Three-dimensional printing of graphene-based materials for energy storage and conversion

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Abstract
Developing high-performance energy storage and conversion (ESC) device relies on both the utilization of good constituent materials and rational design of assembly structure. Graphene-based materials, due to their superior properties like high electrical/thermal conductivity, large surface area, and unique optical properties, have been extensively reported for ESC applications. The emerging three-dimensional (3D) printing techniques, especially extrusion-based direct ink writing technique, have brought a revolutionary improvement in structure control accuracy and designing capability to graphene-based macro-assemblies, triggering a boost in functionalities and performances of graphene-based ESC devices. In these circumstances, understanding the very recent progress of 3D-printed graphene materials and their design philosophy to bring new concepts for material designs and address the requirements for high-performance ESC devices are urgently important. In this review, we aim to outline recent developments in 3D printing of graphene-based materials and their applications in ESC applications. Basic requirements and theoretical analysis for preparation printable inks are discussed, as well as feasible GO ink preparation strategies in existing literatures. The representative explorations of 3D-printed graphene materials in ESC applications like batteries, supercapacitors, solar steam generators, and electro-thermal conversion are also reviewed. This study attempts to provide a comprehensive overview of the progresses and limitations of present 3D printed graphene materials, and seeks to enlighten the opportunities and orientations of future research in this field.

KEYWORDS
3D printing, direct ink writing, energy storage and conversion, graphene

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1 | INTRODUCTION

Energy storage and conversion (ESC) devices with high efficiency, versatility, and adaptability have drawn growing attentions in pursuit of cheap, safe, low-carbon, and sustainable energy alternatives to fossil fuels. The development trend of ESC devices mainly involves three aspects: synthesis of nano-structured active materials, high-accuracy fabrication of macro-architected devices, and the assistance of advanced manufacturing techniques.

Emerging insights into sustainable ESC devices point out that sustainability involves the full life cycle of ESC devices, which includes raw materials, device assembly, use, and recycling. Therefore, enhancing energy density/conversion efficiency, reducing or replacing the usage of limit and polluting materials, improving the service life and cyclic stability, and safety related issues all need to be accounted for to meet the sustainable concerns. Developing such ESC devices that integrate high throughput energy intake and output, high-efficient conversion, low energy consumption, and long lifetime relies on both the exploitation of high-performance constituent materials and the assistance of advanced manufacturing techniques.

Graphene, a single layer two-dimensional (2D) material with covalently bonded sp² carbon hexagonal network, has emerged as a promising material for ESC applications due to its record thermal/electrical conductivity, large surface area, outstanding mechanical properties, and unique optical properties. Apart from pristine graphene, graphene oxide (GO), composing of abundant oxygen-containing groups on its basal plane and edges, is another extensively studied graphene-based materials owning to its good processibility, tunable functionalization, and easy accessibility. The unique structural features and superior properties of graphene and GO allow them to be ideal materials as building blocks for high-performance ESC devices such as the electrodes of batteries and supercapacitors, solar steam generators, and electro-thermal conversion devices. However, the strong π–π interactions and van der Waals force between graphene/GO sheets make them irreversible agglomeration and stacking during assembly, resulting in a severe attenuation of their intrinsic properties in macroscopic assemblies and practical devices. To fully express the superior properties of single layer graphene/GO sheets in macroscopic materials, an important route is to delicately control the structural features over multiple length scales by virtue of high-accuracy assembling and processing techniques.

Additive manufacturing, also known as 3D printing, refers to an industrial production technique that builds 3D objects by adding materials layer-by-layer directly from computer-aid-design files. According to the way the 3D architecture is constructed, 3D printing techniques can be divided into several categories: selective laser sintering of powders, photo-polymerization of light sensitive resins, fused deposition modeling, and extrusion-based ink deposition. These emerging 3D printing techniques enable a growing palette of functional structures with highly programmable structural feature over a wide range of length scales, which is difficult to achieve by conventional methods and therefore open new avenues for fabricating advanced ESC devices. Specifically, 3D printing makes it possible to customize the microstructure as well as composition of printed ESC devices with high accuracy and efficiency. This programmable designing and manufacturing capability greatly enhance the structural diversity and complexity as well as performance and functionality for ESC devices. Moreover, the additive nature and precise material deposition process of 3D printing technique also improves the materials utilization ratio and avoids hasty depletion, which accords well with the developing trend of sustainable ESC devices. Owning to the amphiphilic properties of GO sheets and their unique viscoelastic properties, GO dispersion has been widely exploited as a printable ink material for extrusion-based 3D printing technique like direct ink writing (DIW). The rheological behaviors of graphene-based ink are dependent on the concentration of graphene, the lateral size of graphene, and the utilization of solvent, which can be easily adapted to meet the requirements for different printing techniques and applications. Apart from its own superior properties, graphene-based ink also exhibits good compatibility with various functional additives like nanomaterials, inorganic particles, polymeric additives, and biological materials, which further extends its functionalities and application range. Correspondingly, graphene-based materials with various structures including nanowires, aerogel microlattices, and complex networks have been successfully printed, exhibiting well-expressed properties such as high electrical/thermal conductivity, large surface area, and good structure stability. Exploration of utilizing 3D printed graphene-based structures in ESC devices has also been extensively reported. As an emerging technique, 3D printing demonstrates outstanding structural manipulation and fast prototype ability, which holds great potential for micro- and macro-structure design for high-performance ESG devices. Correspondingly, 3D printed graphene-based devices usually share elaborately designed structural features and composition distribution that conform to the related applications. This customization procedure renders 3D printed graphene-based devices with outstanding work performance and service life, and also significantly reduces materials waste during fabrication, ensuring their sustainability. However, fundamental
guidance for preparation of printable ink is still limited, so is the designing philosophy in printing practical ESG devices. Besides, applying 3D printing technique to fabricate graphene materials also faces difficulties such as limited achieving structures, complicated procedures, and poor mechanical properties.

