Electrochemical (bio)sensors enabled by fused deposition modeling-based 3D printing: A guide to selecting designs, printing parameters, and post-treatment protocols

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Abstract

The 3D printing (or additive manufacturing, AM) technology is capable to provide a quick and easy production of objects with freedom of design, reducing waste generation. Among the AM techniques, fused deposition modeling (FDM) has been highlighted due to its affordability, scalability, and possibility of processing an extensive range of materials (thermoplastics, composites, bio-based materials, etc.). The possibility of obtaining electrochemical cells, arrays, pieces, and, more recently, electrodes, exactly according to the demand, in varied shapes and sizes, and employing the desired materials has made from 3D printing technology an indispensable tool in electroanalysis. In this regard, the obtention of an FDM 3D printer has great advantages for electroanalytical laboratories, and its use is relatively simple. Some care has to be taken to aid the user to take advantage of the great potential of this technology, avoiding problems such as solution leakages, very common in 3D printed cells, providing well-sealed objects, with high quality. In this sense, herein, we present a complete protocol regarding the use of FDM 3D printers for the fabrication of complete electrochemical systems, including (bio)sensors, and how to improve the quality of the obtained systems. A guide from the initial printing stages, regarding the design and structure obtention, to the final application, including the improvement of obtained 3D printed electrodes for different purposes, is here provided. Thus, this protocol can provide great perspectives and alternatives for 3D printing in electroanalysis, and aid the user to understand and solve several problems with the use of this technology in this field.

Keywords: Addictive manufacture, electrochemical systems, 3D printed electrodes, printing parameters, 3D printing for (bio)sensing.

1 OVERVIEW

With the Industrial Revolution 4.0, 3D printing technology has become a priority subject and a hot topic for different research areas, especially for (bio)sensors, which is a central area in many applications. The exponential growth in the number of articles in the recent literature demonstrates the potential of 3D printing in the Analytical Chemistry field, including the fabrication of electrochemical (bio)sensors. This technology enables quick and easy production of objects with freedom of design, reduces waste generation, and can be used anywhere in the world. Moreover, it has enormous potential for large-scale fabrication in a mechanized (or automatized) process.

According to the International Standards Organization/American Society for Testing and Materials standards (ISO/ASTM 52900:2015)[1,2], seven different 3D printing techniques currently are available, including (1) material extrusion, (2) material jetting, (3) binder jetting, (4) sheet lamination, (5) vat photopolymerization, (6) powder bed fusion, and (7) directed energy dispersion. After a search in the Web of Science® database using as keywords "*3D print*", "analytical chem*" or electrochem* or volt** or *sensors*, and associated with the seven described techniques, it can be observed that major part of the published works (53.4%) report the use of material extrusion techniques, while the second most used technique, material jetting, is corresponding to only 17.8% (information obtained on 27th January 2022). These data indicate the relevance of material extrusion techniques in comparison to others (Figure S1A). Material extrusion includes direct ink writing (DIW), which employs a liquid-phase ink of a specific viscosity injected through small nozzles under controlled flow rates, and fused deposition modeling (FDM), which typically employs thermoplastic filaments or pellets that are extruded through a heated nozzle. From these two, Web of Science® database using the keywords *"3D print*", "analytical chem*" or "electrochem*" or* *"volt*"* or "*sensors"*, associated with *FDM* and *DIW* provided the proportion of published works between the last two, where FDM corresponds to more than 68% of the works (Figure S1B), highlighting its importance. Furthermore, FDM is considered the most affordable 3D printing technique and because of the wide range of printable materials has enabled the fabrication of electrochemical cells and electrodes using nonconductive/conductive filaments in several geometries and dimensions, which can be applied for uncountable applications in Analytical Chemistry, especially for miniaturized point-of-need or/and disposable sensors. Nevertheless, there are many variables that a beginner user of FDM 3D printers will find to succeed in the fabrication of miniaturized electrochemical sensing devices, such as the employment of conductive filaments, printing orientation, feasible designs considering dual and single extruder printers, and especially post-treatment protocols to enhance the electrochemical activity of 3D printed electrode surfaces (e.g., electrochemical, chemical and reagentless procedures) before measurement or (bio)chemical modification.

In this context, considering the experience of our research groups, we propose a tutorial perspective on the use of FDM 3D printing technology for the fabrication of improved electrochemical (bio)sensing devices. Our intention is not to publish another review on 3D printing, but rather to present a guide to broaden reader's professionals of different areas interested in taking advantage of this powerful technique to fabricate electrochemical (bio)sensors with improved properties using FDM. To achieve this goal, the tutorial will present the main steps to the development of 3D printing electrochemical sensors or cells. These steps were schematized in **Figure 1**, to serve as a step-by-step guide.

