3D Assembly of Graphene Nanomaterials for Advanced Electronics

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Since the discovery of electricity and the creation of the first transistors two centuries ago, the field of electronics has evolved rapidly to become omnipresent. Today, electronic devices are challenged by new demands in function and performance: they are expected to be lightweight, highly efficient, flexible, smart, implantable, and so on. To meet these demands, the materials and components in devices need to be carefully selected and assembled together. In this regard, the controlled assembly of 3D graphene structures holds tremendous potential to achieve these levels of multifunctionality and outstanding properties. Advanced processing approaches, such as 3D printing, allow the fabrication of a variety of 3D graphene-based materials that present outstanding properties and a high degree of multifunctionality. Herein, the recent progress in the fabrication of graphene-based devices for advanced electronics using controlled assembly is reported. The benefits of controlling the microstructure of graphene nanomaterials for enhanced properties and functionalities are highlighted, and the various fabrication methods and their implications on the organization of materials are reviewed, as well as selected electrical devices. The approaches described here are opening up new avenues for the fabrication of health or structural monitoring devices, autonomous machines, and interconnected objects.

1. Introduction

Smart electronics groups a category of electrical devices that can interact to some extent with their environment and operate autonomously. Such devices include smartphones, touch screens, and keyless locks. However, there is an ever-increasing demand for smarter electronics that exhibit multifunctionalities, superior mechanical properties, biocompatibility, transparency, high computational speed, and low power needs but high power generation, high precision, etc. These stringent requirements challenge electrical materials and their current fabrication methods.[1]

Since the discovery of electricity production and storage in the 19th century, the fabrication of electronic devices has undergone tremendous development.[2] Today’s chips and electrical components are micro and nanoelectromechanical systems (MEMS and NEMS) prepared via lithography on silicon wafers, at resolutions of a few hundreds of nanometers. Although such MEMS and NEMS can make up complex electrical circuits in small devices such as smartphones and hearing aids, they have several limitations. For example, they are necessarily opaque and stiff and primarily made of metal and welded onto a rigid substrate. Although strategies could be found to create flexible substrates with rigid islands to receive the electrical parts,[3] or to transpose silicon technology to flexible electronics by means of the nanoscale dimensions,[4] electrical components themselves remain stiff, black, and connected by metallic welding and soldering. In addition, traditional thermosetting epoxies and metals used in electronics pose limits for implantable systems. For example, the high mismatch in Young’s modulus between metallic electrodes and the brain in the case of neuron stimulation can lead to severe immune reactions in the surrounding tissues and further impair neurological functions.[5,6] To address the demands for new properties, scales, and functions in electrical devices, researchers have put a lot of effort into developing alternative strategies.

A convenient path to combine multiple functional and structural properties is the elaboration of composite materials. For instance, polymer composites with electrically conductive fillers can couple the mechanical properties of the matrix with
the electrical conductivity of fillers that form percolating networks.\textsuperscript{7,20} Due to its ultimate thinnest dimensions, and excellent electron mobility, graphene might be one of the best materials for smart electronic devices.\textsuperscript{19–24} However, pure 2D graphene has limited applications in electronic systems due to its zero bandgap. Other forms of graphene hold tremendous potential, in particular 3D graphene, that is, a 3D interconnected network of graphene. As arranging matter in 3D space offers infinite degrees of freedom, these 3D graphene-based nanomaterials greatly expand the available design space and open new potential applications. Indeed, it has been demonstrated in other systems that 3D organization of matter can yield unusual combinations of properties such as self-shaping materials,\textsuperscript{12–14} strong and tough composites,\textsuperscript{15–17} as well as unusual physical phenomena such as ballistic transport, iridescence, and plasmonics.\textsuperscript{18–20} Thus, in the context of advanced electrically conductive devices, the recent research efforts to control the 3D organization of graphene at nanoscopic, microscopic, and macroscopic length scales is remarkable. Although numerous reviews have tackled the assembly of smart electronics,\textsuperscript{21} flexible electronics,\textsuperscript{22} 3D printed electronics,\textsuperscript{23–27} self-assembly,\textsuperscript{28} and nanomanufacturing,\textsuperscript{29} there is a knowledge gap about the synthesis, fabrication, and controlled microstructure in 3D graphene-based electronic nanomaterials with multifunctional properties.

The objective of this progress report is thus to provide an overview of the most recent research on 3D assembly of 3D graphene nanomaterials and to emphasize their potential for advanced electronics (Figure 1). More specifically, this study aims at highlighting the most efficient fabrication methods of 3D graphene nanomaterials, at demonstrating the importance of the 3D organization to generate multiple functions, and to provide concrete examples of devices. First, we introduce the direct synthesis of 3D graphene using chemical vapor deposition (CVD) on porous templates. Then, we describe how 2D graphene can be manipulated using external magnetic fields to create a 3D interconnected graphene network with amplified and unusual properties. In the following section, 3D printing technologies applied to 3D graphene and the resulting microstructures are reviewed and discussed. Finally, selected electrical devices are presented to underline the potential of these carefully organized 3D materials for electronic applications.

