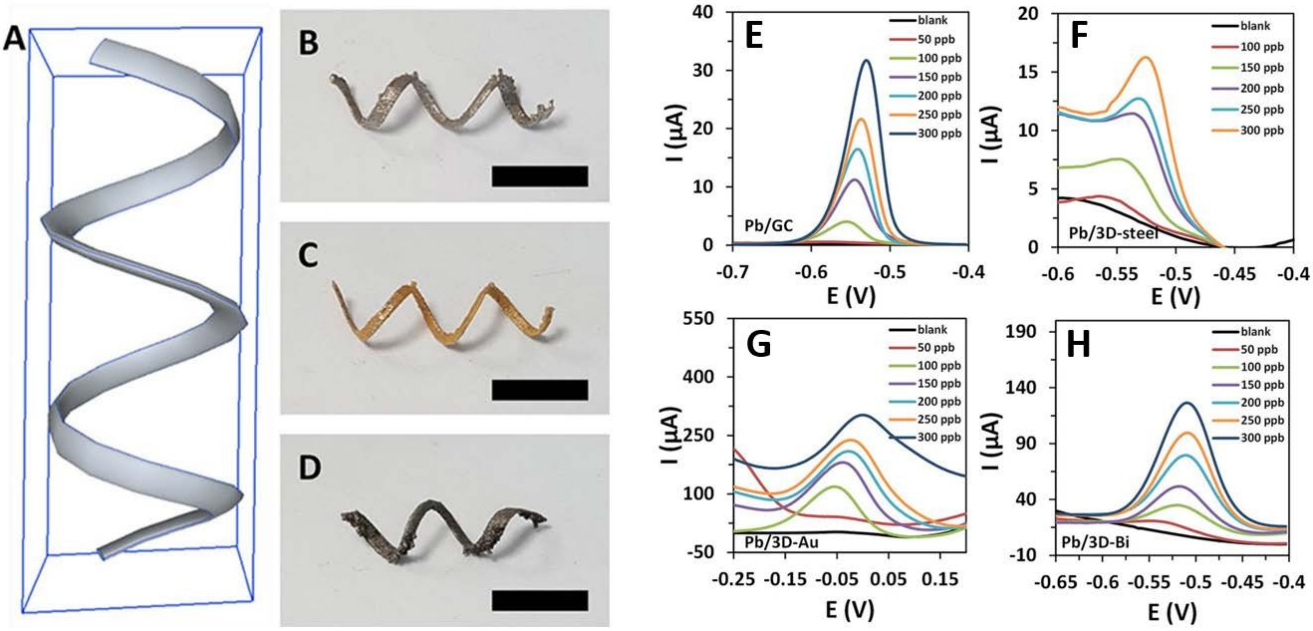
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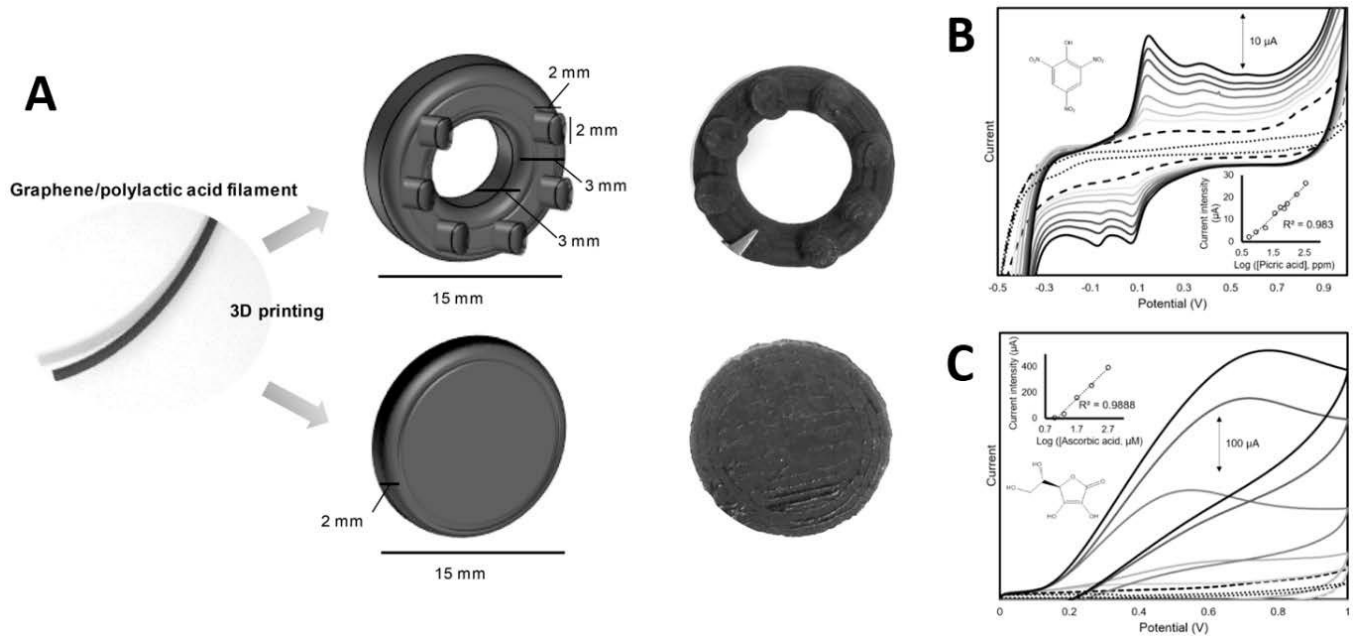
Figure 3


A
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Current intensity (µA)
R² = 0.983
Log ([Picric acid], ppm)
C
Current intensity (µA)
R² = 0.9888
Log ([Ascorbic acid, µM)
100 µA
Current
Potential (V)