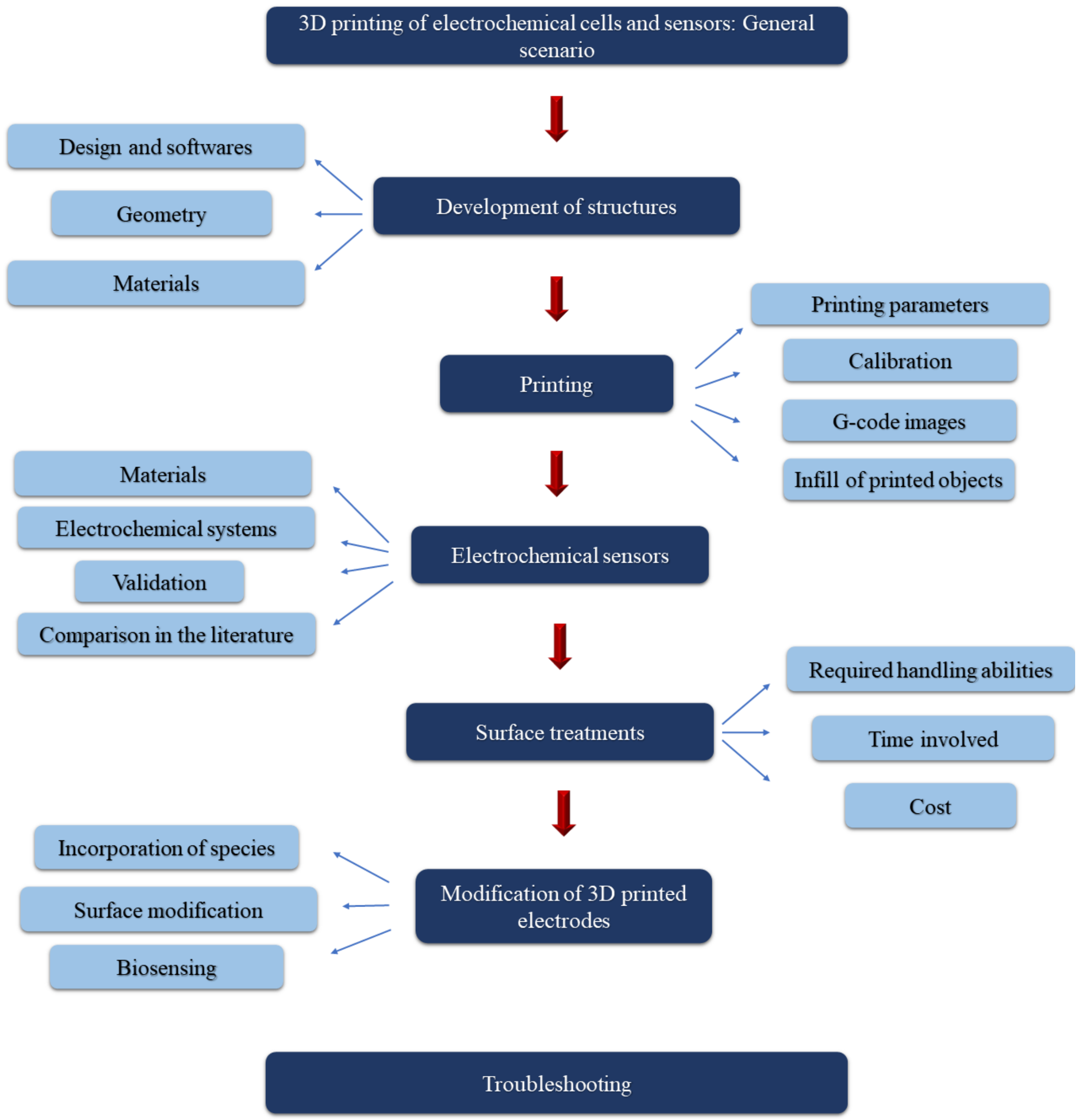

Figure 1. Scheme of the main steps to follow in the development of 3D printing electrochemical sensors or cells.

In summary, the focus of this feature article is to present a tutorial guide for the fabrication of electrochemical sensing devices by FDM 3D printing, which can contribute to the spreading and popularization of 3D printing in the Analytical Chemistry and Electrochemistry fields. From perspectives, robust and large-scale produced 3D printed electrochemical sensors combined with biological agents (enzymes, aptamers, DNA, etc.) or chemical modifiers (molecularly imprinted polymers, metal-organic frameworks, and their composites, etc.) can be envisaged for the development of improved electroanalytical systems.

2 DESIGN AND MATERIALS

The 3D printing technology has been widely used for easy and quick manufacturing of new designs of sensors, electrochemical cells, and other devices. The versatility, possibility of different geometries and dimensions, molding, and miniaturization are the main advantages of this approach for electroanalysis[3]. The FDM has been the most used 3D printing technique for the printing of electrochemical devices by layer-by-layer deposition[4]. Nowadays, it is possible to find a wide range of different 3D printers for this purpose[5]. Also, there are some important aspects of 3D printing that need to be considered and defined, such as the device design (shape and size), the materials employed (polymeric filament), and the printing orientation and parameters.

The design and structure of printed objects will directly depend on the goals of the researcher and final applications, which can be easily molded using properly computer-aided design (CAD) software. This also allows for designing and printing miniaturized and portable electrochemical sensors or complete cells, and their coupling with other devices and systems. Depending on the 3D printer available, it is possible to print entire electrochemical systems at once, using multiple headed 3D printers which allow the handle of filaments with different properties, as explored by Katseli *et al*.[6] The three electrodes were printed in a single-step way using a conductive filament, extruded by one of the heads, coupled with a platform fabricated with non-conductive filament extruded in the second head. Alternatively, complete electrochemical systems can be obtained using a 3D printer equipped with only one head. For instance, the parts of the electrochemical system can be printed separately and then assembled all together at the end, forming an entirely 3D printed electrochemical system, as explored by Richter and collaborators[7]. Different parts of the electrochemical system (cell body, cell base, cell cover, screws, and threads) were printed using a non-conductive filament and the electrodes (working, counter, and reference) using a conductive filament. In the assembly of the system, the working electrode was fixed between the base and the cell body using the screws and threads also produced by 3D printing. Counter and reference electrodes were fixed at the cover of the cell, closing the electrochemical system.

Regarding the employed materials, poly-lactic acid (PLA) remains the most used base polymer for the development of electrochemical devices, due to the ease of printability and requiring lower printing temperatures when compared to other polymeric materials. In addition, PLA is environmentally friendly and suitable for light-duty. As a disadvantage, we can mention its poor mechanical properties[5,8]. Acrylonitrile butadiene styrene (ABS) is also very employed; however, during printing, it produces toxic styrene fumes with an unpleasant odor, which can make its use difficult in a research environment.

Polyethylene terephthalate (PET/PETG) is an interesting material that can be used in 3D printing, providing improved mechanical resistance to the objects, when compared to ABS. However, it is not easy to print as PLA, due to its lower adhesion in the bed and tendency to warp. Nevertheless, this is a promising material for printing materials with high durability and resistance[5]. Thermoplastics such as polytetrafluoroethylene (PTFE) and polyether ether ketone (PEEK) are commonly used in scientific research, but both materials have high melting points (>350 ^{o}C) and most 3D printers cannot apply such high temperatures (limitation of the equipment). There are some specialized machines to print this material, however, they are costly and specific only for this type of filament.

Other thermoplastic materials can also be employed, such as Nylon®, polyvinyl alcohol (PVA), thermoplastic polyurethane (TPU), flexible thermoplastic elastomer (TPE), polycaprolactone (PCL), polypropylene (PP), polyether imide (PEI) and Taulman Tritan high-tensile polyester (TRITAN)[9]. Though Nylon® presents high thermal and mechanical resistance, in addition to excellent flexibility, this material adsorbs/absorbs moisture with facility and its printability is challenging, requiring high extrusion temperatures[5]. TPU/TPE and PP provide similar characteristics in 3D printing, including high flexibility and elasticity (slightly better in TPU), with similar extrusion temperatures[9], however, PP is not readily adhered on glass surfaces, thus, some deformations in the printed material can be observed[10]. The thermoplastic PVA is also an interesting available option. This material is a biodegradable polymer, widely used in the pharmaceutical field as drug release material after 3D printing of capsules[11,12]. PCL is another biodegradable polymer usually employed in 3D printing, this thermoplastic is an excellent option when low extrusion temperatures are required. In contrast, PEI demands very high extrusion temperatures[13]. If high mechanical resistance is required, TRITAN is a good option. This material is considered by the manufacturers as the most resistant and strong filament of all the market of 3D filaments, however, it requires very high extrusion temperatures, and the cost of this material is also increased. A table summarizing the main characteristics aforementioned for raw polymeric materials employed in FDM 3D printing is presented in the supporting information as Table S1. In addition, a combination of different thermoplastic materials can also be employed[3].

In parallel, 3D printing materials and filaments are increasingly available, and there are several options of commercial filaments ready-to-print. In this sense, conductive filaments based on carbon materials (i.e., graphene and carbon black) have become common, as well as new filaments based on metals, such as steel, copper, and zinc[14–16]. For the production of electrochemical sensors and biosensors, a conductive material is needed, which turns the commercial materials into an interesting alternative. However, the expensive price, unknown information about its exact composition, and the presence of impurities can affect the reliability and the use of some commercial filaments.