Hereby, we review the recent advances in 3D printing of graphene-based materials and their applications in ESC devices (Figure 1). Starting from a brief introduction of the extrusion based DIW technique and its basic requirements, we outlined the rheological behaviors of GO dispersion and comprehensively reviewed present strategies for preparation of printable GO inks used for DIW. Research of 3D printed graphene structures in energy-storage applications like batteries and supercapacitors and energy-conversion applications like solar steam generator and electro-thermal conversion are also reviewed and discussed. This review closes with a summary and outlook, pointing out the existing limitations as well as future designs and developments of 3D-printing technology in graphene-based materials for ESC applications and beyond.

FIGURE 1 Overview of feasible strategies for preparing printable GO inks and 3D printed graphene-based materials used for energy storage and conversion applications. Printed batteries. Reproduced with permission from Ref. 82 Copyright 2016 Wiley-VCH. Printed supercapacitors. Reproduced with permission from Ref. 101 Copyright 2020 Wiley-VCH. Solar steam generators. Reproduced with permission from Ref. 111 Copyright 2020 Royal Society of Chemistry (RSC). Electro-thermal conversion. Reproduced with permission from Ref. 38 Copyright 2016 American Chemical Society (ACS). Graphene oxide model. Reproduced with permission from Ref. 20 Copyright 2015 Springer Nature

2 | FABRICATING 3D STRUCTURE BY DIW

2.1 | Basic requirements of DIW

The term “direct ink writing” describes fabrication strategies that employ a computer-controlled translation device, for instance, an ink-deposition nozzle, to fabricate materials with designed architecture and composition.43 Typical DIW process can be divided into three steps: (1) the flow of the ink through the syringe barrel and printing nozzle; (2) the ejection of the ink from the nozzle, and (3) the deposition of the ink onto the underlaying printed layers (or substrate) (Figure 2).44 In order to set patterning materials in three dimension, a printable ink should meet the specific requirements for each of these steps. Specifically, a printable ink must exhibit a well-controlled viscoelastic response, so that it can be smoothly extruded through a nozzle in the form of a continuous filament and be able to “set” immediately once it is deposited to retain the shape features even they span gaps in the underlying layers. These criteria ensure the accurate replication of the digital model. Colloidal gels are therefore excellent candidates for DIW because their viscoelastic properties can be easily tailored over many orders of magnitude under mechanical stimulation.45 In this section, we will analyze the basic requirements of printable inks from the viewpoint of printing procedure.

First, the ink should be homogeneous and able to flow smoothly along the nozzle, which help to avoid jamming or clogging in the deposition nozzle.45,46 The viscosity of the ink should be low under high shear rate, so that the pressure needed to extrude ink is moderate, especially when using micronozzles. This requirement is particularly crucial for fabricating miniaturized devices, where the smaller diameter of micronozzles is demanded for higher resolution.47,48 From a rheological perspective, a shear thinning behavior, that is, viscosity decreases over increasing shear rate, is expected for printable inks as it favors the flow of the ink through nozzles under moderate extrusion pressure.

When the ink is ejected from the nozzle, it must immediately turn into a solid-like filament to retain its shape after deposition.45 To meet this requirement, inks employed in DIW are usually yield stress fluids: they behave as elastic or viscoelastic solids under a threshold value of stress, known as yield stress, while they flow like viscous liquids when the yield stress is exceeded. In this way, inks can flow smoothly through the nozzle as they were violently sheared within the nozzle, and “solidify” quickly once they were deposited as the stress slumped. Tardy recovery process would cause filament bending and stretching during
FIGURE 2 Schematic of the main steps of direct ink writing (DIW) process and their corresponding rheological requirements. Reproduced with permission from Ref. 44 Copyright 2021 RSC

deposition. In order to achieve good shape accuracy and minimize structure distortion, this fluid-to-solid recovery process should be as fast as possible. Kalyon et al. 49 discovered that when flowing in a cylindrical nozzle, inks usually exhibit a three-zone velocity profile that consists of an unyielded core moving at a constant velocity surrounded by yielded shells experiencing laminar flow and a thin slip layer at the nozzle wall. Thus, when the ink is extruded out from the nozzle, a rodlike filament with a rigid-core/fluid-shell architecture comes into being, which is beneficial to shape retention and helps to fuse different layers at contact points.

After the deposition process, the printed structure must maintain its shape until full solidification is completed, usually by solvent removal. The requirements in this final step of DIW is that inks must have a high yield stress to prevent the stacked filament from slumping under their own weight.44 In order to print overhanging structure, a high storage modulus at rest is also required to limit bending and drooping of suspended parts. For instance, to print a woodpile structure with a height of 10 mm from aqueous GO ink, which is widely used as electrodes for electrocatalysis and supercapacitors, a high yield stress around 100 Pa and a storage modulus larger than $10^4$ Pa is usually desirable.

