International Journal of Chemistry; Vol. 17, No. 1; 2025
ISSN 1916-9698 E-ISSN 1916-9701
Published by Canadian Center of Science and Education

Main Processes and Materials for 3D Printed Electrochemical Sensors: Focus on Carbon Composites

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Received: December 25, 2024 Accepted: February 6, 2025 Online Published: February 10, 2025

doi:10.5539/ijc.v17n1p45 URL: https://doi.org/10.5539/ijc.v17n1p45

Abstract

Electrochemical sensors can detect the quantity of substances of interest, aiding human activities in various fields such as medicine, environment, engineering, chemistry, biology, and others. The recent advancement of versatile 3D printing techniques has allowed their application in numerous areas, including electrochemical sensors. Given the low cost of printers that use polymer filaments, increasing studies have been published in recent years exploring the addition of conductive materials, generally carbon-based, into their filament for electrochemical applications. This work presents a bibliometric analysis on the subject and reviews studies of this range of materials and processes for their production. Despite the complexity of possibilities, some common objectives necessary for the optimized production of 3D printed sensors stand out. They are: defining suitable reagents and processes to ensure a homogeneous dispersion of composites; optimizing the ideal dosage between materials, ensuring a good balance between conduction and printability; executing appropriate surface treatment; configuring the orientation and appropriate printing parameters; studying and selecting materials with a good detection limit for correct modification for specific applications. It is expected that future works will continue to investigate the various factors that affect the properties of these materials, increasingly optimizing the performance of 3D printed sensors.

Keywords: sensors, 3D printing, conductive filament, carbon, graphene

1. Introduction

A sensor is commonly defined as a "device that receives and responds to a signal or stimulus," where a signal can be understood as information, whether of quantity, property, or condition, which is generally converted into an electrical signal (Fraden, 2016). Sensors are used in various applications, encompassing different classes such as optical, pressure, humidity, chemical, electrochemical, and other sensors. Electrochemical sensors can directly measure the electrical properties of a target analyte or the effect of the analyte on the electrical properties of another material (Fraden, 2016). In this way, information about the analyte, such as the presence of a chemical or biological element and even its quantity, can be discovered.

Electrochemical sensors can be used in environmental, biological, or industrial applications of interest (Fraden, 2016; Lowinsohn and Bertotti, 2006). They determine the amounts of salts in water, pesticides in water, glucose in blood, viruses in urine, among other specific objectives of each sensor (Fraden, 2016; Siqueira et al., 2023; Stefano et al., 2022).

A simplified example of electrochemical analysis that we can illustrate is a conductometry test, used to define the amount of salts present in water. In water without salts, the addition of a certain salt will increase its conductivity, and by measuring this conductivity variation, we can identify the amount of salt present in the water. However, some factors can interfere with the measurement; appropriate frequencies and currents, sensor materials are studied and selected to provide accurate results (Fatibello-Filho, 2022; Ewing, 1969).

Another more common example is the analysis of substances present in an analyte through redox reactions by a pair of electrodes, being a positive pole and a negative pole, cathode and anode, respectively, inducing a current to the analyte. With appropriate experimental parameters, such as voltage and electrode materials that allow the oxidation and reduction of the analyte, the electron transfer in these reactions can be measured in the system and provide information about the analytes present and their quantities (Fatibello-Filho, 2022; Ewing, 1969; Skoog et al., 2018). This analyte could be a virus present in a patient's urine, blood, or saliva, such as COVID-19, which, when interacting with the antibodies present on the electrode properly designed for this purpose, will chemically react, altering the system's electron transfer. This typical current change will identify whether the patient has the virus or not (Stefano et al., 2022).

Electrochemical electrodes used as sensors can be made of various materials; some popular examples include metallic electrodes, carbon paste electrodes, and screen-printed carbon electrodes, which are printed on paper for subsequent disposal after use, presenting low cost (Fatibello-Filho, 2022; Ewing, 1969; Skoog et al., 2018; Palenzuela, C. L. M. & Pumera, M., 2018).

Recently, with the advancement and availability of 3D printing techniques and conductive filaments, research on 3D printed electrochemical sensors has significantly increased in recent years. 3D printing of electrochemical sensors presents a series of advantages such as low production cost, rapid prototyping, increasing manufacturing speed, and producing a versatile method with sensors of various geometries for diverse applications (Palenzuela, C. L. M. & Pumera, M., 2018; Pohanka, 2016; Kwok, et al., 2017; Hamzah et al., 2018).

Without intending to review extensive general fundamentals of electroanalytical chemistry, which can be found in specific books, this work is limited to reviewing the most used methods in the production of 3D printed electrochemical sensors. Given the versatility and low cost of printing techniques with carbonaceous polymer composite conductive filaments (Ambrosi & Pumera, 2016; Wei et al., 2015; Abdalla & Patel, 2021), today they are the most used methods and materials for 3D printing sensors (Abdalla & Patel, 2021). Therefore, these processes and materials will be emphasized in the discussion.

2. Bibliometric Review

To conduct a selective search, we used the composite term "3D printed electrochemical sensors" on Elsevier's Scopus and ScienceDirect platforms and Clarivate's Web of Science (WOS) database. The bibliometric data from these databases are presented and compared. The connection between works and the co-occurrence of terms among them are analyzed using the Vosviewer software (VOSviewer, 2024).

For discussion purposes, care was taken to individually select works that cover various aspects of the topic, such as different processing routes, different materials used, and different applications. As related works were reviewed and discussed, new references were found, and specific new searches were conducted to contribute specifically to each example of the general topic of "3D printed electrochemical sensors."

All these discussed aspects are fundamental for the understanding and development of new materials. According to Callister and Rethwisch (2010) and Askeland and Wright (2015), there are four fundamental pillars in materials engineering: processing, structure, properties, and application of these materials. The chosen processing of each material will affect its structure and properties, thus dictating its performance in the application.