On the other hand, several works have reported the development of new carbon-based conductive filaments[17–21] with lower costs compared to commercial filaments. Lab-made filaments are generally fabricated using thermoplastic polymers (i.e., PLA, ABS, polystyrene, polypropylene, polyethylene terephthalate glycol-modified, Nylon®, among others) and conductive materials (i.e., graphite, graphene, carbon black, carbon nanofiber, carbon nanotubes, and metals), by the mixing and melt extrusion of the components. An extruder machine can be used for the heat and manufacturing of the filament in a process similar to the 3D printing extrusion. All the components need to be homogeneously dispersed in the polymeric matrix without a cluster. In addition, the components proportion evaluation is required to maintain good electrical conductivity and good printing quality. For this, the filament needs to present enough conductive material; however, the excess of this material can compromise the thermoplastic, mechanical, and printability properties (stiffness, viscoelasticity, tensile, and yield strength) of the filament[18]. Also, the fabrication of new filaments enables some interesting advantages, such as the tailoring of conductivity, since the commercial filaments can present a limited amount of conductive material; and the possibility of including electrocatalysts within the filament, aiming at the improvement of its electrochemical performance.

Herein, we have focused on the most robust designs reported in the literature that can be obtained by a single-extruder FDM 3D printer, which is more accessible worldwide. The selected configurations will be presented in detail, highlighting the simplicity of the devices and the wide range of applications.

3 PRINTING

FDM technologies are in growth for the construction of electrochemical devices and (bio)sensors. In the FDM process, three-dimensional (3D) objects are constructed layer-by-layer from a CAD file on a computer-controlled platform. In this process, a thermoplastic polymer is heated to a temperature that is slightly above the melting point and extruded through a nozzle and deposited on a heated platform. The 3D printer movement is computer-controlled in x-, y- and z-direction. When the deposition of the first layer is completed, the second layer is printed over the first layer. This process continues until the part-manufacturing is concluded[8,22].

Nevertheless, FDM technology displays some limitations, such as an insufficient quality of the printed objects due to its structural defects (high porosity) and unsatisfactory sealing properties[8,23]. In this regard, studies to enhance printing quality have been explored through the optimization of printing parameters[23–25]. Several parameters affect the mechanical properties of printed parts, such as infill, layer height, orientation, temperature, among others. All parameters can modulate the morphological and structural characteristics of 3D printed electrochemical devices.

Recently, Abdalla and coworkers[25] have shown that the effects of different printing layer thickness and orientations can affect the resistivity of conductive 3D printed materials and, consequently, the electron transfer kinetics. On the other hand, Goordev *et al.*[23] reported that the porosity of FDM-materials depends on the extrusion multiplier, which is a parameter to control extrusion flow rate. In fact, there are other printing parameters almost unexplored in the literature[26–31] that can affect the electrochemical performance of 3D printed devices. The following printing parameters can be evaluated: temperature, speed, orientation, layer thickness, extrusion multiplier and perimeter number. For those more enthusiastic 3D printer users, we discuss how each printing parameter can be explored in order to obtain improved electrochemical devices, including some sugestions for future works, in Supporting Information (Sections S3. Printing parameters: Temperature, speed, orientation, and layer thickness and S4. Printing parameters: Extrusion multiplier and perimeter number).

4 3D PRINTING IN ELECTROANALYSIS

4.1 Electrochemical Sensors

Electrochemical sensors are capable of monitoring electrochemical reactions at the electrode/solution interface. The most common conventional/commercial electrodes are carbon-based (glassy carbon and boron-doped diamond) and metals-based (gold and platinum)[32]. However, relatively low reproducibility and stability (surface contamination) and high manufacturing cost are serious drawbacks of such electrodes [33]. Because of the aforementioned, electrodes manufactured *via* 3D printing technology appear as an alternative to conventional electrodes due to features such as low-cost, high versatility, great potential for large-scale production (disposable). 3D-printed-based electrodes also have the advantage to be obtained with conductive filaments of different compositions, in addition to being of easy surface modification increasing its application for the study of specific reactions[3]. In this regard, 3D-printed electrodes have been increasingly employed in the most diverse electrochemical processes in industrial and academic fields[3,34].

To manufacture 3D printed-based electrochemical sensors, conductive filaments are required. This type of filament presents in its composition a blend of an insulation material (thermoplastic polymer greatly important for the printing process) and a conductive material (mostly graphene, graphite, and carbon black). Conductive filaments are commercially affordable and the most used to date were Black Magic® (graphene-based filament) and Proto-Pasta® (carbon black-based filament). Both filaments use the thermoplastic polymer PLA which represents around 90% of its final composition. Another highly used thermoplastic polymer is ABS. While PLA is an environmentally-friendly material, since is a biodegradable polymer, ABS is a petroleum-based non-biodegradable plastic[3]. Also, it is possible to employ other thermoplastic filaments as aforementioned, such as PETG, Nylon®, PVA, TPU, TPE, PCL, and PP, and the choose of the best material can be performed based on the main characteristics of each material, presented in Table S1, in accordance with the researcher's needs. The combination of different thermoplastic materials is also possible[3]. In this sense, some review articles previously published have highlighted that electrodes manufactured from commercially available conductive filaments have great potential for the determination of the diverse type of analytes[3,4,34,35].

In some cases, the 3D-printed sensors which were manufactured using commercial filaments provide poor conductivity which can lead to low electrochemical performance. This fact is related to the low conductive sites present in such devices (generally only around 10% is conductive material in the filament composition). Thus, two approaches are mostly explored aiming to enhance the conductivity of the 3D-based sensors: (i) the use of surface treatments (an issue addressed in section 5) and (ii) the use of lab-made manufactured filaments with a higher percentage of conductive material. The second approach explores to load the polymer thermoplastic with conductive materials, such as graphite[17,36–38], graphene[21,39,40], carbon black[19], carbon nanotubes[41], and metallic nanoparticles[20,42], being possible to combine one or more of the aforementioned conductive materials[21,43] leading to the production of the composite. The printability and the electrochemical performance of the sensors obtained by such lab-made filaments are the most important parameters evaluated to check the proportion of conductive material inserted in the structure of the thermoplastic polymer. For instance, Foster and colleagues[17] reported an interesting way to manufacture a nano-graphite-based home-made filament (NG/PLA) aiming the production of improved sensors for the simultaneous detection of lead(II) and cadmium(II). The authors investigated a range of NG/PLA filaments containing 1, 5, 15, 20, 25, 30, and 40 wt% NG, and they concluded that 25% wt% NG loaded PLA provided better printability and electrochemical properties for both metals sensing. Such electrode was employed later for the manganese sensing in water samples achieving satisfactory results[36]. Stefano et al.[44] also investigated the manufacturing of lab-made filaments and explored their use as a platform for biosensing. The production of the filaments involved the incorporation of graphite in a PLA matrix, obtaining a 40% wt. graphite filament, as summarized in Figure 2. The electrodes obtained from this filament did not require laborious surface treatment (only a simple surface polishing treatment) and were employed for the sensing of uric acid and dopamine, and the development of an immunosensor for SARS-CoV-2.