Developing processes for realizing multifunctional low-power, high-efficiency electronics is anticipated to empower everyday smart objects, homes, and health care devices with electronic capabilities. In the new paradigms of the Internet of Things and continuous monitoring, it is expected that billions of objects will be connected to participate in autonomous decision-making.\textsuperscript{30–32} These capabilities will impact healthcare, transportation, architecture, production, communication, etc. The controlled 3D assembly of graphene nanomaterials using 3D printing technologies is a promising path toward the fabrication of such interconnected devices.

2. Direct Synthesis of 3D Graphene by Chemical Vapor Deposition

As a 3D interconnected continuous network, 3D graphene nanomaterials are primarily ideal for energy storage applications.\textsuperscript{33} Indeed, their foam-like structure was found to allow high energy density, high-power performance, and long cycle life.\textsuperscript{33} Unlike pure carbon materials that have limited energy density, electroactive materials such as conducting polymers and metal oxides can attain very high specific capacitance.\textsuperscript{33–35} Thus, in terms of energy density, conducting polymers and metal oxides can be very efficient. However, one of the main limitations of these materials is their poor mechanical stability and thus short cycle life. This challenge, that is, poor cycle life, can be addressed effectively using 3D graphene nanomaterials. For instance, Chabi et al. used chemical vapor deposition (CVD) to prepare flexible interconnected graphene foams to be used in energy storage devices.\textsuperscript{36} They reported 100% capacity retention after 10 000 cycles of charge–discharge (Figure 2a,b). However, the resulting graphene foam had a very limited specific capacitance of only 3 F g\textsuperscript{−1}. To solve this issue, they instead prepared a 3D graphene–polypyrrole composite as electrode. The resulting hybrid electrode showed a specific capacitance of 660 F g\textsuperscript{−1} with

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an excellent capacity retention after 80,000 cycles of charge-discharge. The main reason behind this superior cycle life is the mechanical robustness and integrity of the produced composite foam. Similarly, Wang et al. used CVD to produce 3D graphene-multiwalled carbon nanotube (CNT) composites with a high specific capacitance of 286 F g⁻¹ and capacity retention.[37] A recent in situ study on the mechanical-electrochemical relationship in such nanomaterials showed that there is a strong correlation between the mechanical properties of the graphene foam and its electrochemical properties, especially cycle life.[38] The study proposes that the excellent cycle life of 3D graphene nanomaterials is a direct result of the mechanical robustness and flexibility of the interconnected graphene network. As the 3D graphene structure possesses compressible and flexible properties, it can accommodate the volume change during repeated charge-discharge cycles, resulting in extended cycle life.

Graphene foam, a 3D network of graphene flakes, was first synthesized by a CVD method using nickel foam as a template (Figure 2c–e).[19] Figure 2c shows a schematic illustration of CVD synthesis of graphene foam. Briefly, the Ni template is first annealed at high temperatures, e.g., 900–1000 °C. Then, a carbon source such as CH₄ or ethanol is injected into the furnace under a hydrogen and argon environment. The resulting graphene foam inherits its macroscopic and microscopic features such as porosity level and pore distribution, dimensions, and grain sizes from the parent nickel foam. Apart from Ni, polystyrene has been used as a template for the synthesis of graphene foams (Figure 2d,e).[38,40] Graphene foams have been used widely for supercapacitor applications, and although they show unprecedented mechanical robustness, electrical conductivity, and flexibility, they still fail to exhibit high energy density and capacity. One successful approach to attain both high energy density and high power density is to create 3D graphene–based hybrid electrodes such as 3D graphene–polymer and 3D graphene–metal oxide composites. Some examples are 3D graphene–polypyrrole, 3D graphene–polyaniline, 3D graphene–MnO₂,
3D graphene–cobalt oxide.\textsuperscript{[31,41,42]} For example, Choi et al. used a template-assisted approach to fabricate 3D graphene/MnO\textsubscript{2} electrodes for use in supercapacitors.\textsuperscript{[40]} This composite demonstrated a high energy density of 44 Wh kg\textsuperscript{-1} and very good cycle life. Similarly, Ambrosi and Pumera reported the synthesis of 3D graphene/Co\textsubscript{3}O\textsubscript{4} electrodes with a specific capacitance of 1100 F g\textsuperscript{-1} (at 10 A g\textsuperscript{-1}) and an excellent cycle life.\textsuperscript{[63]}

3D graphene composites can be prepared via a multistep synthesis procedure with CVD synthesis of the graphene foam followed by the deposition of the electroactive material by chemical oxidation, electrochemical deposition, or hydrothermal synthesis, among others. This templating approach is interesting due to its scalability and the extremely good properties of the final materials, displaying high mechanical stability and cycle life after a long time of charge–discharge cycles.\textsuperscript{[137,38,44]} However, although templating allows flexibility in chemicals and substrates and the possibility to reach submicrometric resolutions,\textsuperscript{[45–47]} the percolating network remains solely determined by the initial foam connections. Also, CVD is an energy- and cost-intensive method that is not easily applicable to large objects of complex and intricate shapes. With the expectation of the fabrication of electrical components and circuits for all devices around us, there is a need to find alternative processing pathways.