Searching for the term "3D printed electrochemical sensors" yielded approximately 489 search results on the Scopus platform (Elsevier, Scopus, 2024) and 669 on the Clarivate platform (Web of Science, 2024), while ScienceDirect (Elsevier, Science Direct, 2024) found 10,700 results, with 1,991 works registered in the last year alone (2023). The difference is due to the different content existing between the platforms, as well as the different filtering mechanisms.

The Scopus and Clarivate platforms appear to be more selective and also provide data analysis tools on the site, indicating the number of articles by area of interest, year, country, authors, among others. These platforms also offer a robust tool for exporting data for analysis in specific software like VOSviewer (2024), which is used here. On the other hand, the ScienceDirect database presents a much larger number of works but with more challenging filtering and data analysis, although it also allows exporting data for analysis in complementary software.

Figure 1 presents a comparison of the number of works published in recent years in the area of interest on the three platforms. It can be observed that interest in the topic has been growing rapidly and relatively steadily.

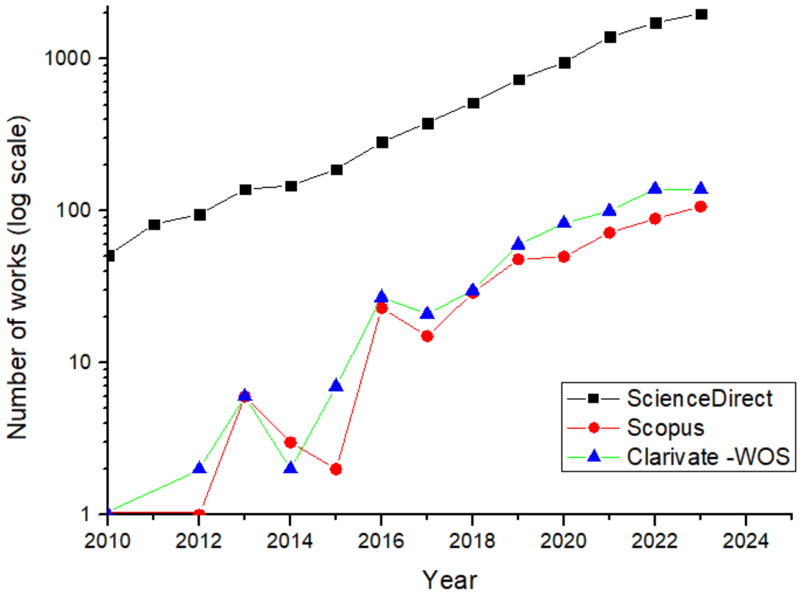

Figure 1. Comparison of the number of works published in recent years with the term "3D printed electrochemical sensors" on the platforms ScienceDirect (Elsevier, Science Direct, 2024), Scopus (Elsevier, Scopus, 2024), and Clarivate (Web of Science, 2024)

Figure 2 (a) provides an overview of the number of publications by country (Elsevier, Scopus, 2024), with Brazil being a major contributor to the topic. Figure 2 (b) shows the number of publications by scientific field, suggesting the relevance of the subject in areas such as chemistry, engineering, medicine, energy, environment, among others (Elsevier, Scopus, 2024).

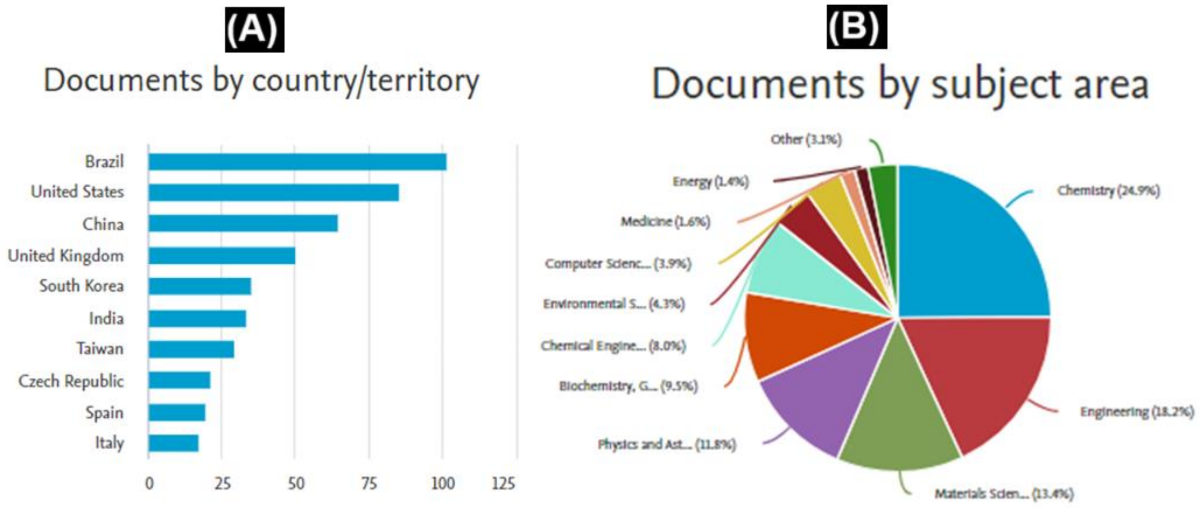

Figure 2. Comparison of the number of works published by country (a) and by scientific field (b), searched with the term "3D printed electrochemical sensors" on the Scopus platform (Elsevier, Scopus, 2024)

Figure 3 shows the number of times each work cites others, illustrating the connection between groups of works and their authors. The lines and positions represent the proximity of connections, and the size of the sphere representing each author's works corresponds to the number of citations.

It can be observed that the most cited works are well connected with each other, where they mutually cite each other, creating a relatively new network, as is the case with the topic in question. If the topic were older, there would be many citations to fundamental previous works, which is not the case here. Therefore, it is confirmed that 3D printed sensors are a new topic in the electrochemical area. Some of these found works will have their content discussed in the following sections.