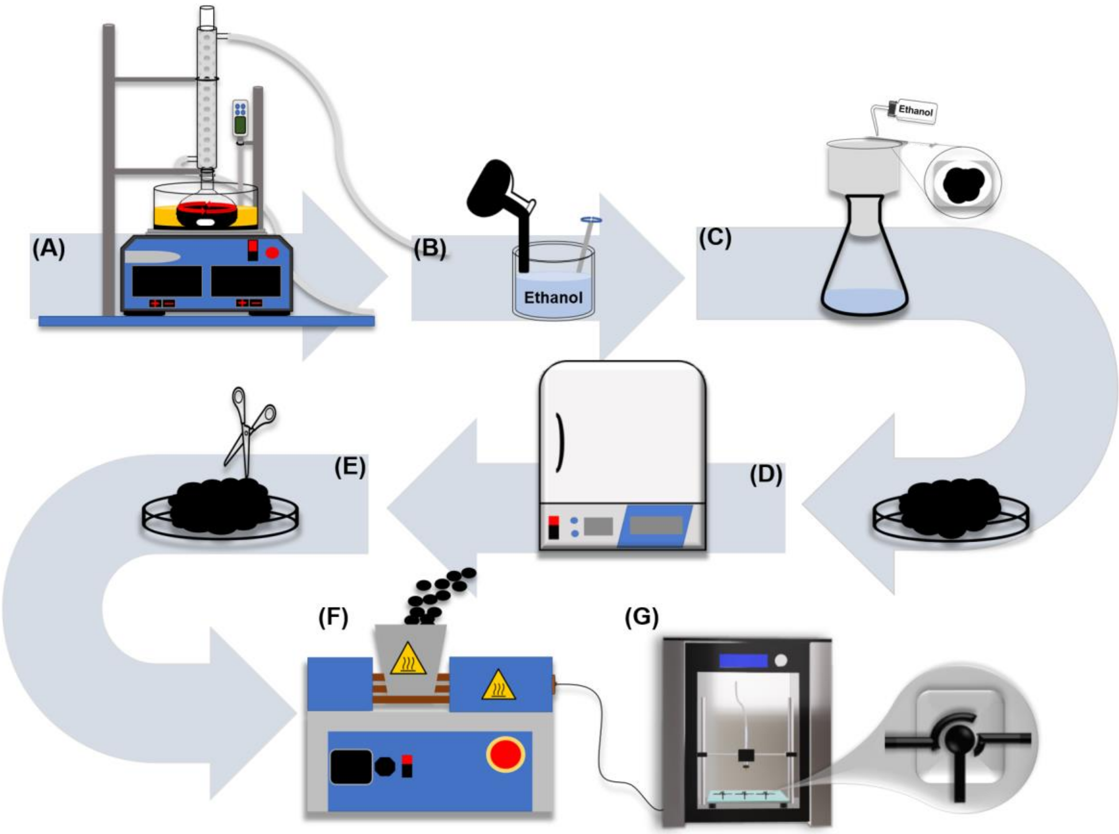

Figure 2. Scheme of the lab-made filament production. **(A)** incorporation of graphite powder on PLA and a reflux system under constant stirring and heating; **(B)** recrystallization of the composite (Gpt-PLA) in ethanol; **(C)** filtration of the composite constantly washing with ethanol; **(D)** drying step on the oven at 50 ºC; **(E)** cut into small parts; **(F)** composite extrusion step and **(G)** 3D printing of the electrochemical sensor. Adapted with permission from Stefano, J. S.; Guterres e Silva, L. R.; Rocha, R. G.; Brazaca, L. C.; Richter, E. M.; Abarza Muñoz, R. A.; Janegitz, B. C. New Conductive Filament Ready-to-Use for 3D-Printing Electrochemical (Bio)Sensors: Towards the Detection of SARS-CoV-2. *Anal. Chim. Acta* **2021**, 339372 (ref 44). Copyright 2022 Elsevier.

Sensors produced from lab-manufactured filaments often provide comparable and even better performance than conventional electrodes, such as glassy carbon and boron-doped diamond electrodes. However, it is noteworthy to mention that if a researcher wants to start working in this research field, he/she will be faced with time-consuming procedures that use large amounts of toxic organic solvents (i.e. methanol, xylene, chloroform, among others) turning such procedures non-environmentally-friendly in research labs. On the other hand, 3D-based sensors using filaments with improved electrical properties provide an extremely low cost per electrode (around $0.20) and can be considered a disposable device. However, the use of cleaning procedures is also possible and reuse is also viable.

4.2 Sensors Arrangement and Electrochemical Cells

The 3D printing technology allows precise control over the customized three-dimensional structures, such as porosity and dimension. Such technology has been used for the development of electrochemical devices, which can be fabricated in several shapes and sizes (miniaturization), leading to the construction of versatile and point-of-need structures. The production of these apparatus does not require sophisticated and expensive instrumentation, which does not limit access to laboratories and research groups. Considering the freedom of design provided by the FDM-based 3D printing, a myriad of devices can be prototyped, and several examples can be found in the literature[3,35,45]. Two recent reviews focused on presenting different electrochemical cells fabricated by 3D printing were published and can be accessed if the reader wants to see a great variety of designs[29,46]. Figure 3 illustrates some examples of electrochemical cells and electrodes and a brief description of each design is also presented.

A complete electrochemical system can be designed and developed by the use of 3D printing technology. Electrochemical cells can be molded and fabricated using non-conductive filaments while the use of conductive filaments allows the fabrication of electrodes, forming a complete electrochemical system, as presented recently by two works published by our research group[7,47]. Richter *et al.*[7] reported a completely 3D printed electrochemical sensing platform developed in a single step using the FDM technique. PLA or ABS could be used for the container, cover, and screws of the electrochemical cell, which had the capacity for 5 mL of solution. The cell was designed as a cylinder, fixed to a base with screws (Figure 3.1). The possibility to remove the cell base enabled the fitting of the working electrode, also 3D printed in rectangular plate-shape. All three electrodes were 3D printed using a conductive filament composed of a mix of PLA (thermoplastic) and carbon black (conductive material). A hollow cube with four faces of thickness of either 0.75 or 3.0 mm was printed and each side (face) was cut and used as working (rectangular plate), counter, and pseudo-reference electrodes. The piece of printed material used as a pseudo-reference electrode was partially covered with silver ink to provide potential stability. This sensing platform was successfully applied for dopamine detection, demonstrating the potential application of 3D printing technologies for the development of complete electrochemical systems.