3D graphene–based electrode materials can also be prepared by direct 3D printing,\textsuperscript{[48]} hydrothermal method, and electrochemical exfoliation.\textsuperscript{[49–51]} Randomly distributing 2D graphene nanosheets in a solvent or a matrix has been done extensively already.\textsuperscript{[52–53]} However, those materials generally do not exhibit the performance of the 3D graphene foam composites, essentially due to limitations in concentration of 2D graphene that can be mixed in a liquid matrix, the subsequent rise in viscosity resulting in defects, and the insulating polymer layer between graphene nanosheets. Using dilute concentrations in exfoliated graphene but controlling its assembly using external fields is an interesting alternative for generating tailored 3D percolating networks and enhancing the properties. In the following section we describe the use of magnetic fields to direct the assembly of 3D percolating networks using functionalized 2D graphene.

3. Magnetically Directed Assembly of 3D Graphene Networks

Directed assembly of nanomaterials can be achieved via the use of external fields. Magnetic fields are more convenient than electrical fields as they are remote, scalable, and cheap, using permanent magnets or solenoids. However, while all matter can align with a very strong magnetic field, viable fabrication processes need to employ low-strength magnetic fields, below 500 mT.\textsuperscript{[54]} Therefore, the first step toward magnetically directed 3D structures using graphene is to functionalize graphene nanosheets, typically using magnetite (Fe\textsubscript{3}O\textsubscript{4}) or maghemite (γ-Fe\textsubscript{2}O\textsubscript{3}) nanoparticles (Figure 3). The functionalization can be done by coprecipitation. In this case, graphene nanosheets are mixed with a solution of iron sulfate and ammonia and refluxed at high temperature to grow the iron oxide nanoparticles on their surface (Figure 3a).\textsuperscript{[55–58]} Alternative methods of coprecipitation use microwave irradiation to trigger the reaction.\textsuperscript{[59]} Others have explored the sol–gel synthesis (Figure 3b)\textsuperscript{[60,61]} or the attachment of preformed iron oxide by electrostatics (Figure 3c).\textsuperscript{[62,63]} As graphic particles are hydrophobic and without surface charge, electrostatic adsorption is done using intermediate polyelectrolytes such as proteins\textsuperscript{[62]} or polymers.\textsuperscript{[63]} For graphene, this modification is usually carried out using graphene oxide (GO) to ensure good dispersibility and prevent aggregation, followed by its reduction after assembly.

Composites containing magnetic fillers are generally prepared by comixing the fillers with a liquid matrix that is subsequently consolidated. 1D alignment is then achieved by casting the mixture in a unidirectional field, while the matrix is drying or curing (Figure 3d).\textsuperscript{[61,62]} whereas 2D biaxial orientation requires rotating magnetic fields (Figure 3e).\textsuperscript{[62,67]} Magnetic field gradients can also be used to localize fillers via the magnetophoretic force.\textsuperscript{[68]} Virtual magnetic molds can be used for high spatial resolution localization by using a ferromagnetic template to generate the magnetic field (Figure 3f).\textsuperscript{[62,66]}

Using magnetic fields is thus a convenient manner to manipulate fillers in a matrix and this can be applied to design the percolating path of graphene to enhance the performance of composites. The homogeneous distribution of magnetic and electrically conductive materials in a matrix already provides advantageous properties in terms of electromagnetic shielding and wave attenuation\textsuperscript{[57,58,69]} as well as biological functions.\textsuperscript{[70]} But the real advantage of using magnetic fields to control the orientation or the localization of fillers is the enhancement of mechanical and electrical properties. 1D and 2D orientation of magnetic graphene-based nanomaterials was demonstrated to result in increases in the strength and conductivity parallel to the direction of alignment.\textsuperscript{[61,71]} 2D vertical alignment also provides lower tortuosity and faster transport of ions, a key feature for ionic batteries.\textsuperscript{[65]} Finally, localization increases the local concentration, leading to locally higher electrical conductivity and stiffness, whereas the rest of the material stays insulating, transparent, and flexible.\textsuperscript{[62]}

To illustrate how the percolation control using magnetically directed assembly can further enhance properties and allow for multifunctionality, we present a 3D graphene composite that is flexible, transparent, and shows high sensitivity to strains.\textsuperscript{[62]} The percolation network of magnetic graphene is designed using meshes as virtual magnetic molds. Varying the mesh geometries and local graphene orientation, the percolation threshold $\phi_p$ and the percolation exponent $t$ from the percolation Equation (1) can be tuned

$$\sigma = C(\phi - \phi_p)^t$$  \hspace{1cm} (1)

where $\sigma$ is the conductivity, $\phi$ the volume fraction in conductive filler, $\phi_p$ the percolation threshold, $t$ the exponent, and $C$ a constant. The thinner the mesh lines, the larger the mesh gaps, and with horizontal stacking, the lower $\phi_p$ is and the higher $t$ is (Figure 4a,b).\textsuperscript{[62]}. With simultaneously low $\phi_p$ and high $t$, a reduced concentration of graphene can be used to achieve a high level of conductivity, allowing for flexibility, high dispersibility, and optical transparency, combined with electrical conductivity. In addition, at graphene concentrations close to the percolation threshold and where the conductive curve is sharp, that is, with a high exponent $t$, the composites...
are highly sensitive to local strain, making them interesting for mechanosensing (Figure 4c).