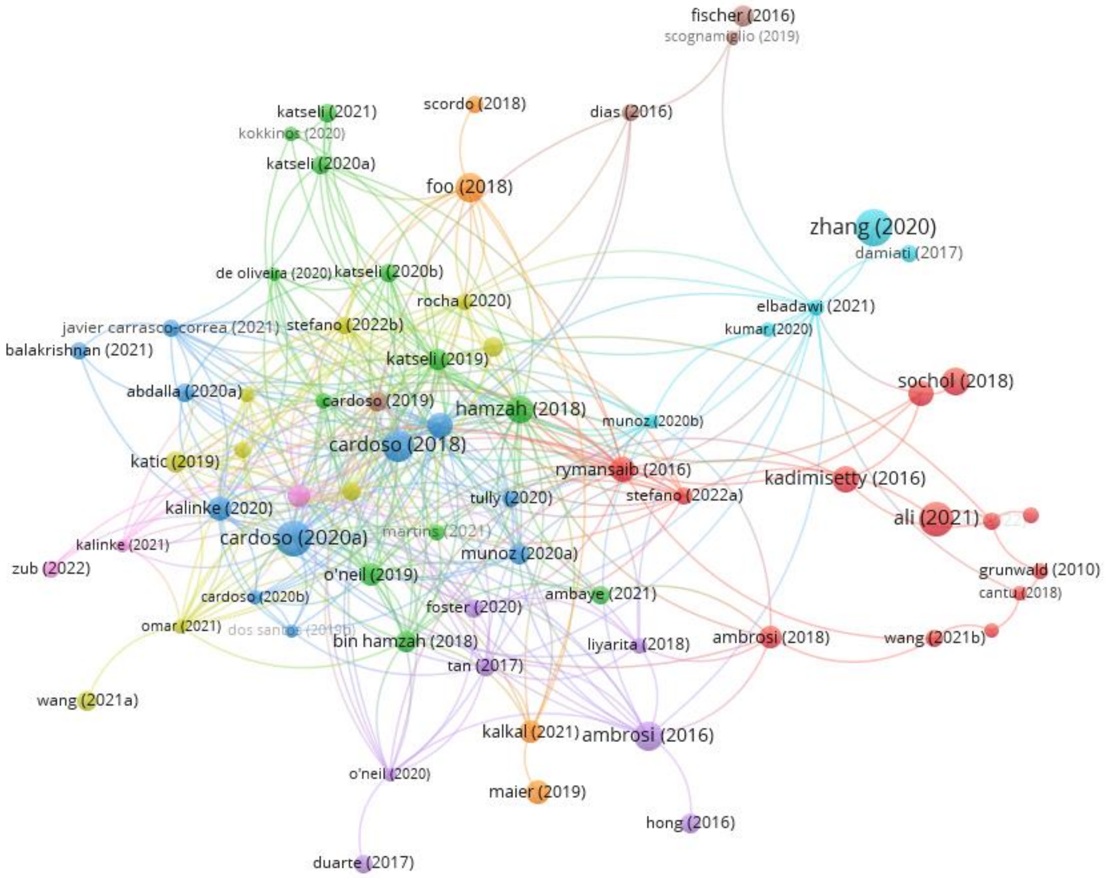

Figure 3. Diagram of the relationship between authors' citations of each other for works searched with the term "3D printed electrochemical sensors" on the Clarivate platform (Web of Science, 2024), carried out in the VOSviewer software (2024)

Figure 4 shows the correlation between the most frequently found terms among the analyzed works. It can be observed that all these groups of terms are connected, though some more than others, forming distinct clusters.

Of the three recurring word groups mapped, one suggests a discussion more focused on the technique, presenting terms such as: 3D printing, technology, and fabrication. Another group appears to focus more on materials, with terms like: PLA, polylactic acid, and carbon, indicating important materials currently used for 3D sensor printing, such as carbon and PLA. Lastly, a group with terms like: cyclic voltammetry, sample, determination, concentration, and detection limit, suggests a discussion more focused on the signal response of these sensors and their effectiveness and performance.

The term co-occurrence map among the works illustrates the connection between different study pillars of materials, as mentioned by Callister and Rethwisch (2010) and Askeland and Wright (2015), which are the relationships between: processing, structure, properties, and application of materials. In the next section, all these fields of interest will be discussed among the selected works.

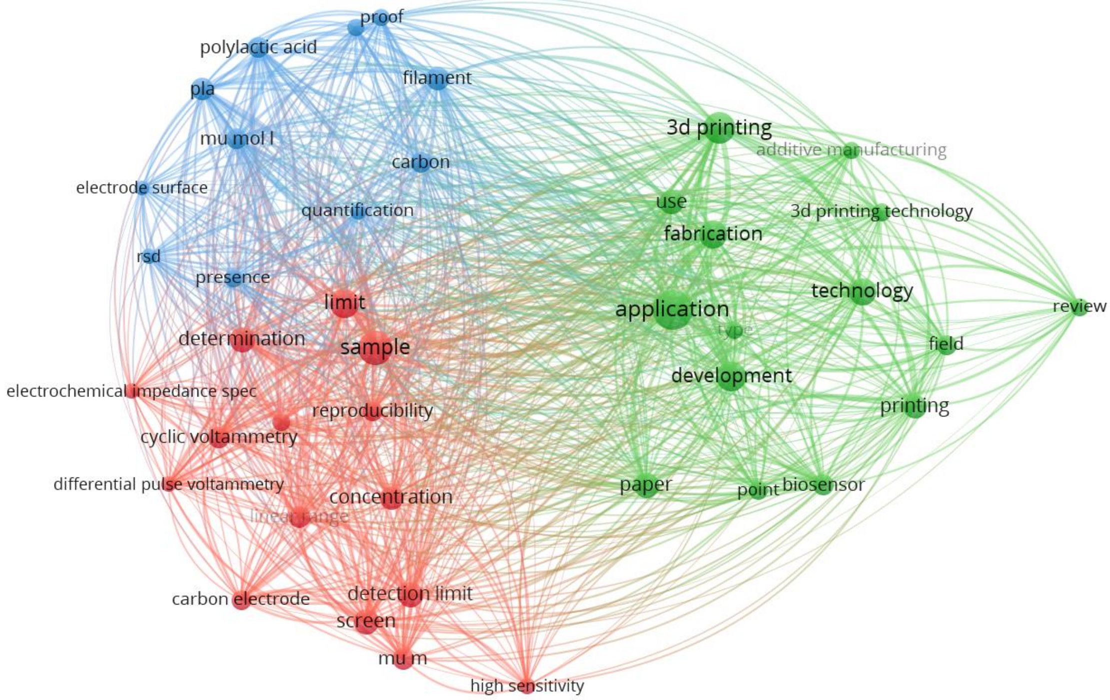

Figure 4. Word co-occurrence map for works searched with the term "3D printed electrochemical sensors" on the Clarivate platform (Web of Science, 2024), carried out in the VOSviewer software (2024)