As aforementioned, the versatility of 3D printing technology allows the manufacture of different cell designs, and thus another approach is presented by Silva and colleagues[47]. A cylindrical-shaped cell designed to work with cylindrical-shaped electrodes was constructed without the need for screws to assemble the base. The cell cover was developed in a specific configuration to enable the insertion of the three cylindrical electrodes (Figure 3.2). The three electrodes were printed using a conductive filament of graphene/PLA (G/PLA). The surroundings of the electrodes were covered with nail polish to delimitate the working area. To avoid parallel reactions, the counter electrode was fabricated with an increased area, in the shape of an arc surrounding the working electrode. The 30 mL cell (including the cover) was printed using PLA filament. The electrodes were hollow cylinder-shaped, enabling the connection with the potentiostat cables (Figure 3.2), where one of the extremities was closed, which was used as the electrode surface. The working electrode surface was modified with an enzyme layer containing tyrosinase and applied for catechol determination in water samples. This electrochemical 3D-printed system was also employed for the detection of serotonin in synthetic urine and a low LOD of 0.032 μmol L^{-1} was achieved.

Showing the versatility of FDM-based 3D printed structures, the before-discussed electrochemical cell[7] was adapted to be used with conventional reference ($Ag/AgCl/KCl_{sat}$) and counter (platinum wire) electrodes[16,36]. This electrochemical set-up was employed to perform square-wave anodic stripping voltammetry for the simultaneous detection of cadmium and lead[16] and square-wave cathodic stripping voltammetry for manganese detection[36].

The literature shows other types of fully 3D printed-based set-ups[48–50]. For instance, Kokkinos' research group reported two similar devices (Figure 3.3 and 3.5) fabricated by a dual extruder 3D-printer using non-conductive filament (PLA, white colour) to manufacture the cell compartment and conductive filaments (carbon-loaded/PLA[48] and carbon-loaded/ABS[49]) to print the working, counter, and pseudo-reference electrodes within the cell. Both devices were employed for the analysis of pharmaceutical and environmental samples. A preliminary version proposed by the same research group can be seen in Figure 3.7 that shows the three electrodes embedded in a single device, however, without a cell compartiment.

Ferreira *et al.*[50] proposed a different fully 3D printed electrochemical set-up used for the voltammetric screening of drugs (Figure 3.6). A desktop FDM 3D printer was used to produce the ABS-based cell, which was composed of three parts: solution vessel, stick, and cover with two embedded 3D-pen-printed CB/PLA electrodes (counter and pseudo-reference). This cell enables the use of any planar working electrode (boron-doped diamond, graphite sheet, and 3D printed CB/PLA electrodes) which is easily assembled at the base of the compartment.

The freedom of design provided by the FDM-based 3D printing technology also enables the production of a wide range of devices in varied configurations. Li and co-authors built a multi-material 3D printed fluidic device (Figure 3.8) for measuring pharmaceuticals in biological fluids with the acquisition of analytical features comparable to a conventional system[51]. O'Neil and co-workers[52] also reported a microfluidic flow cell through a single-step manufacture utilizing multi-material 3D printing (Figure 3.4), which was evaluated for catechol detection.

Crapnell and collaborators (Figure 3.10)[53] proposed a single-step 3D printing procedure to obtain a fully printed electrochemical cell, using PLA filament for the cell and CB/PLA for the electrodes. The proposed cell was explored for the simultaneous detection of ascorbic acid and acetaminophen. Another fully 3D printed electrochemical system with three electrodes on planar base (similar to a conventional screen-printed electrode strip) was fabricated by a dual extruder 3D printer (Figure 3.14)[54]. Escobar *et al*. (Figure 3.11)[55] developed an integrated platform based on a polyamide in which the electrochemical cell presented three independent compartiments to accommodate working, reference and counter electrodes (composed of carbon nanotubes and PLA). The authors proposed this novel design to work in oxygen-free conditions. Another interesting cell was proposed by Poltorak and co-workers (Figure 3.12)[56]. The cell consisted in an integrated platform to perform experiments in a four-electrode arrangement with interface between two immiscible electrolyte solutions. The proposed cell made possible the electrochemical study of ephedrine at polarized liquid-liquid interface with low cost and minimized consumption of organic phase.

Cardoso *et al.* (Figure 3.9)[57], Mendonça *et al.*[58] and Dias *et al*. (Figure 3.13)[59] have explored the aforementioned freedom of design to produce FDM-based batch injection analysis (BIA) cells. Such versatile BIA cells could be produced at a very low cost and are enable the coupling of different types of planar electrodes (boron-doped diamond electrode, screen-printed electrode, graphite sheet, and gold CDtrode), as well as conventional electrodes (glassy carbon, platinum, cooper, and gold electrodes).

Therefore, it is possible to conclude that even with low budgets the research groups worldwide can exploit the FDM-based 3D printing technology because of its low cost and accessibility. In addition, as shown above, it can be used to solve different analytical problems where the researcher's imagination is the limit.