Magnetically directed assembly of graphene thus allows us to design percolating networks that are very beneficial. Further, magnetically directed assembly is fast, inexpensive, and scalable but requires functionalization of graphene prior to the assembly. To compromise, 3D printing technologies have been explored to control the assembly of 3D graphene using bare graphene nanosheets, in a variety of chemical systems and applications. Although other methods have been used, such as layer by layer (LBL) deposition[72,73] and ice-templated self-assembly,[41] 3D printing is unique thanks to its customization potential and the growing interest from industry. In the following section we introduce 3D printing technologies and their application to controlled 3D graphene nanomaterials.

4. 3D Printing of 3D Graphene Nanomaterials

3D printing technologies are already widely applied to polymers and metals and there is increasing research on the 3D printing of composites[74–76] and electrical materials.[77–79] Here we describe the main 3D printing methods applied to graphene nanomaterials and how they can control the 3D organization at multiple levels, and discuss their respective advantages and drawbacks.

4.1. 3D Printing Technologies

3D printing has been applied to produce 3D graphene–based architectures such as graphene aerogels,[80] reduced graphene oxide (rGO) nanowires,[81] and 3D graphene.[42,82] 3D printing

![Image](image_url)
Precise preparation and composite materials thanks to the control over the local deposition. Indeed, composite inks can be printed over a variety of substrates, single-component inks can be mixed in dual nozzles prior to printing, or multimaterial printing can be used to layer and spatially deposit inks of different compositions. These strategies are advantageous in comparison to conventional processing of graphene-based composites, in which agglomeration, phase separation and restacking can occur when blending multiple components. The preparation of the inks and in particular their viscosity and homogeneity are critical parameters to ensure good integrity of the printed parts Precise preparation and selection of the ink and its viscosity are key to fabricating defect-free and mechanically robust 3D graphene-based nanomaterials. Ink preparation is however outside the scope of this article and has been tackled in other reviews. Composite inks can be directly printed using inkjet printing, direct ink writing (DIW), fused deposition modeling (FDM), or stereolithography (SLA), also known as vat photopolymerization (Figure 5).

### 4.1.1. Inkjet Printing

During inkjet printing (Figure 5a–c), liquid drops are deposited on demand and layer-by-layer onto a substrate Inkjet is suitable for printing graphene as the low viscosity requirement for the ink allows the exfoliated nanosheets to remain disperse, preventing aggregation. Also, as exfoliated graphene nanosheets have a large aspect ratio, they remain highly conductive at low concentrations. Typically, the inks contain graphene, a solvent, and a binder. After inkjet printing, the solvent evaporates, leaving a thin layer of conductive material on the substrate. As an example of graphene-based ink formulation, Secor et al. produced graphene using an exfoliation method, then mixed it with ethyl cellulose Although thermal annealing at 250 °C is required to obtain low resistivity, which makes the process incompatible with low-temperature substrates, they could achieve a resistivity of \( \approx 4 \times 10^{-4} \, \Omega \, \text{cm} \) in their printed layers without annealing (equivalent conductivity of \( 2.5 \times 10^4 \, \text{S} \, \text{m}^{-1} \)). In another formulation, exfoliated graphene was dispersed in N-methyl-2-pyrrolidone (NMP) and the conductivity of the printed material reached \( 10^4 \, \text{S} \, \text{m}^{-1} \) with a printing resolution of around 50 μm.

### 4.1.2. Direct Ink Writing

Other ink compositions may be suitable for DIW (Figure 5d,e). DIW offers many benefits, including printing at room temperature, scalability, and versatility. Furthermore, it is compatible with multimaterial printing, to offer the distinct advantage for integrating multiple functionalities in a 3D printing format. For example, Chi et al. used DIW to prepare 3D graphene hydrogel–polyaniline nanocomposites to be used in a supercapacitor. Another recent example is the fabrication of a composite dough made of amine-terminated CNTs and rGO. The composite dough showed a high storage modulus, shear-thinning properties, and shape retention, which allowed it to be processed by DIW to build a 3D stacked device with a nacre-like bioinspired microstructure for high mechanical properties and conductivity.

### 4.1.3. Fused Deposition Modeling

To use the FDM method (Figure 5f,g), a solid composite filament has to be prepared beforehand using thermoplastic polymers. Then, the filament is melted at the tip of the nozzle to decrease the viscosity and allow for the extrusion of the material that will form an object in LBL fashion. Examples of graphene-based FDM materials are composites of thermoplastic polyurethane or acrylonitrile–butadiene–styrene (ABS) and multiwalled CNTs, or ABS and graphene oxide (GO), followed by chemical reduction to convert GO back to graphene in the printed structure. The presence of the graphene enhanced the modulus as well as the printing capability by increasing the resistance to buckling.

### 4.1.4. Stereolithography

Stereolithography (Figure 5h–j) is a vat polymerization technique that uses a light source to cure the liquid resin in a predefined pattern. Lin et al. used a solution intercalation process to add
GO nanofillers into a liquid photopolymer to fabricate 3D truss structures.\(^{[89]}\)

4.2. 3D Printing and Controlled Organization

Controlled microstructures and 3D organization in the 3D printed materials are desired to increase the level of functionalities and the performance of graphene-based composites, as discussed earlier, which are augmented from the capabilities of conventional 3D printing. Controlled 3D organization in 3D-printed graphene nanomaterials can be realized at the macro-, micro-, and nanolevels using a combination of features. In the following, we review how the printing process can determine the microscopic and macroscopic organization, how self-assembly of graphene can occur during the fabrication, and how directed assembly can also be added to the procedure (Figure 6).