2.2 Rheological properties of printable ink

Several mathematical models have been proposed to describe the concept of printability by measurable rheological parameters. For colloidal gels with shear thinning behavior, their flow behavior is usually described by the Herschel–Bulkley model50

$$\tau = \tau_y + K \dot{\gamma}^n,$$

where $\tau$ is the shear stress, $\tau_y$ is the yield stress, $K$ is the viscosity parameter, $\dot{\gamma}$ is the shear rate, and $n$ is the flow index. This model assumes that the ink cannot flow under stress smaller than $\tau_y$, and it represents a shear-thinning fluid if $n < 1$ and a shear-thickening fluid if $n > 1$. Herschel–Bulkley parameters ($n, K, \tau_y$) have been widely used to predict the shear rate profile and pressure distribution in printing ceramics by DIW as well as the finite element analyses for colloidal inks.44,45

The shape retention ability of printed structure is mainly dependent on the yield stress and storage modulus at rest of the ink. To quantitatively evaluate the required yield stress for DIW, M’Barki et al. 51 deduced the minimum yield stress on account of the effect of gravity and capillary forces as below:

$$\sigma_{y}^{\text{dyn}} \geq \gamma R^{-1} + \rho gh,$$

where $\sigma_{y}^{\text{dyn}}$ is the dynamic yield stress, $\gamma$ is the surface tension of suspension, $R$ is the diameter of nozzle, and $\rho gh$ stands for the gravity that acts on the printed filament. This model describes printability better than models purely based on gravitational slumping. Smay et al.52 applied the elastic beam theory to overhanging ink filament to determine the proper storage modulus required to maintain printed shape. It can be
expressed as:

$$G' \geq 1.4\gamma \left(\frac{L}{D}\right)^4 D,$$

(3)

where $G'$ is the storage modulus of ink, $\gamma$ is the specific weight of the ink, and $L$ and $D$ are the length and diameter of the overhanging part of filament, respectively. Applying this equation enables us to calculate the minimum storage modulus required to print designed structure.

3 | DESIGNING PRINTABLE GO INKS

3.1 | Rheology of GO dispersion

In recent years, graphene- and GO based inks have been extensively exploited for 3D printing due to their attractive properties like excellent mechanical properties and electrical/thermal conductivity. Compared with graphene, GO-based inks are more popular due to their following advantages: (1) GO can be easily produced on a large scale by chemical exfoliation strategies like modified Hummer’s methods. (2) GO is hydrophilic and can be easily dispersed in common solvents like water, glycerin, and DMF, which is easy to process. (3) Commercial GO usually appears in the form of colloidal dispersion, which can be directly modified into printable inks with low cost. (4) Chemical structure and properties of printed GO structure like C:O ratio and conductivity can be easily regulated by chemically or thermally reducing, rendering GO inks more compatibility to different applications.

GO aqueous inks are the most widely used GO based inks due to their highly adjustable rheological properties as well as low cost and environmental friendliness. GO aqueous dispersion is a non-Newtonian fluid with typical shear thinning behaviors and a wide range of storage modulus ($G'$) and loss modulus ($G''$) that are highly dependent on its concentration and lateral size. Increasing either the concentration or lateral size of GO would increase both $G'$ and $G''$ over orders of magnitude. Besides, GO aqueous dispersion can simultaneously form a nematic liquid crystalline phase over a critical concentration, which helps to improve the processability of GO inks. By controlling the concentration and lateral size of GO, the rheological properties of GO inks can be freely tailored to fulfill the requirement for different processing and fabrication techniques such as DIW.

Naficy et al. investigated the rheological behaviors of GO dispersion with different concentrations (Figure 3). For GO inks with ultralow concentration (0.05–0.25 mg ml$^{-1}$), $G''$ is slightly larger than $G'$, representing a viscosity dominated liquid-like behavior. As the concentration increases to the range of 0.25–0.75 mg ml$^{-1}$, elastic $G'$ and viscous $G''$ start to crossover, where $G'$ becomes larger than $G''$ at lower shear rate and reverses at higher shear rate. In this range, GO inks behave like a soft solid due to the increased $G'$ at low shear rate, while above the crossover point, $G''$ dominates and GO inks exhibit a liquid-like behavior. Further increase the concentration to larger than 0.75 mg ml$^{-1}$, a shear rate independent plateau can be found for $G'$ at low-rate range, where $G'$ is prominently larger than $G''$. For concentrations up to 13.3 mg mL$^{-1}$, $G'$ is about a magnitude higher than $G''$ in measured shear rate range, behaving like an elastic gel. In this range, GO inks can flow through printing nozzles under high shear stress and solidify quickly after deposition, which can be directly assembled layer by layer to form 3D architecture. However, the yield stress ($< 10^3$ Pa) and $G'$ ($< 30$ Pa) of GO inks in this range are insufficient for printed structure to avoid slumping under large self-weight or to retain overhanging 3D structures. Improving yield stress and $G'$ is therefore crucial for freely fabricating 3D GO structures by DIW.

3.2 | Ink formation strategies

During the last decade, various strategies have been purposed to modify the rheological properties of GO inks to meet the requirements for DIW. Based on their gelation mechanisms, we divided these ink formation strategies in previous literatures into four categories: (1) improving GO network strength; (2) inter-sheet crosslinking; (3) adding rheology modifying additives; and (4) modifying printing technique.