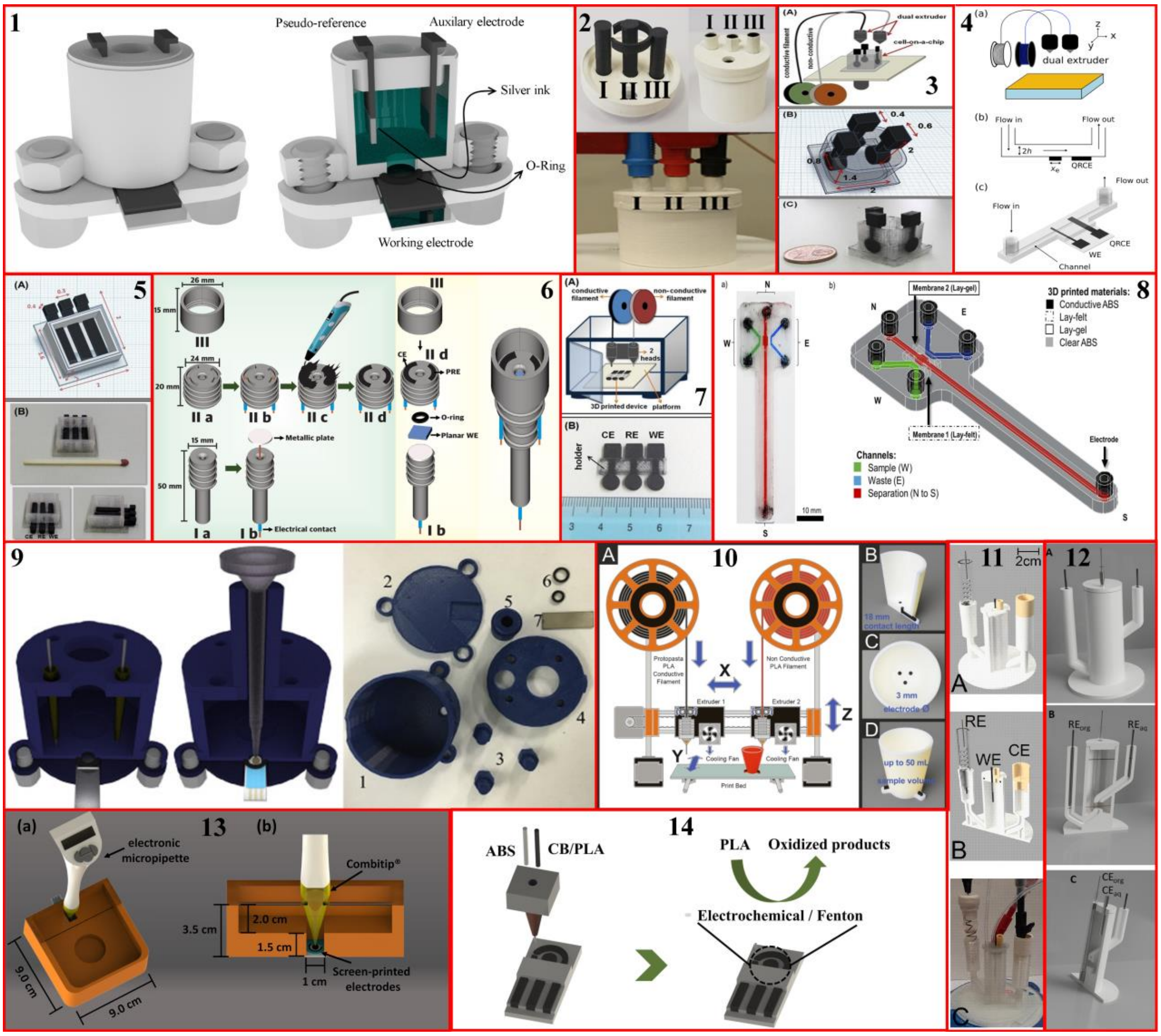

Figure 3. Literature overview regarding sensor arrangement and electrochemical cells manufactured by the 3D printing technology. **(1)** Complete additively manufactured electrochemical cell and its components adapted with permission from Richter, E. M.; Rocha, D. P.; Cardoso, R. M.; Keefe, E. M.; Foster, C. W.; Munoz, R. A. A.; Banks, C. E. Complete Additively Manufactured (3D-Printed) Electrochemical Sensing Platform. *Anal. Chem.* **2019**, *91*, *20*, 12844–12851 (ref 7). Copyright 2019 American Chemical Society; **(2)** 3D printed electrochemical cell and electrodes adapted with permission from Silva, V. A. O. P.; Fernandes-Junior, W. S.; Rocha, D. P.; Stefano, J. S.; Munoz, R. A. A.; Bonacin, J. A.; Janegitz, B. C. 3D-Printed Reduced Graphene Oxide/Polylactic Acid Electrodes: A New Prototyped Platform for Sensing and

Biosensing Applications. *Biosens. Bioelectron.* **2020**, *170*, 112684 (ref 47). Copyright 2020 Elsevier; **(3)** Schematic representation of the 3D printing procedure for the fabrication of the cell-on-a-chip device using a dual extruder 3D printer adapted with permission from Katseli, V.; Economou, A.; Kokkinos, C. A Novel All-3D-Printed Cell-on-a-Chip Device as a Useful Electroanalytical Tool: Application to the Simultaneous Voltammetric Determination of Caffeine and Paracetamol. *Talanta* **2020**, *208*, 120388 (ref 49). Copyright 2020 Elsevier; **(4)** schematic illustration of the single-step manufacture of electrochemical flow cells utilizing multi-material 3D printing adapted with permission from O'Neil, G. D.; Ahmed, S.; Halloran, K.; Janusz, J. N.; Rodríguez, A.; Terrero Rodríguez, I. M. Single-Step Fabrication of Electrochemical Flow Cells Utilizing Multi-Material 3D Printing. *Electrochem. Commun.* **2019**, *99*, 56–60 (ref 52). 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5 SURFACE TREATMENTS

As can be seen, the use of 3D-printing technology for printing electrochemical sensors has provided an advance in electroanalysis. Much of this advance can be attributed to ways found to improve the electrochemical performance of these sensors. As well known, the response of as printed 3D printed sensors can be very poor or negligible for some electroactive species (including for the popular redox probe ferricyanide/ferrocyanide)[3,16,60–63] due to the high amount of insulating polymer at the electrode surface after the printing process. As well known, the filaments usually employed have low amounts of conductive materials, the commercial filament Black Magic® for example presents only 8% of graphene on its composition[64].

The idea of “cleaning” or “activating” the surface of the obtained electrode was of great importance for the growth in the use of 3D printed electrodes in electroanalysis. This step is performed by removing the excessive polymeric material which remains as a film on the surface after the printing process and thus exposing more of the conductive material. In this sense, many approaches have been related in the literature and a discussion on the different methods can be found in the Supporting Information. In this section, we aim to highlight the simplest protocols accessible to any research laboratory to obtain improved 3D-printed electrochemical sensors.

Reagentless approaches including the use of laser and plasma sources are rapid however require a proper instrument to provide the treatment[65–67]. Chemical procedures and their combination with electrochemical treatment seem to be more accessible to generate enhanced results[61,68]. Greener protocols have also been proposed considering the elimination of toxic solvents[69].

Each treatment has its specificities, and searching for improvements in the electrochemical response, many authors proceeded with a combination of the pre-treatments discussed in Supporting Information (Section S5. Surface Treatments). In this aspect, it is common to perform a mechanical polishing prior to other types of activation, either for the obtention of a smoother and more uniform surface or for pre-removing the insulating film of PLA from the surface. Another reason for employing mechanical polishing further to other pre-treatments is that this is a simple procedure, which enables surface renewal and reuse of the electrodes. A simple combination of pre-treatments highly employed in the literature for CB/PLA electrodes consists of the sequence of mechanical polishing and electrochemical activation performed as reported by Richter *et al.*[7]. Figure 4 presents a schematic representation of the steps involved. They developed an electrochemical system completely 3D printed. The electrodes in the form of a hollow cube were obtained and polished in sandpaper (600 grit, followed by 1200 grit) as illustrated in Figure 4B. The cube-shaped structure was easier to polish than a rectangular plane piece, thus the printed cube was cut into rectangular pieces after the polishing procedure, and assembled in a complete additively manufactured electrochemical cell, also developed by the group (Figure 4C), and the reference electrode was previously coated with silver ink. The electrochemical cell was filled with a 0.5 mol L^{-1} NaOH solution, and an electrochemical pre-treatment was then performed involving the application of two constant potentials during 200 s, initially, +1.4 V, followed by -1.0 V (Figure 4D). SEM images (Figure 4E) show the difference between the steps of mechanical polishing and electrochemical treatment, the exposition of CB particles is improved after the second treatment, increasing, even more, the porosity, and consequently an effective area of the electrode.