3. Main Materials Used in 3D Printed Eletrochemical Sensors

Various materials are used for 3D printing in different sectors, with one significant technological sector being the 3D printing of electronic components (Kwok, 2017; Hamzah, 2018; Lee, Jian-Yuan et al., 2017; Lee, Ke Yau et al., 2017; Leigh et al., 2012). Several studies have utilized 3D printed electronic materials for sensing applications (Hamzah et al., 2018).

Electrode materials can be metals, ceramics, polymers, or composites. There are various specific research studies that may use different methods, each with its advantages and disadvantages (Hamzah et al., 2018; Ambrosi & Pumera, 2016).

In sensor applications, it is important that the electrodes do not dissolve or react undesirably with the electrolyte. Therefore, for each desired analyte, some specific electrodes may be more recommended, as they have an appropriate voltage range for the redox reaction of the analyte, capturing its signal without permanent redox changes to the sensor (Skoog et al., 2018). Some potential windows for different electrodes such as platinum, mercury, carbon, and boron-doped diamond in various supporting electrolytes. These potential ranges can be found in the works of Skoog et al. (2018) and Cavalheiro et al. (2012).

One of the most common types of 3D printed electrodes found in the literature are metallic electrodes. In these studies, electrodes are typically printed in stainless steel and coated with gold (Au), bismuth (Bi) (Lee, Ke Yau, et al., 2017), nickel (Ni), platinum (Pt) (Ambrosi & Pumera, 2018), among other less common materials (Hamzah et al., 2018).

Printing metallic electrodes requires expensive and robust equipment, as well as additional manufacturing processes, usually to properly coat the metal for specific sensing applications (Hamzah et al., 2018).

Ambrosi and Pumera (2016) provide a review of various 3D printing techniques. Although the fused deposition modeling (FDM) technique has poorer surface quality compared to powder-based plastic additive manufacturing processes (Hamzah et al., 2018, Bikas et al., 2016), it is the most commonly used 3D printing technique due to its simplicity and the availability of low-cost printers. In fact, the terms carbon, carbon electrode, and PLA are among the most frequently found material terms in the literature when analyzing a large database, as seen in Figure 4.

To achieve conductivity, carbon conductive materials are dispersed in a polymer matrix. Carbon materials and nanomaterials used include graphite, carbon black (CB), carbon nanotubes (CNT), graphene, or reduced graphene oxide (rGO). The chemical structures of these carbon materials are illustrated in Figure 5.

The crystalline structure of graphene consists of a two-dimensional sheet of carbon atoms, where each atom is covalently bonded to three other carbon atoms, forming hexagonal structures (Fatibello-Filho et al., 2022; Callister & Rethwisch, 2010). In reduced graphene oxide, this carbon structure has bonds with other oxygen and hydrogen atoms to a greater or lesser extent, depending on the level of oxidation (Fatibello-Filho et al., 2022; Cavalheiro et al., 2012). As the name suggests, a carbon nanotube consists of a carbon atom plane in a tubular shape, which can be single-walled or multi-walled (Fatibello-Filho et al., 2022; Bikas et al., 2016). Crystalline graphite, in turn, consists of multiple graphene planes stacked on top of each other (Fatibello-Filho et al., 2022; Cavalheiro et al., 2012). Finally, carbon black has a structure similar to graphite, except that its structure is three-dimensional and less ordered, combining amorphous and crystalline carbon structures (Bikas et al., 2016).

The polymer matrix is usually composed of polymers such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyamide (PA), or other less common ones (Hamzah et al., 2018; Ambrosi & Pumera, 2016).

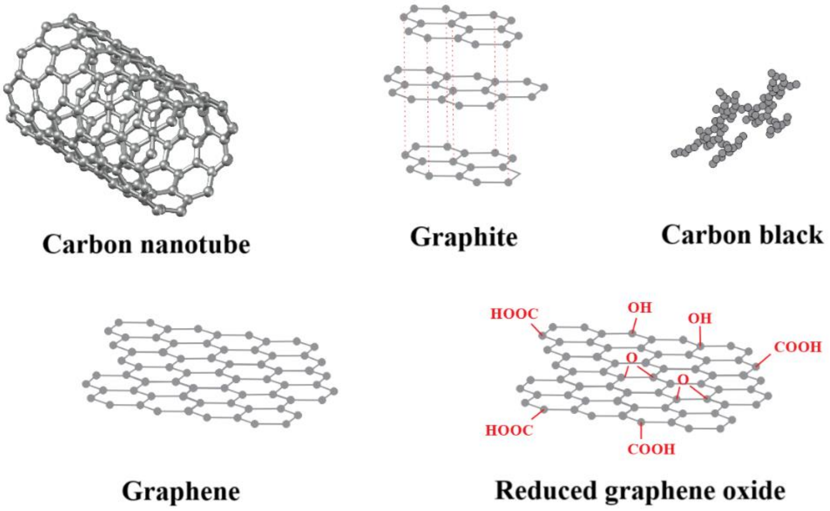

Figure 5. Representation of chemical structures of different carbonaceous materials used as electrochemical sensors

In particular, graphene possesses unique properties, such as a high elastic modulus (~1 TPa (Lee et al., 2008)), a high theoretical surface area (~2630 m^2/g (Stoller et al., 2008)), and notable thermal (~300-500 W/mK (Balandin et al., 2008)) and electrical (~10^2 S/m (Gómez-Navarro et al., 2007)) conductivities.