3.2.1 | Improving GO network strength

The mechanical properties of colloidal dispersions like GO inks are dependent on the colloid volume fraction ($\varphi$) according to the scaling relationship given by

$$y = k \left(\frac{\varphi}{\varphi_{gel}} - 1\right)^x,$$

(4)

where $y$ is the mechanical property of interest (e.g., yield stress $\tau_y$, or storage modulus $G'$), $k$ is a constant, $x$ is the scaling exponent, and $\varphi_{gel}$ is the colloid volume fraction at the gel point, which scales inversely with the lateral size of GO sheets. Therefore, increasing the concentration or lateral size of GO inks can help to improve printability of GO inks. Similar result has been reported by Valles et al., who demonstrated that GO dispersions behave like percolated networks, and their $G'$ increased with the concentration $c$. 
following a power law:

\[ G' = 791c^{2.7} \text{ (} G' \text{ in Pa, } c \text{ in vol\%}) \].

(5)

For GO dispersion with a concentration of 3.90 vol\%, it behaves like an elastic gel and exhibits a high \( G' \) around \( 2 \times 10^4 \) Pa, indicating that the GO network is strong enough to retain the printed shape.

Recently, many advanced strategies, including redispersing solid state GO and solvent exchange drying, have been developed to further concentrate GO inks and therefore improve their printability. Yao et al.\(^{38}\) redispersed freeze-dried GO foam in water and obtained concentrated GO inks with concentration of 8 vol\%. This GO ink exhibits a plateau \( G' \) of \( 10^3 \) Pa with shear stress in a range of \( 10^{-1} \) Pa and \( 10^2 \) Pa as well as a high yield stress of \( 10^3 \) Pa (Figure 4A–C). As a proof-of-concept, they printed a 3D rGO heater by DIW technique, which exhibit good shape retainment and function well as a high-performance thermal supply with high temperature and ultrafast heating rate (Figure 4D–F). Yeh et al.\(^{59}\) also prepared GO dispersions with ultrahigh concentration larger than 10 vol\% by partially replacing water with involatile glycerol in GO dispersion, followed by removal of volatile water solvent through drying. The obtained GO ink exhibit a plateau \( G' \) of \( 2 \times 10^5 \) Pa and a yield stress larger than \( 10^3 \) Pa (Figure 4G–I). This simple “mix and dry” route has made GO inks well accommodate to DIW technique, rendering printed GO simples with high density (1.73 g cm\(^{-3}\)), excellent compression resistance (62.7 MPa), and outstanding electrical conductivity (2073 S m\(^{-1}\)). Apart from colloidal GO dispersion, highly printable GO inks can also be derived from solid GO assemblies. Guo et al.\(^{61}\) achieved a highly plastic state for GO solid assemblies by solvent intercalation, which enables both local and global plastic deformations required for processing techniques like micromolding and 3D printing.

In addition to increase the concentration, utilizing GO sheet with larger lateral size (\( D \)) is an alternative route to modify the printability of GO inks. Ma et al.\(^{62}\) compared the rheological behaviors of GO dispersion with large average \( D \) of 50 \( \mu \)m (labeled as LGO) with GO dispersion with small \( D \) of 5 \( \mu \)m (labeled as SGO). Larger \( D \) renders LGO a lower \( \varphi_{gel} \) as \( \varphi_{gel} \propto D^{-1} \). At the same concentration, LGO dispersion exhibits higher \( G' \) and yield stress than SGO dispersion. As the concentration increases to 2 vol\%, the \( G' \) and yield stress of LGO dispersions increase to
around $10^4$ Pa and 100 Pa, respectively, sufficient to meet the requirement for 3D printing (Figure 5). As a comparison, SGO dispersion with similar printability requires a higher concentration that exceeds 4 vol%. Using LGO inks with low concentration down to 2 vol%, they fabricated 3D graphene monolith with high performance and designable shape through DIW.

### 3.2.2 Intersheet crosslinking

GO behaves like an amphiphilic macromolecule with hydrophobic basal plane and hydrophilic edges composed of oxygen-containing groups like carboxyl and hydroxyl. As a result, various supramolecular interactions like ionic bonding, hydrogen bonding, and $\pi-\pi$ interaction can be used to construct interconnected network in GO dispersions. Many researchers have attempted to prepare printable GO inks by introducing crosslinking agents. For example, by adding small amounts of Ca$^{2+}$ ions, Jiang et al. turned low concentration GO dispersions (0.8–2 vol%) into printable gel inks. The introduction of Ca$^{2+}$ ions can form coordination bonds with carboxyl and hydroxyl moieties and bridge different GO sheets, bringing one order of magnitude increment of $G'$ and yield stress for GO inks (Figure 6A). Similar strategy has been adopted by Tang et al., who used urea as a key precursor to trigger the moderate crosslinking of GO sheet. Under heat and acid conditions, urea began to hydrolyze and release ammonium ions, which induce the formation of hydrogen bonds. The hydrogen bonds between ammonium ions and the GO sheets increased the elasticity and strength of GO gel inks by orders of magnitudes, ensuring their printability (Figure 6B). Jiang et al. have also developed versatile