4.2.1. Printed Macro- and Microstructures

The printing resolution and deposition process can be used to control the macro- and microstructure. Inkjet printing was utilized by Zhu et al. to print GO formulations to create 3D aerogel microlattices at a resolution of 100 μm (Figure 6a).\(^{[84]}\) However, obtaining printable GO is often difficult and demands optimization of the rheological properties. To this aim, fumed silica
nanopowder was successfully added to the pure GO suspensions to increase both the elastic modulus and yield stress, thus making them suitable for 3D printing. In another report, several graphene-based inks were prepared to realize the specific rheological properties needed for the deposition of filaments, piles, rings, and woodpile structures through DIW at a resolution below 200 μm.83

4.2.2. Self-Assembly at the Nozzle

During extrusion of the inks through the printing nozzle in DIW and FDM, shear forces enable the alignment of anisotropic nanoparticles.84,85 This shear-induced alignment has been used to orient GO sheets (Figure 6b).86 Another example of self-assembly made use of the controlled evaporation at the nozzle to

Figure 6. Microstructural control during 3D printing. Printed microstructures: a) image of a 3D-printed microlattice of graphene aerogel and scanning electron micrograph of the microstructure, obtained through DIW; self-assembly at the printing nozzle: b) schematics of the alignment of anisotropic nanomaterials during the printing process and c) schematics illustrating the principle of formation of a pure GO nanowire by evaporation of water at the nozzle of a micropipette filled with an aqueous solution of exfoliated GO nanosheets; self-assembly after inkjet printing: d) microscopic images showing the local arrangement of the CNTs in a printed droplet and schematics of the mechanisms behind it and e) optical images of the deposited graphene films on silicon wafers before (left) and after (right) drying and pattern formation. Bottom images show the precision and controlled patterns obtained by this method; self-assembly after DIW: f) schematics of the assembly in the printed line during drying and scanning electron micrograph of the cross section; directed assembly during SLA: g) schematics of the printing set-up (left) and schematics and electron micrographs of the aligned printed structure made of graphene nanoplatelets. (a) Reproduced under the terms of the CC BY license.84 Copyright 2015, Springer Nature. (b,f) Reproduced with permission.86 Copyright 2016, American Chemical Society. (c) Reproduced with permission.87 Copyright 2014, Wiley-VCH (d) Reproduced with permission.88 Copyright 2019, Royal Society of Chemistry. (e) Reproduced with permission.89 Copyright 2013, Wiley-VCH Co. (g) Reproduced with permission.90 Copyright 2019, The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a CC-BY-NC License 4.0. AAAS.
self-assemble pure GO filaments in a DIW set-up by controlling the liquid meniscus (Figure 6c). [101]

4.2.3. Self-Assembly after Inkjet Printing

When the ink deposited comprises a solvent, the removal of the solvent on the substrate develops significant capillary forces that can promote the self-assembly of the anisotropic graphene-based nanomaterial. The phenomenon is further accentuated by the increase in concentration in the system as it dries. [106] For example, CNTs suspended in aqueous inkjet-printed droplets were found to form a variety of patterns depending on their initial concentration as well as on the evaporation rate determined by the temperature of the substrate (Figure 6d). [99] In the case of droplet deposition, the flow arising from thecoffee ring effect led to an increase in CNT concentration at the outer part of the droplet in a tangential orientation, whereas the CNTs adopted a radial orientation in the middle. [99] Similarly, Li et al. investigated the coffee ring effect of graphene to print a variety of patterns (Figure 6e). [102]

4.2.4. Self-Assembly after Direct Ink Writing

Using aqueous suspensions of GO and printing them using DIW, Li et al. assembled giant horizontally aligned GO sheets on a variety of substrates (Figure 6f). [104] The DIW process led to the deposition of thin lines with aligned GO due to the shear forces at the nozzle, whereas evaporation and the induced increase in concentration led to a horizontal alignment and packing. In this case, the printing was followed by a chemical reduction to enhance the electrical properties and the conduction between the reduced GO sheets. With a print resolution of 200 μm and alignment of the graphene, the fabricated electrode arrays exhibited an architecture with two levels of hierarchy that enhanced their properties.

4.2.5. Directed Assembly during Stereolithography

As electrically conductive and anisotropic particles align when a unidirectional electric field is applied, this strategy has been used to orient graphene nanoplatelets during SLA (Figure 6g). [103] In other systems, ultrasonic waves have been coupled to SLA to simultaneously deposit, orient, and concentrate glass fibers. [107] and magnetic fields and sequential masking have been used to build complex heterogeneous assemblies of magneto-responsive microparticles. [108,109] Although, to the best of our knowledge, there are no reports of these directed-assembly and SLA 3D printing techniques being applied to graphene-based nanomaterials, it could be the case in the future.

4.3. Comparison of the 3D Printing Strategies and Other Alternatives

Each 3D printing strategy has its advantages and drawbacks. Generally, inkjet printing of graphene nanomaterials is a popular choice as it uses the same principle as for our paper printers, rendering the technology highly available and scalable. However, it suffers from low mechanical stability of the final structures. Indeed, due to the inherent nature of thermal and piezoelectric printheads used in inkjet printers, the graphene inks need to have very low viscosity. As a result, the materials printed by inkjet printers are essentially thin and planar instead of complex and thick 3D structures.