It is important to find the best combination of materials to create the composites. It is necessary to study the amount of carbonaceous particles added to the polymer matrix to ensure that the material has good conductivity without losing too much of its flexibility and proper moldability during printing (Hamzah et al., 2018). This ensures that the material maintains an appropriate glass transition temperature (Tg) for extrusion.

Other factors that can also affect the quality of the electrode include its lifespan and surface treatment. In the study by Kalinke et al. (2022), commercial filaments of 1, 2, and 3 years old were analyzed. The electrochemical response is reasonably better for newer filaments; over time, the filaments degrade and lose signal. Pereira et al. (Pereira et al., 2021) conducted a surface treatment on the electrode using plasma, increasing the sensor's sensitivity by approximately 100 times.

4. 3D Printed Process for Sensors

Although the printing process began around the 1980s, it has gained commercial scale in recent years (Wei et al., 2015; Ryder et al., 2002; Bassoli et al., 2007). The 3D printing process starts with designing the sensor using one of several computer-aided design (CAD) software programs. The design is then converted into a file in a standard language called Standard Triangle Language (STL), which interprets the design as a list of coordinates to be read by various slicing software for printing. The software slices the object layer by layer, providing a roadmap for the printer to print the 3D object (Hamzah et al., 2018).

In addition, the slicing software also allows for the configuration of various printing parameters, such as internal porosity, filament diameter, and printing direction. This can result in a sensor with anisotropic properties, leading to different performances depending on the direction of printing (Hamzah et al., 2018; Zhang et al., 2017; Bin Hamzahet al., 2018).

With the model ready, it can be read by the 3D printer, which will heat the material above its glass transition temperature (Tg), achieving the appropriate viscosity parameters. The filament can then be extruded layer by layer until the object, in this case, the sensor, is completed (Wei et al., 2015). Therefore, Tg is a vital parameter to determine for 3D printing applications (Utela et al., 2008).

Although mastering printing techniques is a significant task, one of the main challenges in sensor production is, in fact, the creation of the special conductive filament for each desired application.

5. Production of Carbonaceous Composites for 3D Sensor Printing

Table 1 provides a summary of different studies on carbonaceous polymer composites used for sensors or conductive filaments produced by or for FDM. It also briefly indicates the processing routes, major studies conducted, and key properties obtained from each reference. A more detailed description of these studies and processing methods will be provided in the following sections.

Table 1. Summary of different studies on carbonaceous polymer composites used for sensors or conductive filaments produced by or for FDM

Materials	Summary of the processing route	Some contributions of the work	Main properties obtained	Ref.
Graphene/ABS (0.4~7.4 wt% of graphene)	Oxidation of graphite, high rpm mixing of OG with ABS in NPM solvent, reduction to a graphene-hydrazine composite for subsequent precipitation, extrusion and printing.	Production of the first study of graphene/ABS conductive filament for 3D printing; study of ideal concentration; identification of electrical percolation threshold.	Electrical conductivity in the order of ~1.05x10-3 S.m^{-1}	(Wei et al., 2015)
Graphene/PBT (until 5.5 wt% of graphene)	Graphene mixed in isopropanol; subsequent addition of PBT and stirring at high temperature to evaporate the solvent; followed by extrusion for printing.	Study of ideal concentration; identification of electrical percolation threshold.	Electrical conductivity in the order of ~2x10^{1} S.m^{-1}	(Gnanasekaran, et al., 2017)
Carbon nanotube/PBT (until 13.4 wt% of carbon nanotube)	Carbon nanotube mixed in isopropanol; subsequent addition of PBT and stirring at high temperature to evaporate the solvent; followed by extrusion for printing.	Study of ideal concentration; identification of electrical percolation threshold.	Electrical conductivity in the order of ~3x10^{0} S.m^{-1}	(Gnanasekaran, et al., 2017)
Graphite/PLA	Solubilization and mixing of PLA and graphite in acetone and chloroform solution (3:1 v/v), with magnetic stirring, for subsequent extrusion and printing.	Glucose detection.	Limit of detection (LOD) of 2.4 μmol L^{-1}	(Rocha et al., 2020)
Graphite/PLA	Solubilization and mixing of PLA and graphite in acetone and chloroform solution (3:1 v/v), with magnetic stirring, for subsequent extrusion and printing.	COVID detection and comparison with commercial filaments.	LOD of 1.35 nmol L^{-1} 0.10 mg mL^{-1}	(Stefano et al., 2022)
Carbonblack/PLA (28.5 wt% of carbon black)	Solubilization and mixing of PLA and graphite in acetone and chloroform solution (4:1 v/v), with magnetic stirring, for subsequent extrusion and printing.	Detection of catechol and hydroquinone in water and hydrogen peroxide in milk.	LOD values of 0.02 and 0.22 μmol L^{-1}	(Stefano et al., 2022b)
Carbonblack/ABS (commercial filament)	-	Surface treatment based on cold oxygen reactive plasma.	Up to 100 times greater sensitivity in detecting dopamine after surface treatment	(Pereira et al., 2021)
Carbonblack/ABS (15 wt% carbon black)	Extrusion of commercial Carbon black/ABS pellets.	Electrical conductivity analysis depending on printing Direction.	Electrical conductivity in the order of ~2.39x10^{-2} S.m^{-1}	(Zhang et al., 2017)
Graphene thin films (for comparison, not 3D printed)	Application of graphene thin film by the technique of substrate lifting in graphene suspension.	Analysis of electrical conductivity of the thin film and control of film thickness and properties as a function of the amount of graphene used.	Electrical conductivity in the range of 1x10^{-4}~1.25x10^{-3} S.m^{-1}	(Arapov et al., 2015)

5.1 Graphene Material

Among carbonaceous materials, graphene is one of the materials with the best conductive properties. However, a major issue in producing the composite is the proper dispersion of the material in the polymer matrix without graphene agglomerating. To avoid this problem, it is common to first use graphene oxide (GO), which has better dispersing properties, and then reduce GO to reduced graphene oxide (rGO) (Wei et al., 2015; Zhao et al., 2013; Podsiadlo et al., 2007).