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**Figure 4** (A–C) Rheological behaviors of concentrated GO aqueous prepared by redispersing freeze-dried GO foam. (D–F) 3D printed micro-heater. Reproduced with permission from Ref. 38 Copyright 2016 ACS. (G–I) Rheological behaviors of concentrated GO aqueous prepared by solvent exchanging drying. Reproduced with permission from Ref. 60 Copyright 2020 Elsevier.
GO putty-like inks with excellent processability by mediating GO dispersion with aniline. After addition of aniline, GO could have stronger interaction with aniline molecules than water through π-π interaction, hydrogen bonding, and electrostatic interaction, which induces the aggregation of GO sheets and the formation of strong crosslinked network (Figure 6C). Garcia-Tunon et al.66 designed a pH-responsive GO inks with the aid of a branched copolymer (BCS), poly(methacrylic acid) (PMA), and polyethylene glycol (PEG). The BCS constantly maintains a strong interaction with GO sheets through hydrophobic chain ends and could undergo self-aggregation due to the hydrogen bonding between the methacrylic acid (MA) and ethylene glycol (EG) group under acidic condition. It induces the formation of a GO/BCS 3D network linked by noncovalent interactions and an exponential improvement of $G'$ by five orders of magnitude when the pH is reduced to 3.88. Physical and chemical crosslinking are viable routes to improve the printability of GO inks because it effectively increases the connectivity of GO sheet in inks. In this way, not only the printability of the inks but also the functionalities of printed architectures like mechanical strength and electrical conductivity can be largely enhanced.

3.2.3 Adding rheology modifying additives

Another common ink preparation strategy is adding functional additives to modify their rheological properties to meet the requirements for 3D printing. Various functional additives, ranging from inorganic nanoparticles to viscoelastic polymers, have been adopted to develop printable graphene inks. Zhu et al.67 used nano silica filler to increase the solid content of GO inks and therefore improved their printability and shape retention ability. The addition of 20 wt% silica filler increases the $G'$ and yield stress of GO dispersions by over an order of magnitude. After printing process, the remaining silica filler was removed by hydrofluoric acid etching to obtain neat graphene lattices (Figure 7A). Huang et al.68 prepared gel like graphene inks by adding a mixture of dibutyl phthalate (DBP) and polyvinyl butyral (PVB) as thickening agent,
which exhibited typical shear-thinning behavior and high $G'$. The apparent viscosity of prepared ink was negatively related to the shear rate, ensuring the different viscosity requirements of the inks during extrusion and stacking. The high plateau $G'$ value ($\sim 10^5$ Pa) and yield stress ($\sim 470$ Pa) of composite inks are also sufficient enough to retain self-supporting 3D stacked architectures (Figure 7B).

The utilization of organic gel additives can not only monitor the rheological properties of graphene inks to enable 3D printing but also render printed structures with special functionalities. For instance, Wang et al.\textsuperscript{69} printed a stretchable graphene/polydimethylsiloxane (PDMS) sensor by using PDMS base to adjust the viscosity of graphene inks. Highly concentrated graphene/PDMS inks were smoothly extruded and stacked layer by layer to form 3D architecture. Moreover, the high flexibility and stretchability of cured PDMS endows printed graphene-based structures with enhanced compatibility with broad applications like wearable electronics, piezoresistive sensors, and shape memory composites. Jakus et al.\textsuperscript{70} prepared biocompatible graphene inks by mixing graphene powder with polylactide-co-glycolide copolymer in dichloromethane solvent. This solvent-based graphene ink comprise graphene sheets and the biocompatible, biodegradable, and hyperelastic polyester polylactide-co-glycolide, which can be directly printed into 3D electrically conducting scaffolds primarily for tissue regenerative engineering applications (Figure 7C). By modifying graphene inks with these functional additives, versatile design and functionalities can be achieved by 3D printed graphene-based objects, which greatly extends their applications in energy-related devices, sensors, bioelectronics, and medicine.
3.2.4 MODIFYING PRINTING TECHNIQUE

In addition to tuning the rheological properties of the printing inks, an alternative direction is to modify the current printing technique to enable DIW. Based on the rheological behaviors of pure GO dispersions, the main target is to introduce auxiliary forming techniques to ensure the printed 3D structure is properly maintained. By directly printing GO dispersion onto a cold sink (−25°C), where printed GO filaments were frozen immediately after extrusion from the nozzle, Zhang et al.\(^{71}\) fabricated freestanding 3D GO structures (Figure 8A). Owning to the rapid solidification effect of low temperature, GO dispersion with ultralow concentration down to 0.1 vol% can be directly printed into low density 3D structures. Besides, when the fresh ink was printed out, this not-yet-frozen filament could partially melt the frozen filament underneath and then refreeze together as an integration under the cooling environment. This “melt-and refreeze” process effectively eliminates the interface inhomogeneity between adjacent filaments, enhancing the structural integrity and properties of printed 3D structures. Kim et al.\(^{36}\) printed...
free-standing GO nanowires with overhanging structures by extrusion from a micropipette. Due to the small size of the micropipette (1.3–2.6 μm) as compared with normal 3D printing nozzle (usually larger than 100 μm), the water evaporation at the meniscus forming at the micropipette tip is significantly accelerated, and therefore enables in situ solidification and growth of free-standing nanowires. Notably, the diameter of printed nanowires can be regulated by tuning the pulling speed, enabling the printing of nanowires with a diameter down to 150 nm (Figure 8B).