Fused deposition modeling and stereolithography are more suitable for printing higher viscosity graphene composite inks to create stronger and thicker components. The strength of the printed structure is indeed increased thanks to the polymer network that bonds the layers together and the higher concentration of graphene. [110,111] The obtained materials have been widely used and printed for various devices, namely, energy storage devices [112] lithium ion batteries, [113] flexible circuits, [114] and sensors. [90,98]

Direct ink writing, in turn, is a highly flexible technique as the range of viscosity is large, from liquid to paste. [115–117] As such, suspensions, foams, composite mixtures, and even biological cells can be printed. [118,119] In addition, the nozzle design and extrusion principle also can vary greatly. For example, to further extend the possible materials and architectures, coextrusion of inks of different compositions can be realized using a customized printhead with four nozzles aligned coaxially. [120] Using alternating electrically conductive and electrically insulating inks, capacitive fibers with a multicore–shell architecture could be printed. [120] Furthermore, by changing the nozzle diameter, the thickness of each layer in the capacitor was varied. Although the authors used a liquid ionic conductor for the conductive phase and a silicone elastomer as a stretchable insulator, this strategy is highly adaptable to inks of any composition. In other studies, rotating printheads have been used to create helicoidal orientation of anisotropic fillers, [121] external fields have been applied at the nozzle to direct orientations, [109,122] and laser technologies have been added too. [123] Finally, the shape can be easily controlled in DIW by developing inks with adequate shape retention properties or by using sacrificial substrates. [124,125]

3D printing technologies thus offer a large design space for the fabrication of controlled hierarchically and 3D organized matter. In the field of advanced electronics, 3D printing of 3D architectured graphene allows for the creation of structures and devices with interesting capabilities. Selected examples are detailed in the following section.

5. 3D Graphene for Advanced Electronics

In this section, we describe selected examples of 3D organized graphene for advanced electronics and related energy applications. What is particularly exciting with 3D printing of electronics is the possibility to simultaneously fabricate electrical substrates with embedded circuits and the electrical components, all of which can exhibit unusual combinations of properties. To illustrate this, we present in the following sections the 3D printing of graphene for flexible strain sensors and for high-power components, supercapacitors.

5.1. Sensor Application

With the advent of wearable devices and increasing awareness on individual health monitoring, the need for lower power,
efficient, faster, and smaller electronics has grown rapidly. Skin-mountable sensors, which can either be attached to clothing or adhere to human skin, have presented additional demands of flexibility, light weight, and biocompatibility. Such requirements have fueled research in materials, substrates, and processes to enable novel electronic devices.\textsuperscript{[126–128]} For this purpose, biocompatible flexible strain sensors are sought after due to their broad applications in human-motion sensing, human–machine interface, and soft robotics.\textsuperscript{[129–131]} Graphene has found a central role as the main material for electronic skin (E-skin), wearable, and bioinspired devices. Most flexible strain sensors use either resistive or capacitive sensing mechanisms.\textsuperscript{[132,133]} Resistive strain sensors use conducting materials that undergo microstructural changes during deformation, resulting in variations in the electrical resistance of the material. Capacitive sensors use a dielectric material that is sandwiched between two conducting layers. Applying a strain changes the distance between the conducting layers, thereby changing the overall capacitance. The important parameters for assessing the performance of a strain sensor in the health monitoring perspective are the gauge factor (GF) and the time response. The GF measures the sensitivity and is defined as the change in the electrical resistance $\Delta R/R$, or in capacitance $\Delta C/C$, with applied strain $\epsilon$. The time response of the sensor reflects the ability of the sensor to follow dynamic changes. Usually, when dynamic loads are applied to the sensor, a hysteresis appears. Large hysteresis and nonlinearity are likely to affect the reliability of the measurements. Graphene-based strain sensors exhibit GF in the range of 1.9–6 due to semimetallic properties.\textsuperscript{[134,135]} Rosette-type graphene sensor designs have been successful in detecting principal strains on the skin, but using them on human joints is still difficult.\textsuperscript{[136]} The laser scribe method was used by Tian et al. to fabricate a foam-like graphene tactile sensor that measured a wide pressure range with high sensitivity.\textsuperscript{[137]} In addition to strain and tactile sensors, graphene-based large-area flexible devices, namely, touch panels and biosensors, have been fabricated.\textsuperscript{[138–140]} However, 3D printing methods were not used to make them.