Without proper dispersion, the agglomeration of carbonaceous materials in the filament can lead to defects and even clogging in the print nozzle.

The reduction of GO is strategic in its processing. It is typically done by reaction with hydrazine, which restores up to 80% of the graphene structure, with the remaining structure still containing some residual GO (Wei et al., 2015; Mattevi et al., 2009).

Graphene is usually produced by the Hummers method (Hummers & Offeman, 1958) or a derivative of this method (Muzyka et al., 2017). The literature recommends the use of the term reduced graphene oxide (rGO) when obtained from reduction techniques, as it does not present 100% of the pure graphene structure (Bianco et al., 2013).

The reduction route is attractive due to cost-benefit considerations (Pei et al., 2012). The most efficient product for this route is hydrazine; however, its high toxicity makes large-scale use difficult (Silva et al., 2017). A solution is to use more sustainable reducers, with ascorbic acid (AA), or vitamin C, being a promising alternative that is also being used in the literature (Oliveira et al., 2019; Fernández-Merino et al., 2010).

Another process, also highlighted in recent years, is the production of graphene through the electrochemical exfoliation of graphite in sulfuric acid, where both oxidation of graphite and reduction to rGO occur in a single process (Parvez et al., 2013). In this case, the graphene is filtered and washed to remove the acid, which may contain some agglomeration, and then dispersed in dimethylformamide (DMF) for storage (Parvez et al., 2013).

The production of graphene for incorporation into conductive filaments for 3D printing is the same as for other applications, such as incorporating a thin film into polymeric or glass substrates using methods like transfer, drop-casting, or others (Gnanasekaran et al., 2017; Arapov et al., 2015). For example, Arapov et al. (2015) produced conductive graphene thin films on polymeric and glass substrates using the transfer method, achieving electrical conductivity in the range of $1x10^{-4}$ to $1.25x10^{-3}$ S/m, which is comparable to the values of conductive 3D-printed sensors, as seen in the following section.

Therefore, 3D-printed sensors can be a versatile alternative, replacing the production of sensors obtained by other methods, such as the transfer deposition on substrates.

5.2 Conductive Polymer Filaments with Graphene

According to Wei et al. (2015), their work produced the first commercial graphene filament for 3D printers. The steps for this production are as follows:

a) Oxidation of graphite flakes using the optimized methodology from Marcano et al. (Marcano et al., 2010);

b) The graphene oxide (GO) sheets are then dispersed in N-Methyl-2-pyrrolidone (NMP) medium (Paredes et al., 2008), which is compatible with the ABS polymer used in this case;

c) Two solutions containing GO in NMP and ABS in NMP are mixed in a homogenizer at 1500 rpm for 1 hour;

d) Reduction with hydrazine is then carried out in the GO-ABS solution in NMP without noticeable phase separation, forming the G-ABS solution, where G represents reduced graphene oxide (rGO);

e) To precipitate the G-ABS composite, the solution is added to water, thereby coagulating G-ABS;

f) The composite is then separated by centrifugation, washed, and dried in a vacuum oven;

g) After drying, the composite is extruded into a 1.75mm diameter filament for use in commercial printers.

The high speed of the homogenizer is crucial for proper homogenization, as without the equipment, phase separation was noticeable in the process (Wei et al., 2015).

Wei et al. (2015) tested different amounts of rGO in ABS (0.4, 0.8, 1.6, 2.3, 3.8, 5.6, and 7.4 wt%) and PLA (0.8 wt%). Optimal surface qualities were achieved with samples containing up to 5.6 wt% rGO in ABS, while the 7.4 wt% sample showed discontinuities in extrusion and homogenization. The sample with 0.8 wt% rGO in PLA also exhibited good print quality. According to Wei et al. (2015), by improving the dispersion technique, even larger amounts of rGO could be incorporated into the filaments.

The filament conductivity was measured using the four-probe method on hot-pressed rectangular models and 3D-printed samples. An electrical conductivity of up to 1.05 x 10^{-3} S/m was obtained for 5.6 wt% rGO in ABS for 3D-printed samples. It was also observed that the conductivity is lower for 3D-printed samples compared to hot-pressed ones, likely due to porosity (Wei et al., 2015).

Wei et al. (2015) observed that the variation in electrical conductivity with respect to rGO content follows a percolation model of connections (Stauffer & Aharony, 2018). Conductivity increases dramatically as the rGO content reaches the percolation threshold, forming an infinite network (Stankovich et al., 2006). At least three of the samples presented by Wei et al. (2015) reached this threshold. Thus, the conductive composites presented allow 3D printing to address complex engineering problems using printable electronics (Stauffer & Aharony, 2018).

The Tg of pure ABS is around ~105.8 ºC. In Wei et al.'s (2015) study, the addition of rGO to the polymer matrix resulted in a composite Tg of approximately ~110 ºC, which is close to that of pure ABS. This can affect viscosity during printing, and the viscosity can be studied by adjusting printing temperature settings to achieve optimal parameters.

In a TGA study, Wei et al. (2015) also observed that the lowest degradation temperature of the analyzed samples is around 339.17 ºC. With the printing temperature set at 230 ºC, which is more than 100 ºC below, this ensures a high level of safety regarding this factor. There was also no significant variation in the coefficient of thermal expansion, showing less than 1% expansion from room temperature to Tg.

Other studies or applications have been successfully conducted with graphene/PLA sensors. For example, Foster et al. (2017) used Black Magic® filament (Black Magic®, New York, USA), which contained 8% graphene by mass in the PLA composite, and reported a study for energy storage devices.

Another study, also using Black Magic® filament, Foo et al. (2018) observed that the surface of the 3D-printed electrode exhibited high electrical resistance, which was improved with a gold layer.