4 | 3D-PRINTED GRAPHENE MATERIALS FOR ENERGY STORAGE AND CONVERSION

4.1 | Batteries

Batteries, especially lithium-ion batteries, play an important role in energy storage and conversion because of their performance advantages such as high energy density, low self-discharge, and wide operating temperature. Carbon nanomaterials like graphene are regarded as an ideal electrode material due to their high electrical conductivity, low density, and chemical stability. Conventional electrodes are usually prepared by casting a slurry composed of active materials, conducting additives and polymer binds onto metal current collectors, resulting in 2D planar electrodes. Employing 3D printing technique enables fabrication of 3D electrodes with controllable thickness, shape, and pore structures. Compared with 2D planar electrodes, 3D electrodes have many advantages such as high areal loading, fast ion-diffusion rate, and low tortuosity. Therefore, extensive graphene-based electrodes constructed by 3D printing have been studied and developed in recent years. Hu’s group first fabricated 3D Li-ion battery electrodes by DIW with aqueous GO composite inks. 3D cathode and anode are directly printed from concentrated GO/LiFePO₄ (LFP) and GO/Li₄Ti₅O₁₂ (LTO) aqueous inks (~ 8.5 vol%), respectively, followed
by freeze-drying and thermal annealing (Figure 9A). Here, GO flakes were chose to provide a continuous electrically conductive network for electron transport and offer a large surface area to load active materials. Owing to their well-connected 3D structures, the printed half-cell battery exhibited a capacity approaching the theoretical capacity of LFP and LTO. Notably, the capacity remained plateau during long charge–discharge cycles and no obvious voltage hysteresis was observed, indicating excellent charge transport stability and electrical conductivity of printed electrodes. To further improve the charge transport efficiency of 3D printed graphene electrodes, Hu’s group printed hierarchically porous 3D electrodes by using freestanding holey GO meshes.83 The printed electrode exhibited a trimodal porosity of nanoscale, microscale, and macroscale porous structures that originate from inherently nanoporous holey GO sheets, lyophilization induced pores and 3D printed macro architectures, respectively. This hierarchical porous structure could promote the mass transfer and ionic transport, leading to a superior cycling depth and stability as well as low over-potential (Figure 9B). Similar strategies have also been adopted by Qiao et al.84 and Shen et al.,85 where functional graphene-based electrodes with hierarchical structural features were constructed by 3D printing. Recently, Gao et al. fabricated a thickness-independent Li-S battery electrode composing of vertically aligned 2D “thin electrodes” via 3D printing.86 This well-designed vertical structure provided a short Li ion diffusion distance no more than 10 μm, significantly reducing the Li ion transporting resistance. As a result, all printed batteries exhibited similar rate performance and cycling performance independent of various electrode thickness (250–750 μm). As a newly emerged technique, 3D printing can realize delicately designing and fabricating of electrodes over multiple length scale, taking full advantage of the excellent electrical and thermal properties of graphene. Moreover, 3D printing can fulfill the personalized and large-scale design requirements in the future, showing potential in applications like portable electronics, electric vehicles, and stationary grids for renewable energy storage.87,88
Supercapacitors are treated as a promising candidate for alternative energy storage due to their high power density and almost unlimited cyclability, which can be used as supporting power supply for many applications such as an implantable device, on-chip energy storage, and electric vehicles.89–92 Supercapacitors store the energy within the electrochemical double-layer at the electrode/electrolyte interface via physisorption of ions. Therefore, graphene-based materials have been widely used as supercapacitors electrodes because of their large specific surface area, high electrical conductivity, and chemical stability. In order to improve the ion-accessible surfaces and ion/electron transport efficiency, a series of 3D graphene-based electrodes with interconnected pore structures have been developed, such as fiber,93 porous film,94 nonwoven fabrics,95,96 and aerogels.97–99 3D printing techniques enable us to rationally tailor the architectures of 3D graphene electrodes over multiple length scales, which have been extensively studied recently. Li’s group first 3D printed graphene-based supercapacitors in 2016.100 Printable inks composed of concentrated GO dispersion (∼4 vol%), graphene nanoplatelets, and nano silica fillers were used to directly printed into 3D graphene electrodes with woodpile structure. Here, graphene nanoplatelets were added to improve the electrical conductivity of printed electrodes and maintain their high surface area, which is curial for the capacitive performance. A symmetric supercapacitor cell is assembled from two identical 3D printed graphene electrodes, which exhibited a maximum gravimetric capacitance of 4.76 F g⁻¹ at a current density of 0.4 A g⁻¹. Owning to the ordered pore structure and high electrical conductivity, this printed supercapacitor showed high energy density and power density compared with previous graphene-based supercapacitors (Figure 10A). Similar strategy has
also been adopted by Jiang et al., 37 who fabricated 3D GO electrodes with hierarchical pore structures with a printable GO gel ink. The printed supercapacitor exhibited a high gravimetric capacitance of 213 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\) and retained 183 F g\(^{-1}\) at a high current density up to 100 A g\(^{-1}\). This improved capacitive performance and excellent rate performance can be attributed to the well-designed macro- and mesopore structures and interconnected conductive skeletons constructed by 3D printing.