Traditional manufacturing of sensor devices suffers from many disadvantages such as time-consuming steps, high temperature, high cost, and incompatibility with flexible and stretchable substrates. 3D printing, however, has the potential to overcome some of these challenges. Printing intricate structures and narrow hollow channels has been successfully demonstrated using 3D printing.\textsuperscript{[141,142]} As more progress is being made, 3D printed sensors can achieve higher sensitivity and better selectivity, in particular using 3D organized graphene compositions. To date, there are not many reports on graphene-based physical sensors as most of the research efforts have been concentrated on ink formulations. In most cases, the ink is synthesized and then processed to lay down the electrodes or the entire circuit to achieve the desired functionality. The resulting materials usually present stretchability, high electrical conductivity, sensing and actuation capabilities. Some work has been done on inkjet-printed graphene radio frequency identification (RFID) tags as they have the potential to penetrate various fields ranging from smart packaging, anticounterfeiting bank notes, healthcare to public safety devices.\textsuperscript{[143]} In most cases, graphene flakes were used to form a nanocomposite and printed on flexible substrates, namely, polyethylene terephthalate (PET), polyimide (PI), and paper.\textsuperscript{[144]}

Figure 7 shows a soft flexible actuator fabricated using DIW of a GO film onto a flexible substrate of poly(dimethylsiloxane) (PDMS).\textsuperscript{[101]} The actuator is sensitive to bending, exhibits reproduducible and reproducible voltage variations with the bending, and can be printed into many shapes such as a hand shape.

However, the fields of wearables, human motion sensing, soft robotics, and optogenetics have created additional demand for the fabrication of stretchable and transparent strain sensors. The use of conductive gels, namely, ionogels and hydrogels, has been largely applied to address the issue. Ionic liquids, or ionogels, are salts with low vapor pressure displaying high ionic...

**Figure 7.** Soft actuator with 3D printed electrodes: a) schematics of the actuation principle, b) bending angle as a function of the applied voltage, c) hand-shaped actuator demonstrating gestures and independent control of the fingers, and d) bending angle as a function of time in cyclic actuations. Reproduced with permission.\textsuperscript{[101]} Copyright 2016, American Chemical Society.
Ionogels have been used as gate dielectrics in graphene-based thin film transistors operating at high frequencies. Flexible all-graphene-based transistors were printed with ionic gels as a gate dielectric layer and graphene as a source/drain electrode exhibiting high mobility and good stability. Most of these devices are fabricated using multistep and low-yield processes such as free-form and micromolding. The group successfully printed several materials to fabricate a soft actuator via 3D printing. The group recently demonstrated an interesting approach with a conductive ionogel by creating a soft actuator via 3D printing. The group successfully printed several materials to fabricate a soft robotic actuator with haptic, proprioceptive, and thermoceptive sensing. 3D printing is especially attractive for multimaterial processing as it reduces the cost, time, and effort of manually assembling the cast segments for the device. Porous graphene was infused into an ionic liquid material to obtain high-performance freestanding and binder-free electrodes. In the same work, the authors grew MnO2 nanoparticles with the self-assembly of graphene nanosheets to obtain a “plum pudding” structure.

Although much progress has been made in fabricating stretchable graphene sensors, there are still some challenges to overcome. Most of the demonstrated applications have focused on passive devices. There is a need to build a library of stretchable graphene inks to fabricate active devices that are hysteresis-free. Ray et al. have successfully summarized how material engineering can lead to new substrate- and application-specific properties in materials. New design strategies involving serpentine structures have aided in developing skin-like sensor devices. Scalable production of graphene-based materials is another roadblock. In a recent study, Karim et al. tried to address the issue by reducing GO in solution and then coating it on cotton textile for a wearable motion sensor. The method detailed in the study could be scaled up and adopted by industries.

Figure 8. 3D-printed 3D graphene devices. a) Schematics of 3D-printed DC–DC converter with a 3D graphene supercapacitor and a USB connector and the USB output voltage as a function of the input voltages from the supercapacitor; b) schematics of a stack of 3D graphene electrodes to form a GFSC cell and its integration into a flexible self-charging power pack (FSPP) comprising a flexible photovoltaic cell and a pH sensor and its charging/discharging curves under c) bending and d) different light intensities; e) Ragone plots of symmetric supercapacitors (SSCs) showing the power density as a function of the energy density and f) the volumetric equivalent to illustrate the benefits of the 3D-GCA SSC (in red). (a) Reproduced with permission. Copyright 2019, The Royal Society of Chemistry. (b–d) Reproduced under the terms of the CC-BY license. Copyright 2018, the Authors, Published by Elsevier Ltd. (e,f) Reproduced with permission. Copyright 2016, American Chemical Society.
5.2. Other 3D-Printed 3D Graphene–Based Electronic and Energy Devices

Electronic devices require conductive networks, electronic components, and power sources. Driven by the fast development of portable electronics, stand-alone renewables, the smart grid, and the transport sector, there is an ever-increasing demand for electrochemical energy storage technology, including supercapacitors and batteries. Supercapacitors have unique advantages over lithium-ion batteries in terms of high power delivery and long cycling life, and they are emerging as attractive electrochemical energy storage devices for future energy storage applications. However, supercapacitors usually have lower energy density than lithium-ion batteries.\[33,157\] Intensive research efforts have been devoted to the enhancement of the energy density of supercapacitors while retaining their intrinsic high power density. One promising approach is to use graphene and to design all-graphene-based energy storage devices. Due to their high surface area and excellent mechanical and electrical conductivity,\[158–160\] graphene materials hold tremendous potential to bridge the gap between supercapacitors and batteries. However, 2D graphene has a flat structure with no pore or channels for ion transport, which limits their application in supercapacitors. Recent research has suggested that some specially engineered 3D structures of graphene, such as graphene foam, hold tremendous potential for supercapacitors.\[158–160\] These 3D materials benefit from unprecedented properties such as mechanical robustness, flexibility, and compressibility as well as high electrical and ionic conductivities.\[161\]