As seen in these examples, commercial conductive filaments like Black Magic® have been used in various studies for the fabrication of electrochemical sensors. A summary of various studies using these commercial materials can be found in the work of Cardoso et al. (2020).

5.3 Conductive Polymer Filaments with Graphite

A bit less conductive than graphene but simpler, cheaper, and sufficiently efficient for some applications are graphite filaments in a polymer matrix such as PLA. Rocha et al. (2020) and Stefano et al. (2022) present methods for manufacturing conductive graphite filaments in a PLA matrix. A summary of the processes is described below:

a) First, 40% (~12g of the suggested amount) of the graphite mass is solubilized in 200 ml of acetone and chloroform (3:1 v/v) with stirring at 70°C for 30 minutes, according to Rocha et al. (2020). According to Stefano et al. (2022), with 40% wt of graphite, the best signal response is achieved while maintaining good electrode print quality, and the diluted chloroform will present reduced toxicity. The temperature helps with dispersion. The process should be done in a reflux system to prevent solvents from escaping, within a basin with commercial vegetable oil purchased from local stores. It is also recommended that the process be carried out in a fume hood with proper ventilation. Then, 60% of PLA (~18g, totaling 30g of graphite with PLA) is added to the mixture and kept stirring for an additional 3 hours.

b) After this process, the entire solution is poured into a container with 800 ml of ethanol to cool and recrystallize the material.

c) Once recrystallized, the PLA with graphite is filtered, and the residue of the solution is stored for proper disposal or reuse. The material is washed with ethanol.

d) Subsequently, the material is dried at 50°C for an indefinite period.

e) Once dry, the material is cut into smaller pieces of 2 cm.

f) The chopped material is added to the Filmaq3D extruder for filament production at 200°C.

g) Finally, the electrodes are printed with the 3D printer.

The studied filaments showed better results than commercially available graphene (Black Magic®, New York, USA) and carbon black (proto pasta®, Vancouver, USA) filaments.

According to Stefano et al. (2022), various amounts of graphite were tested, and the best balance of conductivity and printability was achieved with a 40 wt% graphite in PLA matrix. The applications for electrochemical sensors using these filaments are diverse. While Stefano et al. (2022) modified 3D-printed electrodes for COVID detection, Rocha et al. (2020) adapted them for glucose detection.

Although graphite is simpler to process and obtain for incorporation into a polymer matrix, its main disadvantage noted in the studies is the large amount required to achieve adequate conductivity, around 40 wt% relative to the polymer matrix.

5.4 Conductive Polymer filaments with Carbon Black

Returning to the discussion of the conductive properties of 3D-printed sensor surfaces, the study by Zhang et al. (2017) can be mentioned. Their work analyzed different printing parameters and orientations, resulting in sensors with anisotropic properties, with varying conductivities depending on the direction. This study used commercial carbon black/ABS pellets (Guangzhou Plastic Technology Co., Ltd., Guangzhou, China) with approximately 15 wt% carbon black. The sensor achieved a conductivity of up to ~2.39×10^{-2} S/m, nearly five times higher than the graphene filament previously mentioned by Wei et al. (2015).

A similar study confirms the direction-dependent conductive properties by Bin Hamzah et al. (2018), also using carbon black/ABS filaments, but does not report the production of carbon black conductive filament.

Pereira et al. (2021) also presents an interesting study by demonstrating a performance gain of the carbon black/ABS sensor through appropriate surface treatment with cold reactive oxygen plasma. This treatment resulted in up to a 100-fold increase in sensor sensitivity for dopamine detection.

Surface treatment has shown increased performance in various studies in the literature. Typically, by immersing the electrode for 10-30 minutes in different solvents, such as dimethylformamide, acetone, etc., conductive materials are better exposed on the sensor surface, thus increasing its conductivity (Pereira et al., 2021; Cardoso et al., 2020; Browne et al., 2018; Gusmão et al., 2019).

All the reviewed works above and most of the studies and reviews found in the literature (Stefano et al., 2022; Cardoso et al., 2020) analyze and produce sensors using commercial carbon black filaments. As mentioned, the filament is a critical point of high importance for the performance of these sensors.

According to Stefano et al. (2022b), commercial filaments have low content of conductive materials, leading to poor sensor performance. To improve the performance of these filaments, their study produced a new conductive carbon black/PLA material for sensors (28.5 wt% carbon black), with superior performance compared to commercial filaments. The filament was successfully used for various applications, such as hydrogen peroxide detection in milk and catechol hydroquinone in water. The process is similar to the production of composites with graphite discussed earlier in the work of Stefano et al. (2022b) and Rocha et al. (2020).

5.5 Conductive Polymer filaments with Carbon Nanotubes (CNTs)

Gnanasekaran et al. (2017) produced conductive filaments for 3D printing from carbon nanotubes (CNTs) and graphene in a PBT matrix. The production of the graphene used is explained by Arapov et al. (2015). The CNT and graphene materials were dispersed in the PBT matrix using a process summarized in the following steps:

a) 50 mg of CNT and graphene were placed in 100 ml of isopropanol and sonicated in a bath (Bransonic 1510) for 2 hours in an ice bath to prevent temperature rise;

b) The appropriate amount of PBT powder was added and sonicated for an additional hour;

c) Isopropanol was then evaporated at 90 ºC in a water bath while the solution was vigorously stirred to avoid phase segregation;

d) The solution was left to dry at room temperature for 24 hours;

e) Finally, the obtained composites were extruded and printed.

It was observed that a certain degree of non-homogeneity could not be avoided due to the high viscosity of the composite, especially in the later stages of drying. Nevertheless, the method demonstrates good dispersion (Ghisland et al., 2013). The viscoelasticity of the CNT/PBT and graphene/PBT composites showed a more elastic behavior compared to other studies in the literature using different composites, such as ABS. However, it did not significantly alter the final viscosity given the small amount of carbon materials added to the polymer (Gnanasekaran et al., 2017).