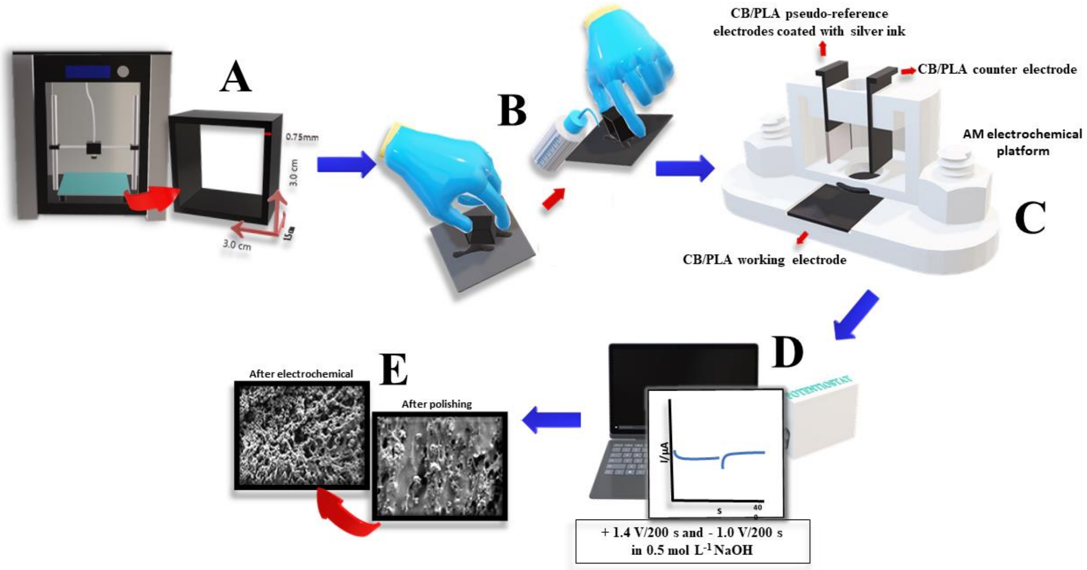

Figure 4. Schematic representation of an efficient and commonly employed pre-treatment performed on a CB/PLA 3D printed electrode: **(A)** 3D printing of the hollow cube (electrodes); **(B)** mechanical polishing in sandpaper; **(C)** assembling of the electrochemical cell; **(D)** electrochemical pre-treatment step; **(E)** SEM images of the electrodes before and after pre-treatment. Adapted with permission from Richter, E. M.; Rocha, D. P.; Cardoso, R. M.; Keefe, E. M.; Foster, C. W.; Munoz, R. A. A.; Banks, C.

E. Complete Additively Manufactured (3D-Printed) Electrochemical Sensing Platform. *Anal. Chem.* **2019**, *91*, *20*, 12844–12851 (ref 7). Copyright 2019 American Chemical Society.

A sequence of pre-treatments was also proposed for graphene-based electrodes (Figure 5) [62]. After printed (Figure 5A), the 3D-printed electrode was treated first by exposition of graphene *via* saponification of the PLA (Figure 5B) using 1.0 mol L^{-1} NaOH for 30 minutes, followed by the electrochemical oxidation (+1.8 V *vs.* SCE during 900 s) of the graphene-to-graphene oxide, and subsequent electrochemical reduction (scan from 0.0 to -1.8 V at 50 mV s^{-1}) of the graphene oxide to reduced graphene oxide (rGO) (Figure 5C). Finally, the rGO-generated electrode was rinsed with deionized water and dried at 70 ºC (Figure 5D). SEM images showed clearly the great exposition of the conductive material at the electrode surface. The rGO-generated surface presents a superior performance than the untreated or partially treated surfaces (containing graphene or graphene oxide), thus, this process is highly advantageous for this conductive filament that contains graphene in its composition.

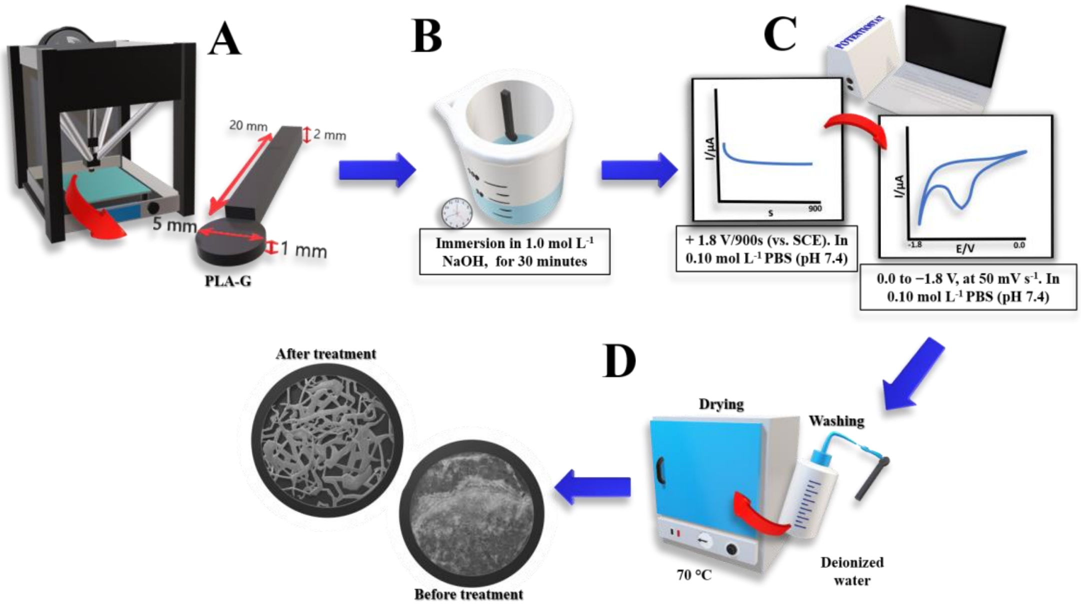

Figure 5. Schematic representation of an efficient pre-treatment performed on a G/PLA (Black Magic ®) 3D printed electrode: **(A)** 3D printing of the electrodes; **(B)** chemical pre-treatment by immersion in 1.0 mol L^{-1} NaOH; **(C)** electrochemical pre-treatment step; **(D)** rinsing of the electrode and drying step at 70 °C; **(E)** illustrative SEM images of the electrodes before and after pre-treatment.

Each pre-treatment has its pros and cons, and the choice of the best treatment should be performed according to the researchers aims, including time, reagents, handling, and instrumentation, and also the interaction of the analyte of interest with the obtained surface. Table S2 summarizes the types of pre-treatments and their main characteristics, such as time-consuming, their performance according to the redox probe employed (peak-to-peak separation), and the types of residues generated if the reader is interested in a more detailed comparison.

6 ANCHORING OF SPECIES

The modification of the filament before printing or anchoring of species after printing, such as metallic micro-and nanoparticles, has been reported to improve the conductivity and electrochemical performance of 3D printed sensors. In the first method, the modified filament can be produced after homogeneous mixing of the base polymer and the conductive material (modifier). This is an interesting strategy that allows the homogeneous distribution of the modifier in the entire filament, as a composite material. In this case, the modification can also be performed extruding commercial filaments in presence of the modifier, aiming its incorporation[70]. However, an extruder machine is necessary for these processes, which could be a disadvantage. On the other hand, the surface modification can be directly performed on the 3D printed electrode by the electrodeposition of metals, followed by the micro- or nanoparticles growth at a specific applied potential. This strategy has been applied for the synthesis of bismuth microparticles on a 3D graphene-based electrode, which allowed the improvement of the detectability of trace metals[71]. The sputtering method can also be used for homogeneous metal deposition on 3D printed electrode surfaces. For example, gold sputtering has increased the conductive properties and decreased the surface resistivity of 3D printed electrodes based on a mix of PLA/graphene[72]. The sensor was used for the polypyrrole nanoparticles attachment on reduced graphene oxide by π-π interaction, hydrogen bonding, and Van der Waal forces.