Entire 3D-printed devices using 3D graphene percolating network supercapacitors are starting to emerge in the literature (Figure 8). Li et al. recently developed a modified 3D printing process assisted by laser to transfer graphene onto nickel foams to prepare electrodes of high conductivity, high retention rate, and large areal specific capacitance (Figure 8a).\[161,162\] They could use those electrodes for charging a USB with a stable 5 V output voltage.\[162\] Another example of a 3D-printed device developed makes use of 3D porous flexible foam-based graphene stacked in a layer structure of highly conductive electrodes of Ag–graphene and conductive epoxy to realize electrochemical and supercapacitive performance (Figure 8b).\[163\] This graphene foam–based supercapacitor (GFSC) is flexible and retains 68% capacitance after 25 000 charge–discharge cycles and under dynamic bending. Furthermore, they incorporated the GFSC between a flexible photovoltaic cell and a 3D-printed CuO pH sensor\[164\] to create a self-charging sensor. The device showed slow discharge at low potential and remained functional during bending (Figure 8c,d).\[163\] Finally, DIW 3D-printed graphene composite aerogel (3D-GCA) lattices were designed to form lightweight, conductive, and electrochemical electrodes with exceptional capacitive retention and power density.\[164,165\] Although the device has power and energy densities comparable to those of other capacitors, its volumetric power and energy densities are significantly higher (Figure 8e,f).\[165\] The authors demonstrated that it can be used to power a red LED bulb for 3 min, a digital timer for 5 min, and a small electric fan for several seconds (see inserts in Figure 8e).\[165\] These selected electronic devices are impressive proofs of concept of the applications of 3D-printed organized graphene-based nanomaterials for new properties and functions in electronics.

6. Conclusions

The future of electronics demands new and unusual combinations of properties and functions that require new materials and new fabrication paths. In this Progress Report, we have underlined how graphene-based composites can be used to realize this future. We have seen that 3D graphene composites with an interconnected network structure are ideal for supercapacitors with high power, low density, and long cycle life. 3D assembly of graphene materials can be achieved via different methods, including CVD and 3D printing. Different synthesis methods have varying characteristics that make them better suited for various applications. For instance, CVD-grown 3D graphene electrodes benefit from mechanically robust and intrinsically interconnected 3D structures that are very useful for electrochemical energy storage devices. In contrast, 3D printing is a highly versatile fabrication tool and allows rapid prototyping. 3D printing technologies such as inkjet printing and direct writing allow excellent geometry controllability and covers a wide range of materials.\[43,84,166\]

Controlling the assembly of graphene within this percolating network, e.g., by means of magnetically directed assembly, can further enhance those properties as well as harness multifunctionalities, including transparency, flexibility, and high sensitivity. In addition, controlled and tailored assembly can conveniently be combined with 3D printing technologies to benefit from local deposition, fast and cheap processing, and multiamaterial fabrication. Several examples of stretchable strain sensors for health monitoring or E-skins for robots and energy storage components demonstrate the potential of this 3D printing and 3D assembly of graphene for future electronic applications.

However, to make a breakthrough in consumable devices, several other challenges are down the road. First, for industrial impact and relevance, it will be necessary to ensure that the fabrication methods proposed are translatable on industrial scale. This means fast, cheap, and scalable processes. Although the obtention of 2D graphene at high scale and high quality can now be achieved,\[167–169\] the difficulty might lie in the combination of the high resolution of the material structure with the large and quick throughput required for commercialization. Second, it might be relevant to develop processes that can be readily applied to already established ones to quicken its industrialization and increase its attractiveness. Further, the future of electronics predicts implantable sensors, robotics, continuous health, and structural monitoring and interconnected objects through physical and wireless networks.\[170,171\] This will pose a big data challenge that needs to be tackled. Artificial intelligence (AI), machine learning, and neuronal networks could be ways to connect and control those elements and to generate autonomous systems. Finally, the methods described in this Report focus on graphene-based nanocomposites. As nanomaterials are being synthesized and created, such as the MXenes\[172–174\] or the multifierroics,\[175\] there are opportunities to further expand the level of multifunctionalities using such building blocks instead of graphene. Those new layered materials can be used in the fabrication methods described in this paper. For example, hexagonal boron nitride sheets can be manipulated via magnetic fields to control thermal
conductivity,[176] and 3D printing of inks containing MoS₂ or MXene sheets is under active research with a few studies reporting their benefits for storage applications.[177–180] Given that MXenes share many similarities with graphene, as a 2D material, it is expected that 3D printing of MXenes would share the same promises as well as challenges as 3D printing of graphene inks. In particular, optimized material systems are still to be developed to enable high packing of electronics in flexible devices. Indeed, high computational power and fast responsiveness generate heat that needs to be dissipated. Heat sinks with brush architecture are one common strategy but require expensive and time-consuming fabrication.[181] Exploring composite structures using highly thermally conductive particles or ballistic modes for heat dissipation would also push forward the application scope of electronic devices.[182]

To conclude, the field of advanced electronics synergizes the efforts of chemists, engineers, material scientists, biologists, and programmers to innovate and satisfy the demand for intelligent and autonomous devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D printing, controlled assembly, graphene-based composites, smart electronics
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