The CNT/PBT composites studied showed better results than the graphene/PBT composites. In their study, the CNT content varied up to ~5.5 wt% in PBT, and graphene up to ~13.4 wt% in PBT. Electrical conductivity values of ~2×10^{1} $S.m^{-1}$ and ~3×10^{0} $S.m^{-1}$ were achieved for CNT and graphene, respectively. It was observed that the individual PBT and CNT/graphene materials had conductivity values of ~1×10^{-12} $S.m^{-1}$ and ~1×10^{2} $S.m^{-1}$, respectively (Gnanasekaran et al., 2017).

As with Wei et al. (2015) work on graphene, the electrical conductivity of polymeric conductive composites with CNTs, such as those by Gnanasekaran et al. (2017), is also governed by the electrical percolation model. A percolation threshold must be reached to define the minimum amount of carbonaceous materials to be added (Gnanasekaran et al., 2017; Stauffer & Aharony, 2018).

It is interesting to note that Gnanasekaran et al. (2017), like others, focuses on the production of conductive filaments. Electrical conductivity is indeed important for electrochemical sensors. However, it is also necessary for the material to interact properly with the analyte, allowing electron transfer. See the following study.

Hussain et al. (2023) compared the properties of different sensors printed from commercial conductive PLA filaments with various carbonaceous materials. The materials were tested for serotonin detection. The results of electrical conductivity and LOD normalized by the carbon content of each composite are presented in the table.

Each type of commercial filament has a different amount of the analyzed carbonaceous material. To make a real comparison, normalizing the electrochemical signal by the carbon content is essential to compare the performance of the carbonaceous material in question. This was not done for electrical conductivity, thus providing a single value for the filament's conductivity. These values are presented in Table 2.

Although the graphite filament had the best electrical conductivity, graphene and multi-walled carbon nanotubes had the best LOD for serotonin.

Additionally, Hussain et al. (2023) analyzed the stability of the sensor in continuous testing. In this case, the carbon black sensor showed the most stability, with minimal signal change after successive tests.

Table 2. Properties of carbonaceous electrochemical sensors in PLA matrix for serotonin detection (Adapted from Hussain et al. (2023))

Material	Carbon Weigh (%)	Electrical Conductivity ($S.m^{-1}$)	LOD normalized for carbon content ($\mu mol.L^{-1}$)
Carbon Black/PLA	~45.4	~25.10^{-1}	3.4
Graphite/PLA	~25.4	~1.10^{0}	3.9
Graphene/PLA	~21.3	~38.10^{-1}	0.7
Carbon nanotube-multiwalled/PLA	~14	~30.10^{-2}	2.3

As presented in the process of composites with carbon nanotubes, as well as in previous materials like graphene, graphite, and carbon black, producing them is a complex task. There are many steps and processes involved in creating materials suitable for conductive filaments for 3D printing of sensors.

In general, the polymer matrix needs to be dissolved and solubilized with the carbonaceous materials adequately dispersed in a solution, which will later precipitate into a carbon-polymer composite.

It is important to emphasize that the study of proper dispersion of carbon materials in the polymer matrix, without clumping, is crucial to ensure good conductivity. Choosing the appropriate routes and reagents for each case is a challenge, as those that aid in the proper dissolution of polymers and dispersion of carbons often have some level of toxicity.

To mitigate these factors, environmentally friendly reagents have been experimented with in recent research. For example, Sharif et al. (2024) tested for the first time the use of Cyrene, a solvent with a lower environmental impact, for the production of 3D-printed electrochemical sensors.

All these factors need to be considered to successfully produce optimized materials for 3D manufacturing of electrochemical sensors.

6. Conclusions

It has been observed that studies related to 3D-printed electrochemical sensors are recent and growing in recent years, as 3D printing techniques have become more accessible. Various works have been found using carbonaceous composite materials and polymer matrices for 3D printing sensors, along with a significant citation of these materials in bibliometric data analysis.

Some examples of studies focused on the production of filaments made from specific materials, while others used commercial filaments and concentrated on studying modifications and their applications. There have been works that studied printing parameters and others that examined the influence of filament age on the electrochemical signal. Overall, there is a broad diversity of studies and future possibilities for improving these materials.

By individually studying some of these works, it was possible to identify some of the main conductive materials used. These include graphene, carbon nanotubes, graphite, and carbon black, which have been used in various polymer matrices such as ABS and PLA.

There have been numerous routes, materials, and treatments found for the production of these sensors and filaments, as well as for various types of applications. As observed in the works, defining an appropriate route is a complex challenge that depends on each specific application and study of interest, as well as the available raw materials and infrastructure equipment.

However, the review of these diverse studies and materials contributes to defining some general, desirable goals to be achieved, regardless of the application. These goals are:

a) Selection of appropriate reagents and processes to properly dissolve and disperse the materials to form a homogeneous composite;

b) Optimization of material dosages to reach the electrical percolation threshold and ensure a good balance between conductivity and printability;

c) Execution of proper surface treatment to reduce surface resistivity;

d) Use of an appropriate printing direction to ensure better conductivity;

e) Study of material selection with a good detection limit for correct modification for specific applications;

It is hoped that the review presented here will synthesize and provide suitable examples for a good discussion and understanding of the production of 3D-printed electrochemical sensors from polymeric carbonaceous composites. Thus, presenting the state of the art on the topic and contributing to the pursuit of future optimizations in the manufacturing of these sensors.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) – Finance Code 001.

Authors contributions

Prof. Dr. Devaney R. do Carmo and Ms. Luís M. Genova was responsible for study, drafted the manuscript and revising. Ms. Abner S. B. Sales, Ms. Danubia Santiago Martins, Dr. Murilo Santos Peixoto and Natália A. N. Rodrigues was responsible for discussion and drafted the manuscript.

Funding

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) – Finance Code 001.

Competing interests

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.

Informed consent

Obtained.

Ethics approval

The Publication Ethics Committee of the Canadian Center of Science and Education.

The journal's policies adhere to the Core Practices established by the Committee on Publication Ethics (COPE).

Provenance and peer review

Not commissioned; externally double-blind peer reviewed.

Data availability statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Data sharing statement

No additional data are available.

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