Recently, many researchers have combined 3D printing technique with other physical/chemical treatments to further enhance the performance of printed supercapacitors. Li’s group functionalized 3D printed graphene aerogels by electrochemical oxidation in 0.5 M KNO\(_3\) solution at a potential of 1.9 V for 3 h.101 This electrochemical functionalization process introduced abundant surface functional groups that provide extra pseudocapacitance onto printed electrodes. As a result, functionalized electrodes exhibit a benchmark areal capacitance of 2195 mF cm\(^{-2}\) at a high current density of 100 mA cm\(^{-2}\) as well as an ultrahigh intrinsic capacitance of 309.1 µF cm\(^{-2}\) even at a high mass loading of 12.8 mg cm\(^{-2}\). Moreover, kinetic analysis revealed that the capacitance of 3D printed electrode is primarily (93.3%) attributed to the fast kinetic process, demonstrating the important role of 3D-printed structure in boosting the kinetics and intrinsic capacitance of pseudocapacitive supercapacitors (Figure 10B). Yao et al.102 further electrodeposited pseudocapacitive MnO\(_2\) onto 3D printed graphene aerogels. The macroscopic porous structures constructed by 3D printing facilitated uniform deposition of MnO\(_2\) throughout graphene aerogels and enhanced ion diffusion during charging/discharging even at ultrahigh mass loading of MnO\(_2\). A 4-µm-thick graphene aerogel with MnO\(_2\) loading of 182.2 mg cm\(^{-2}\) were fabricated and exhibited a record high areal capacitance of 44.13 F cm\(^{-2}\). More importantly, the areal capacitance of this printed electrode increases linearly with the mass loading of MnO\(_2\) and electrode thickness, indicating that the capacitive performance is not limited by ion diffusion (Figure 10C).

Another developing tendency of supercapacitors is to fabricate microsupercapacitors that integrate both high areal capacitance and energy density to fulfill the growing demand for integrated and miniaturized devices.103 In this regard, 3D printing possess advantages such as high manufacturing accuracy, flexible design capability, and high processing efficiency. Correspondingly, various 3D printed graphene based microsupercapacitors have been developed in recent years.103-106 For instance, Wu’s group developed aqueous planar microsupercapacitors via an all-3D-printing strategy.104 The printed microsupercapacitors exhibited ultrahigh areal capacitance (2381 mF cm\(^{-2}\)) and energy density (331 µWh cm\(^{-2}\)), as well as a wide voltage window up to 2.0 V. Moreover, 3D printed microsupercapacitors can be feasibly integrated in parallel or in series with various voltage and current outputs, which further extended their compatibility to multiple applications. These findings validate the advantages of fabricating high-performance supercapacitors by 3D printing technique, which could actualize complicated electrode design and extend the application area of supercapacitor devices.

### 4.3 Solar steam device

Solar steam generation (SSG) system, which utilizes abundantly available solar energy and self-floating photothermal materials to generate steam, is a clean and sustainable approach for sterilization of waste and seawater desalination.107-109 The main challenge for SSG is achieving high sunlight absorption efficiency and fast water transportation simultaneously. 3D graphene-based macrostructure features exceptional optical absorption ability and high thermal conductivity for high-efficient solar absorption and conversion, as well as an interconnected porous structure and tunable hydrophilicity to facilitate fast water transportation, which makes it outperform multiple other materials developed for SSG. Hu’s group first utilized 3D printing technique to architect an all-in-one device with concave structure for high-efficiency SSG.10 By virtue of the switchable multiple-component printing nozzle, an integrated structure successively consisting of the carbon nanotube (CNT)/GO layer, GO/nano-fibrillated cellulose (NFC) layer, and GO/NFC wall was constructed (Figure 11A). Here, the CNT/GO layer contributes to high-efficient solar-thermal conversation due to its broadband solar absorption and excellent photothermal conversion; GO/NFC layer helps to transport water and wick water upward to the contiguous CNT/GO layer because of its porous mesh-like structure; the porous and hydrophilic GO/NFC wall can effectively draw water from the bottom owning to the capillary and serves as an thermal barrier to alleviate thermal losses. This delicately designed and constructed SSG evaporator therefore exhibited a high solar steam efficiency of 85.6% under 1 sun illumination (1 kW m\(^{-2}\)). Wang et al.11 also developed a 3D GO-based biomimetic SSG evaporator using DIW technique. Their printed evaporator integrated a rippled upper surface decorated with stomata-like pores to enhance sunlight absorption and vapor evaporation, and a substructure comprising vertically orientated vessel-like channels for water transportation. This elaborated multiscale structure endows 3D printed evaporator with a good solar-thermal conversion efficiency up to 94.5% at an illumination of 1 kW m\(^{-2}\) (Figure 11B). The construction of fast and
scalable SSG system through 3D printing has opened up a new way to realize high-efficiency solar-thermal conversion with minimum energy loss, which holds great potential to be applied in the fields of sterilization and desalination.