The electrodeposition method can also be used for the modification of 3D printed sensors with redox mediators, making possible its application for the catalysis and electrooxidation or reduction of species of interest. In this case, nickel and copper electroplating has been performed on 3D printed PLA/graphene electrodes, followed by the electrochemical synthesis of oxy-hydroxide redox mediators in alkaline media. This strategy improved the electrocatalytic activity of the 3D-printed sensor for glucose and sucrose detection, and as future perspectives include oxygen or hydrogen evolution reactions (OER or HER) and other electrochemical applications[73].

Regarding OER and HER reactions, Prussian blue and its analogs have been extensively used. The Prussian blue film is normally electrochemically deposited on the electrode surface by cyclic voltammetry in presence of both iron and potassium hexacyanoferrate in the solution[74]. Recently, an interesting strategy has been reported, in which the iron impurities present in commercial graphene conductive filament were used for the electrochemical synthesis of Prussian blue film on the 3D printed electrode, aiming the non-enzymatic sensing of hydrogen peroxide[75]. Besides that, 3D-printed G/PLA electrodes modified with nickel oxide have improved the OER activity as reported in the literature[76]. The nickel oxide electrodeposited in association with iron impurities of the filament provides the enhancement of electrochemical catalysis. These works demonstrate that iron and other "impurities" of the commercial filaments are not necessarily a problem, since they can be explored for the improvement of the electrochemical devices.

Another possibility is the immobilization of biomolecules on 3D-printed electrodes for the development of biosensors. The immobilization of enzymes (i.e., glucose oxidase, horseradish peroxidase, tyrosinase, glutaraldehyde, alkaline phosphatase) has been widely applied for this approach[6,47,77–79]. The immobilization can be performed directly on 3D printed electrode surfaces by cross-linking between its oxygenated functional groups or using immobilization agents, such as the Nafion® film or EDC/NHS couple (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride and N-hydroxysuccinimide). Nafion® has been used as a binder for several materials (carbon nanotubes, nanoparticles, and biomolecules). Related to a new approach using

EDC/NHS couple, it can be highlighted the immobilization of specific antibodies anchored on carbon black-based 3D sensor, which allows a stable and covalent immobilization on the electrode surface. The immunosensor was applied for the detection of *Hantavirus araucaria* protein[80]. In addition, the anchoring of antibodies has also been reported on graphite-based 3D printed electrodes using EDC/NHS, this platform was successfully employed for the detection of SARS-CoV-2 *spike* protein[44]. These works demonstrate the innovation and versatility of the 3D technology applied for the development of biosensors. From perspectives, robust and large-scale produced 3D printed electrochemical sensors combined with biological agents (i.e., enzymes, antibodies, aptamers, DNA, and among others) or chemical modifiers (molecularly imprinted polymers, metal-organic frameworks, and their composites) can be envisaged for the development of improved electroanalytical devices.

7 CONCLUSION AND PERSPECTIVES

In this feature article, we present a tutorial perspective on the use of FDM 3D printing technology for the fabrication of enhanced electrochemical (bio)sensors. The guide was created to help and expand the professional knowledge of the reader from different areas to use this high-potential technique in the manufacture of improved electrochemical (bio)sensors, providing more independence for the choice of materials, techniques, and parameters. 3D printing has become a priority subject and a hot topic for different areas of research. Its development has grown along with the immediate industrial revolution 4.0, and bringing with it the advancement of the production of 3D printed electrodes applied especially for (bio)sensors, which are central to many applications. Increasingly popular due to their easy operation, 3D printers are becoming a part of research labs, which has led to the rise of the development of 3D printed electrodes.

Using relatively low-cost materials and developing devices that are simple to assemble aggregates a wide range of designs and objects, performed by FDM 3D printing, useful in the electroanalytical field with applicability in (bio)sensing. As it is a very versatile technique, it is possible to develop microfluidic devices, complete electrochemical cells, and electrodes, in varied shapes and compositions, thus providing new applications according to the purposes of analytical chemistry. In addition, the possibility of using different types of materials for the construction of objects further increases the innovation potential of the devices, apparatus, and cells such as mechanical resistance, robustness, flexibility, transparency or opacity, hydrophobicity, or recyclability. The obtention of an extruder can additionally provide the opportunity of fabricating new conductive filaments by the mixture of thermoplastic filaments with a diversity of conductive materials (carbonaceous, oxides, metals, among others).

In this context, another practice that has been growing is the hyphenated techniques using 3D printing, where two or more analytical techniques are coupled to obtain a more efficient, complete, and faster final device than when separated. An example of hyphenation found in the literature is electrochemistry with microfluidics, a technique that has also been explored regarding its construction from 3D printing. Currently, these devices present analytical performance close to classical methods, such as chromatography, in addition to presenting improvements such as miniaturization, allowing the construction of portable and versatile (bio)sensors, with low sample consumption. In addition, new and improved strategies for manufacturing electrodes are emerging, such as the application of other techniques in electrode post-printing, increasing its versatility and analytical performance. Thus, 3D printing is a growing field in electroanalysis, and, though its use has been exponentially growing in the last years, there is space for novel strategies, materials, and designs providing innovative applications in this field.

In conclusion, what determines the final quality obtained is the knowledge regarding the 3D printer and its main processes involved in the 3D printing of objects, considering the development of structures, materials used, and printing parameters. 3D printed devices for electrochemical detection can be used for a variety of applications, including pharmaceutical, food, environmental, medical, and industrial. The construction of low-cost, miniaturized hyphenated devices has numerous advantages and is a promising field for further investigation. The development of new conductive filaments, especially those modified with carbon nanoparticles, offers a wide range of modifications and applications enabling the application of 3D printed electrodes in various areas of analytical chemistry. Finally, this is a topic that, despite being well disseminated, is still on the rise and there is still a lot to be studied and developed, which makes it a hot topic with promising characteristics.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

S1. The number of publications in the Web of Science® database regarding different 3D printing techniques and different material extrusion techniques (Figure S1); **S2.** Raw polymeric materials used in FDM 3D printing and its main characteristics (Table S1); **S3.** Printing parameters: Temperature, speed, orientation, and layer thickness; **S4.** Printing parameters: Extrusion multiplier and perimeter number (Figure S2); **S5.**

Surface treatments and activations of 3D printed electrodes; **S6.** FDM 3D printed electrochemical sensors pre-treatments and main characteristics (Table S2) (PDF)

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