4.4 Electro-thermal conversion applications

High temperature is essentially important in materials synthesis, processing, and functionalization, which is usually achieved by energy-consuming furnaces or hotplates. Therefore, developing advanced electro-thermal conversion devices with high accessible temperature and stable heat supply as well as high conversion efficiency and low heat dissipation is of great significance. The 2D hexagonal honeycomb structure formed by strong sp2 hybridized carbon–carbon bonds endows graphene with extremely high thermal conductivity and excellent electrical conductivity, making it a promising candidate for electro-thermal conversion applications. By utilizing 3D printing technique, graphene-based materials with various 3D shapes and structures as well as designable porous structures that can cultivate heat and incorporate functional additives can be flexibly customized. Hu’s group printed a horseshoe-like 3D heater with highly viscous GO ink. Driven by electrical Joule heating, the printed heater can generate a high temperature up to 3000 K at an ultrafast heating rate up to 20,000 K s\(^{-1}\). Moreover, the printed heater also exhibited an excellent stability during repeatedly on-off turning tests for more than 2000 cycles and staying 1500 K for more than 24 h. By using 3D printing, the heater can be designed into arbitrary shapes with submillimeter accuracy, showing great potential as high-efficiency and high-precision heater used for micro device and irregular structural materials. As a proof-of-concept, Hu and co-workers used 3D printed microheater as a high-temperature platform for in situ synthesis and dispersion of metal nanoparticles. Assisted by the high-temperature thermal shock (~2000 K) originated from the ultrafast heating rate of microheater, metal nanoparticles with diameter around 10 nm can
be uniformly deposited on rGO structures with designed shape (Figure 12A).

Apart from high-temperature heaters, electro-thermal conversion can also be coupled with thermal-triggered functional materials to extend its application in sensing, actuating, and phase change energy storage. Guo et al. fabricated shape memory aerogels with ultrafast response up to 50 ms at low electrical field of 0.1 V mm\(^{-1}\) by incorporated commercial shape memory polymers with 3D printed graphene aerogels. The rapid electrothermal conversion and the extremely short heat transportation distance provided by the graphene skeleton are responsible for this high responsive speed. In addition, owning to the high stretchability of printed graphene framework, this nanocomposite aerogels also exhibit large elongation (~100%), high fixing (~97%), and high recovery ratio (~98%) at 100% tensile strain (Figure 12B). This combination of fast response, large deformation, and designability of 3D printed graphene-based aerogels hold great opportunities for applications in smart devices and micro robotics.

5 | SUMMARY AND OUTLOOK

We have briefly reviewed the recent developments of 3D printing techniques, especially DIW technique, in fabricating graphene-based materials for ESC applications. The extrusion based DIW technique requires a printable ink with a shear thinning behavior to be smoothly extruded and good mechanical properties, that is, moderate elastic modulus and yield stress, to retain printed structure. In order to construct 3D graphene structure by DIW, various strategies have been developed to prepare printable GO inks, which are divided into four categories: improving GO network strength, inter-sheet crosslinking, adding rheology modifying additives, and modifying printing technique. By using graphene-based inks, 3D graphene architectures with tunable structural features over multiple length scales can be facilely designed and fabricated through DIW. This structural design capability boosted a series of ESC applications with enhanced performances and diverse functions, and some remarkable results are reviewed and summarized in this paper. Specifically, in
graphene-based energy storage devices such as electrodes for batteries and supercapacitors, 3D printing technique enables building electrodes with delicately designed hierarchical porous structure and interconnected skeleton to attain both high energy density and high-power density. In graphene-based energy conversion devices such as solar steam generators and electro-thermal conversion devices, flexible structural designability covering diversified geometry, multiscale size, and multicomponent regulation is achieved by 3D printing, which greatly improved the conversion efficiency and extended their functionalities.

Despite various superiorities, there are existing challenges of applying 3D printing techniques for graphene-based ESC devices. First, most existing strategies involve posttreatments to remove remaining solvent and additives, which is not only time- and energy-consuming but also harmful to the performance of final devices. Besides, removal of solvent usually results in a porous structure, leading to poor mechanical performance and less loading of active materials. Second, the 2D topology and ultra-high aspect ratio of GO sheets set an inherent energy barrier for preparing GO dispersion with high solid content (> 10 vol%) due to the intensive extruded volume effect. As a result, printed GO structures suffer an unavoidable shape shrinkage and distortion, which alters the structural accuracy.

In future work, the design of micro- and nanoscale 3D-printed objects used for miniaturized ESC devices might be one of the most important tendency. More efforts should be dedicated to improve the controllability and accuracy of 3D printing techniques. As to graphene-based materials, one route to realize high-resolution printing is combining DIW technique with other processing procedure. For example, present DIW relies on a coarse uniaxial shear field to regulate the orientation of graphene sheets inside a filament, lacking of precise control of orientation structure. By coupling a rotational nozzle or microfluidics system, printed architecture with programmably defined sheet arrangement like orthogonal and helical configuration can be achieved. Another feasible strategy is developing high solid content inks from near-solid state of graphene materials. Recently, a superplastic state of solid-state graphene assemblies has been observed by a few research groups, where a small amount of intercalated solvent can active the collaborative sheet slippage to achieve large plastic deformation. This plastic graphene dough holds great potential to be developed into near-solid printable inks, which might lead us to printed graphene structures with enhanced structure accuracy and even highly densified graphene structures. Moreover, incorporating graphene inks with other functional additives might also stand as an alternative to further extend the functionalities of 3D printed graphene materials. Ultimately, we can envision that 3D printed graphene architecture with programmable micro- and macro-structures and tunable properties will facilitate the development of high-performance and sustainable ESC devices.

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**CONFLICT OF INTERESTS**

The authors declare no conflict of interests.

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